COMPOSITE MATERIALS

Introduction

Composite materials are made by combining two or more materials to give a unique combination of properties. Many common materials are indeed “composites,” including wood, concrete, and metals alloys. However, fiber-reinforced composite materials differ from these common materials in that the constituent materials of the composite (eg the two or more phases) are macroscopically distinguishable and eventually mechanically separable. In other words, the constituent materials work together but remain essentially in their original bulk form (apart from the thin hybrid interface between the phases).

The main component of a composite is the matrix material. The reinforcement (qv) can be fibers, particulates, or whiskers. The fibers can be continuous, long, or short. In advanced composites, the fibers (ie the reinforcing phase) are present as unidirectional strands or woven fabric and provide strength and stiffness to the composite. The matrix acts as a load transfer medium assuring rigidity and protects the fibers and the whole composite from environmental attack. Short chopped fibers and mat are used in nonstructural polymer matrix composites. In these cases the fibers provide comparatively less strength and stiffness to the composite.

Fiber-reinforced polymer matrix composites are the most common advanced composites. Early glass-fiber-reinforced composites resins were used in the 1930s to build parts of boats and aircraft. Since the 1970s, application of composites has widely increased owing to the development of new fibers such as carbon, boron, and aramids (see High Performance Fibers). Thermosetting polymers such as epoxy, polyester, and urethane resins are, among the others, the most widely used matrices of advanced composites. (see Thermosets). In the 1980s the development of new, cost-effective thermoplastic polymers such as PEEK (poly-ether-ether-ketone) and PEI (Poly-ether-imides) allowed the development of a new class of high performance composites (see Engineering Thermoplastics, Overview; Polyimides).

Thermosetting and thermoplastic matrix composites are in many ways superior materials compared to common metals and ceramic materials. Their reliability is confirmed by their large use in the aerospace industry. Mechanical advantages of polymer composites are expressed in terms of two main parameters (ie specific modulus and strength) reflecting the key role of density on the selection of high performance materials. The specific modulus $E_s$ is defined as the ratio between the Young’s modulus $E$ and density $\rho$ of the material. The other parameter, the specific strength ($\sigma_s$), is defined as the ratio of the ultimate strength $\sigma_{ult}$ and the density

$$E_s = \frac{E}{\rho} \quad (1)$$

$$\sigma_s = \frac{\sigma_{ult}}{\rho} \quad (2)$$
The coefficient of thermal expansion (CTE) of composite structures can be made close to zero by selecting suitable materials and lay-up sequence. Dimensional stability is, in fact, one of the key requirements that many metals cannot satisfy (owing to their higher CTE) in aerospace applications. A CTE that can be tailored for a specific application gives rise to an increased amount of design flexibility with respect to common metals. In Table 1 the relevant thermomechanical properties of common and fiber-reinforced composite materials are reported. The last three columns of Table 1 explain why specific stiffness, strength, and CTE are, among the others, the key parameters in the selection of composite materials in aerospace applications where both performance and cost are a concern. High specific performance of composite materials allows weight saving, with consequent increase in payload and fuel savings. Composite materials can be highly fatigue- and corrosion-resistant, with enhanced life and reduced maintenance costs. The following drawbacks represent limits in using polymer-based composites:

1. The high cost of fabrication of composites for aerospace applications is still a critical issue. Today most of the effort and investment in this area is devoted toward improving processing and manufacturing techniques in order to lower costs. Medium performance composites, on the contrary, can be made using manufacturing techniques such as sheet molding compound (SMC), structural reinforced injection molding (SRIM), and resin transfer molding (RTM), in which both the cost and the production time have been consistently optimized to compete within the automotive industry.

2. Unlike metals, fiber-reinforced composites are anisotropic, that is, their properties depend on both the fiber orientation and the lay-up sequence in the laminate. In-plane quasi-isotropic materials can, however, be made by opportune selection of a lay-up sequence (e.g., a \([0/\pm 45/90]_2\) lamination sequence realizes in-plane equivalent properties from an engineering point of view) or when continuous random mats of fibers are utilized as the reinforcing system (this is the case in parts obtained by SRIM or RTM). In both cases, however, the fibers remain perpendicular to the third direction, and it is this drawback that renders the design procedures far more complicated and intensive than those normally utilized for isotropic materials. In other words, while monolithic materials such as aluminum require only two elastic constants to establish the stress–strain relationship in each body point for a given system of forces acting on it, composite materials require many more elastic constants. For example, in unidirectional composites (where all the fibers lay in one direction) under plane stress conditions (no out-of-plane loads) four elastic constants are required. In addition, the mechanical characterization of a composite structure is far more complex than that of a metal structure if one considers that the techniques for the evaluation and measurement of some composite properties, such as fracture toughness and compressive strength, are still debatable.

3. The reinforcing fibers in composites offer unique properties but create complications in recycling. Thermoplastic composites have the potential of primary and secondary recycling since the reprocessing of waste can result in a product with the same or comparable properties, whereas thermoset
<table>
<thead>
<tr>
<th>Material</th>
<th>Density, mg/m³</th>
<th>Young's modulus, GPa</th>
<th>Specific modulus, (GPa·m³)/mg</th>
<th>Ultimate strength, GPa</th>
<th>Specific strength, (GPa·m³)/mg</th>
<th>CTE, 10⁻⁶/°C⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>7.85</td>
<td>200</td>
<td>25.5</td>
<td>0.38–1.79</td>
<td>0.048–0.23</td>
<td>30–51</td>
</tr>
<tr>
<td>Aluminum</td>
<td>2.7</td>
<td>70</td>
<td>25.9</td>
<td>0.09–0.572</td>
<td>0.033–0.21</td>
<td>64–71</td>
</tr>
<tr>
<td>Titanium</td>
<td>4.5</td>
<td>110</td>
<td>24.4</td>
<td>0.24–1.17</td>
<td>0.053–0.26</td>
<td>25–38</td>
</tr>
<tr>
<td>Aramid</td>
<td>1.44</td>
<td>131</td>
<td>91</td>
<td>3.6–4.1</td>
<td>2.5–2.85</td>
<td>Id:−6.0, td:180³</td>
</tr>
<tr>
<td>Graphite</td>
<td>1.78–2.15</td>
<td>228–724</td>
<td>106–407</td>
<td>1.5–4.8</td>
<td>0.70–2.70</td>
<td>Id:−1.8, td:30</td>
</tr>
<tr>
<td>Glass</td>
<td>2.58</td>
<td>72.5</td>
<td>28.1</td>
<td>3.45</td>
<td>1.34</td>
<td>15</td>
</tr>
<tr>
<td>Alumina</td>
<td>3.95</td>
<td>379</td>
<td>96</td>
<td>1.38</td>
<td>0.35</td>
<td>22</td>
</tr>
<tr>
<td>Unidirectional AS4 graphite–epoxy (V_f = 70%)</td>
<td>1.64</td>
<td>161</td>
<td>98.2</td>
<td>2.77</td>
<td>1.68</td>
<td>Id:−3.84×10⁻², td:26</td>
</tr>
<tr>
<td>Unidirectional E-glass–epoxy (V_f = 50%)</td>
<td>1.93</td>
<td>38.34</td>
<td>19.86</td>
<td>0.93</td>
<td>0.48</td>
<td>Id: 7.37, td: 28.62</td>
</tr>
<tr>
<td>Cross-ply AS4 graphite–epoxy (V_f = 58%)</td>
<td>1.57</td>
<td>77.45</td>
<td>48.98</td>
<td>–</td>
<td>–</td>
<td>1.56</td>
</tr>
<tr>
<td>Cross-ply E-glass–epoxy (V_f = 40%)</td>
<td>1.8</td>
<td>21.05</td>
<td>11.69</td>
<td>–</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

³Id = longitudinal direction, td = transverse direction.
Composite scraps usually are tertiary recycled (in order to recover the fibers so they can be reused in molding compounds) or essentially burned off.

(4) Repairing composite parts is a very complex process and not always accessible.

(5) Most of the effectiveness of nondestructive techniques for the inspection of metal parts (such as eddy currents, X-ray) is lost when it comes to detection of flaws and cracks in composite structures, unless appropriate modifications are made to the instrumentation hardware or the inspection procedure. Ultrasound, laser (shearography), and acoustic emission techniques are usually preferred for inspecting the crack initialization (see Nondestructive Testing).

Many of the above drawbacks forced the composite industry to focus significant effort on the development of manufacturing procedures in which the fabrication process is controlled with the highest level of real-time monitoring tools. It is well established that the quality of a composite structure depends almost completely on the process quality. Controlling the manufacturing process depends, first of all, on a deep knowledge of the overall physical and chemical changes occurring within the part. Mathematical modeling then provides estimates of optimum process parameters for a given manufacturing process to produce a high quality product.

### Composite Manufacturing Techniques

Composite parts are made using either thermoset or thermoplastic resins with some form of reinforcements. Techniques for manufacturing polymer matrix composites are covered in Composites, Fabrication (qv). Filament winding and robotic winding are used for making pipes and tanks. Pultrusion is used for low cost high volume productions. Autoclave processing is used when high quality panels and structures sometimes having complex shapes are required. RTM is used extensively to make small and large complex structural parts in a cost-effective manner using low cost tooling. Compression molding processes are widely used in the automotive industry for high volume production capabilities and injection molding (qv) is adopted when the production rate is a critical issue, mainly for consumer and automotive applications.

Filament winding consists of drawing resin-impregnated fibers that are wound over a mandrel. Winding patterns are decided at the design stage depending on the desired properties of the product. The winding process of a high quality pressure vessel is shown in Fig. 1.

Pultrusion is a simple, continuous process in which resin-impregnated fibers are pulled through a die to make a part. During passage through the heated die resin-impregnated yarns consolidate due to the incoming cross-linking reaction. Objects with constant cross-section and smooth finish can be obtained.

Autoclave processing is used with prepregs with lay-up realized by automated means or by hand. The assembly is vacuum-bagged in order to minimize the presence of volatile substances (responsible for void/defect growth during the
process) and placed inside an autoclave. After the process cycle, consisting, generally, of a sequence of heat and pressure inputs, the part is removed from the tool. It takes several hours generally to complete the process.

In RTM a low viscosity resin is injected under low pressure into a closed mold which contains the fiber preforms or fabrics used as reinforcements. RTM has gained increasing importance, because of its potential for making structural components (due to the use of continuous fibers) in a cost-effective manner.

Compression molding of sheet molding compounds (SMCs) or bulk molding compounds (BMCs) is typically used in the auto industry mainly because of the similarity to stamping technology. In the compression molding operation, the SMC is cut into rectangular shapes and “charged” on the bottom half of a preheated mold. The SMC covers only a part of the mold (between 30 and 90%) while the remaining surface is filled by forcing flow of the “charge” by pressure. When the mold is closed, lying down, and has a constant displacement rate (ie 40 mm/s) the upper half of the mold, the SMC, starts to flow inside the mold, filling the cavity. The molds are generally preheated to about 140–150°C.

Injection Molding (qv) has been generally used for thermoplastic materials for many years. Only during the last decade, because of the increasing demanding has it been considered and successfully applied in the thermoset industry. The mold injection, the subsequent cross-linking of the system, and the final demolding and expulsion of the part takes between 30 and 60 s; therefore this process is
particularly considered when very high volume production is requested. In some cases, using multiple-cavity molds for the consolidation of different element parts at the same time can further increase the production rate.

Many other techniques have been developed over the years. However, each manufacturing process consists of four basic steps, wetting/impregnation, lay-up, consolidation, and solidification, which in case of composites require low energy compared with those for traditional materials. In fact, composites do not have high pressure and temperature requirements for part processing as compared with metal. This is the reason why composite processing techniques such as those described above have the potential of producing complex, high strength, high stiffness, and near-net-shape structures. Therefore the applications of polymer matrix composites range from the aerospace industry to the sporting goods. Composites are the material of choice in space applications owing essentially to two factors: high specific modulus and strength, and dimensional stability. Graphite–epoxy composites are increasingly used in bicycles, sometimes allowing frames to consist of one lightweight piece, or in golf club shafts, using the saved weight in the head. Tennis and racquetball rackets with graphite–epoxy frames are now commonplace. The military aircraft industry has mainly led the use of polymer composites in structural applications while in commercial airlines the use of composites has been conservative because of safety concerns. The graphite–epoxy and aramid honeycomb tail fin of Airbus A310-300 is an example of using composites in the primary structure in commercial airlines. The weight of the tail fin was reduced by 300 kg, together with the number of parts, which decreased from 2000 to 100. Infrastructure applications of polymer composites include bridges—due to low weight, corrosion resistance, longer life cycles, and limited earthquake damage. The application of fiber glass in boats is well known even when hybrids of Kevlar–glass/epoxy are now receiving attention because of the improved weight savings, vibration damping, and impact resistance.

Today’s automobile industry uses low amounts of composite parts owing to the unavailability of cost-effective manufacturing techniques. Nowadays about 8% of automobile parts are made of composites.

**Process Modeling**

During the fabrication process (e.g., RTM, autoclave, filament winding) a combination of pressure–temperature steps are applied with given histories in order to assure well-consolidated parts with minimum defects. The solidification or curing process involves a number of physical, chemical, and mechanical phenomena in the composite materials. Generally speaking, the formation of a structure due to cross-linking reactions or to the melting and consolidation of thermoplastic polymers is the macroscopic effect of heat and pressure inputs: in real terms continuous changes in degree of cure or crystallinity, gelation (the formation of an infinite polymer network as a consequence of chemical reaction) and vitrification (the passage from a molten/rubbery to a glassy state) occur. As a consequence of the above phenomena, the evolving chemical and thermal shrinkage give rise to the development of stress and strain within the part, whereas the presence...
of volatiles in the form of residual plasticizing agents or unreacted resins can eventually induce void growth and resin–fiber debonding.

In all, thermal shrinkage, chemical shrinkage, time–temperature–degree of cure dependent resin properties, viscosity, and structural relaxation shrinkage are the matrix properties to control. Therefore, since the evolution of polymer properties is strongly influenced by processing history, each parameter has to be investigated at each stage of the manufacturing process. Moreover considering that the level of temperature reached during the manufacturing of composite parts does not affect the fiber content, investigations are almost always carried out on the polymer system matrix. Significant progress has been made in quantitatively evaluating process-related parameters such as mold shape, mold material and surface, void content, fiber volume fraction, lay-up sequence. However, considerable work remains to be done to account for constituent resin-related properties. In particular, when new resins are developed a number of experimental tests are necessary to completely characterize the resin (such as toughened epoxies) so as to perform a general analysis of the physical and chemical phenomena and to code it by mathematical tools.

Mathematical modeling of a manufacturing process provides a tool for the process control with minimum costs and high quality production. Typical aerospace manufacturing processes for composites are characterized by a two-step cure cycle. In such a cycle the temperature of the material is increased from room temperature to the first dwell temperature and this temperature is held constant for the first dwell period (∼1 h); during this stage the material reaches the minimum value of viscosity to fill the mould and/or compact the whole system. The temperature is then increased again to the second dwell temperature and held constant for the second dwell period (∼2–8 h). Post-cure reaction takes place during this second stage. Following this second dwell period the part is cooled down to room temperature at a constant rate or by air to allow the extraction from the mould. It is during the polymerization reaction that the strength and related mechanical properties of the composite are developed, together with incipient flaws (eg voids, resin–fiber debonding) and residual stresses.

The transient heat transfer phenomena induce peculiar property changes at each body point. In this respect, the temperature profiles and the chemorheological functions (viscosity, degree of cure/crystallinity) need to be included within the energy balance equation:

\[ \rho C_p \frac{dT}{dt} = \nabla (K \nabla T) + \rho \dot{Q} \]  

where \( \rho \) is the density, \( C_p \) is the specific heat, \( t \) is the time, \( K \) is the thermal conductivity, and \( \dot{Q} \) is the rate of heat generated either by the exothermic polymerization reaction in the case of a thermosetting matrix system or by the crystallization process for thermoplastic matrix.

From the micro-mechanical point of view, the process modeling strategies must consider simultaneous interplay of the following “intrinsic” factors: initial and boundary conditions in terms of pressure and temperature, fiber content and stacking, sequence of layers (ie ply-to-ply orientation), thermal shrinkage, chemical shrinkage, time–temperature–degree of cure dependent resin properties, and
structural relaxation shrinkage. The above factors can play a different role when an even more complex scenario arises for thick composite parts. Therefore a detailed analysis of temperature distribution during the process is crucial for the determination of the complex evolution of the properties at each material point of the composite part. A simple analogy could be made with metals in order to understand this complex scenario. The evolution of the structure for metals inevitably leads to a distribution of grain size as a result of the different temperature profiles experienced during the forming process. In the case of polymeric matrices, the same assumption can be reasonably made considering that each material point will undergo a completely different temperature profile, owing to the relative position occupied in respect to the heat source. For this reason, a thermosetting system matrix necessarily presents a distribution of polymerization reactions at each body point, according to the experienced thermal histories; in the case of thermoplastic systems, because of the strong dependency of the crystallization process upon the temperature profile, a distribution of grain size through the thickness (i.e., skin–core fine to coarse structure) is obtained. The temperature distribution can be suitably determined using finite element analysis (FEA) software; the temperature at a given point in the structure depends on the boundary and initial conditions, as well as the materials’ properties evolution. In fact, as the evolution of the structure is highly dependent on the thermal history, within a thick composite different material properties arise at each material point.

The correct analysis then would be an investigation of the temperature distribution with appropriate boundary conditions for the determination of real temperature profile as a function of the material point. This analysis would be coupled with a structural analysis, which takes into account the whole set of constraint conditions imposed by the mould, as in the case of RTM, or any other tool for a different manufacturing process. Figure 2 illustrates the flow-chart of a generic process modeling procedure.

![Graph](image)

**Fig. 2.** Experimental data for glass-transition temperature and DiBenedetto model predictions: □, experimental data; ——, fitting model.
Different material parameters need to be quantified to be able to perform the thermostructural analysis. The complex interactions of the different phenomena occurring during the manufacturing process could be schematized as follows.

(1) Both crystallization and polymerization reactions are temperature-activated phenomena, allowing the transformation of the system from a liquid-like to an almost solid-like material. The structure evolution can be suitably monitored by a degree of conversion parameter, which follows an analytical kinetics model.

(2) Thermal (specific heat, thermal conductivity) and viscoelastic properties of the material change during the process owing to both temperature variations (as for traditional materials) and level of conversion.

(3) Variation of the specific volume can be originated by three different phenomena:
   a. thermal expansion (or contraction) due to positive (negative) temperature change,
   b. chemical/physical shrinkage due to the densification (polymerization/crystallization) of the material according to the conversion level, and/or
   c. contraction due to the thermodynamic instability associated with the nonequilibrium kinetics of glass transition (structural relaxation).

The experimental evaluation and the modeling of each contribution still represent a difficult task for many researchers, and at the same time it is the main issue for the correct prediction of

(1) the residual stress formation and warpage effect in thick composite parts
(2) voids and flaw formation, and
(3) resin flow behavior dependent compaction and consolidation feature.

Coupled with the energy equation along with the specific initial and boundary conditions, the mathematical description of the above factors (through the use of suitable submodels for a given manufacturing process) allows the complete analysis of a generic manufacturing process, providing at the same time a fundamental “tool” for the production of high quality parts.

**Cure Kinetics and Glass-Transition Model**

As stated above, during the cure, at each level of conversion, a thermosetting material could be assimilated to a completely new material with specific thermomechanical properties. Then, the possibility of following with a monitoring variable the level of conversion reached by the system during the manufacturing process represents an important issue.

Thermal analysis provides useful information upon which to construct an adequate kinetics model under both isothermal and dynamic temperature
conditions. The mathematical model selected on the basis of the experimental data generally represents the primary component in studies on the optimization of thermoset molding processes (resin transfer molding, reaction injection molding, prepreg cure, etc). Reliable methods are required to predict the degree of conversion and to control the evolution of the exothermic heat of reaction. Correct kinetics models are also essential to predict the evolution of the structure under more complicated temperature profiles; or to correlate the changes in thermal and mechanical properties of the neat resin through all the manufacturing processes. Thus, the knowledge of the level of conversion of the polymer matrix is fundamental information to monitor the evolution of properties. Curing raw data needed to implement the kinetics models can be obtained, by nearly standardized procedures, through isothermal and dynamic differential scanning calorimetry (DSC) tests.

There are essentially two kinetic models used to describe thermoset-curing reactions.

(1) **Phenomenological Models** (macroscopic level) assume that there is an overall order of reaction and fit this model to the experimental kinetic data. This type of model provides no information about the kinetic mechanism of the reaction and is predominantly used to provide models for industrial applications.

(2) **Mechanistic models** (microscopic level) are derived from a rather complex analysis of the individual reactions occurring during the cure, and require detailed measurements of the concentrations of reactants, intermediates, and products. Mechanistic models are much more complex than empirical models, but are not restricted by changes in the composition of the system.

Despite the efforts that have been made in recent years, in the exploitation of kinetic models for polymerization of thermosetting resin systems (see Table 1), two main problems still arise:

(1) no general model for the cure mechanisms of all systems is available (although many authors in the past have already searched for a generalized model), and

(2) in many cases, for a given resin system, different models are needed to describe isothermal and nonisothermal experimental condition.

The first problem still represents a severe limitation on the industrial application of any monitoring or control system that requires significant prior knowledge of the cure kinetics, which will affect either the time or cost of production. Acquired thermal data are generally fitted with chose kinetics equation to establish the best set of kinetics parameters to predict the conversion evolution for a generic temperature history at every location.

In Table 2, the most used kinetic equations are reported. Advances in the description of cure kinetics were recently used to model the cure of an RTM epoxy
Table 2. Mathematical Models for Cure of Resins

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Expression</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Order (1)</td>
<td>$\frac{d\alpha}{dt} = A \exp\left(\frac{E_a}{RT}\right)(1 - \alpha)$</td>
<td>$k = \text{Rate constant}$</td>
</tr>
<tr>
<td></td>
<td>$k = A \exp\left(\frac{E_a}{RT}\right)$</td>
<td>$E_a = \text{Activation energy}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A = \text{Rate coefficient}$</td>
</tr>
<tr>
<td>$n$th order (2–4)</td>
<td>$\frac{d\alpha}{dt} = k(1 - \alpha)^n$</td>
<td>$n = \text{Reaction order}$</td>
</tr>
<tr>
<td>Polynomial (5)</td>
<td>$\frac{d\alpha}{dt} = k(a_0 + a_1 \alpha + a_2 \alpha^2)$</td>
<td>$a_0, a_1, a_2 = \text{Constant}$</td>
</tr>
<tr>
<td>Autocatal. −1 (6,7)</td>
<td>$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^n)(1 - \alpha)^m$</td>
<td>$n, m = \text{Reaction orders}$</td>
</tr>
<tr>
<td></td>
<td>$k_1, k_2 = \text{Rate constants}$</td>
<td></td>
</tr>
<tr>
<td>Autocatal −2 (8)</td>
<td>$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha)^n(1 - \alpha)(B - \alpha)$</td>
<td>$n, m = \text{Reaction orders}$</td>
</tr>
<tr>
<td></td>
<td>$k_1, k_2 = \text{Rate constants}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$B = \text{Stoichiometry factor}$</td>
<td></td>
</tr>
<tr>
<td>Mechanistic (9)</td>
<td>$\frac{\alpha}{\alpha_{gel}} = f(\text{concentration})$</td>
<td>$\alpha_{gel} = \text{Conversion at gelation}$</td>
</tr>
<tr>
<td>Self-acceleration (10)</td>
<td>$\frac{d\alpha}{dt} = k(1 - \alpha)(1 - C\alpha)$</td>
<td>$C = \text{Constant}$</td>
</tr>
</tbody>
</table>

resin system by Karkans (11). The kinetics equation used can be stated as

$$\frac{d\alpha}{dt} = k_1(1 - \alpha)^{n_1} + k_1\alpha^{n_2}(1 - \alpha)^{n_1}$$  \hspace{1cm} (4)

where $k_1$ and $k_2$ are kinetic reaction rate constants, having an Arrhenius temperature dependence.

$$K_i(T) = k_i \exp\left(-\frac{E_i}{RT}\right)$$ \hspace{1cm} (5)

and $n_1, m,$ and $n_2$ are the model parameters and $E_i (i = 1, 2)$ the activation energy.

According to the Rabinowitch theory (12) the reaction is driven by two parallel phenomena, the chemical mechanism and the diffusion-controlled mechanism, as

$$\frac{1}{k_i} = \frac{1}{k_c(T_c)} + \frac{1}{k_d(\alpha,T_c)}$$ \hspace{1cm} (6)

where $T_c$ is the curing temperature and $k_d$ is the rate of the diffusion-controlled mechanism based on free volume models as proposed by Simon and Gillham (13).
In the above equation \( b \) is an adjustable parameter to achieve a suitable fit, while the parameter \( f \) encapsulates the driving force of the diffusion-controlled mechanism by means of the Doolittle (14) equation, to model the free volume as follows:

\[
f(\alpha) = (4.8 \times 10^{-4}) [T_c - T_g(\alpha)] + 2.5 \times 10^{-3}
\]  

The diffusion-controlled mechanism occurs during vitrification in the latter stage of the reaction. It is obvious that for a chemical reaction to occur, reactive groups are required to be close to each other and also to be oriented so that eventually the cross-link can be formed. In the early stages of the cure, when the material is very much in a liquid state, the rate of cure is predominantly controlled by chemical kinetics; this essentially means that in the “reaction zone” the temperature of the system is capable of activating a reaction between monomers. Since these processes are very fast owing to the short characteristic times of the liquid state compared to the time of experimental observations, the rate coefficient for the reaction is constant at constant temperature, hence the validity of Arrhenius-type analysis. Theoretical models of this stage of the cure have been extensively discussed by Mita and Horrie (15) using a reptation theory model, and by Rozenberg (16), who also tried to determine the topological area of the reaction associated with reactive groups that are isolated within the gelled structure. Experiments have demonstrated that analytical methods are not sensitive enough to detect these unreacted groups and for this reason it is not possible to evaluate their concentration during the final stages of the curing process. It is clear then, that the overall reaction rate cannot be a function of the temperature alone, but that a dependency on a structural parameter has to be included, which at certain isothermal temperatures will lower the reaction rate, limiting the extent of the reaction.

The glass-transition temperature can be regarded as a suitable structural parameter for following the progressive evolution of the cross-linked system in case of diffusion-controlled mechanism; therefore, a suitable model is needed. The evolution of the glass-transition temperature is modeled according to a widely accepted DiBenedetto equation (17), stated as follows:

\[
T_g(\alpha) = \frac{(1 - \alpha)T_{g0} + \lambda\alpha T_{g\infty}}{(1 - \alpha) + \lambda\alpha}
\]  

where \( T_{g0} \) and \( T_{g\infty} \) are the glass-transition temperatures for the uncured and fully cured resin, respectively; \( \lambda \) is the adjustable parameter for a given resin system. Figure 3 reports the experimental determinate values of the glass-transition temperature along with the found model predictions.

Most of the time, the complete kinetics model can result in a multiparameter model characterized by nonunique set of best parameters. Therefore, reliable
Fitting techniques based on nonlinear least square fitting algorithms are generally required to determine a suitable set of kinetic parameters. Along with traditional techniques, novel programming algorithm techniques, recently widely used to solve complex problems of optimization in the area of industrial engineering, are being used for kinetics model definition. Appreciable results have been achieved using a hybrid algorithm in the case of a complex empirical model characterized by 14 fitting parameters. This two-stage fitting procedure was implemented considering an “evolutionary type” algorithm (genetic algorithm) to identify the most probable region of the minimum for the least square function followed by a traditional non-linear least square method (ie Lavenber–Marquardt) to determine the precise value of each fitting parameter.

Experimental reaction rate profiles as obtained by thermal analysis tests are reported in Figure 4 for different temperature rates. Cure conversion profiles along with kinetics model predictions, respectively, for dynamic and isothermal conditions are given in Figures 5 and 6.

**Shrinkage**

**Thermal Shrinkage.** As for traditional materials, temperature variations during the manufacturing process are associated with local thermal expansion or contraction depending on the sign of the change. For thermosetting systems, it is reasonable to assume that the lower degree of cure leads to a higher mobility of the evolving cross-link structure compared with the fully cured state. Moreover, the content of free volume frozen within the structure will necessarily affect the dimensional stability of the system because of the temperature variation during
the processing. The effects of volume variation related only to temperature change are known as thermal shrinkage.

The evolving structure of the polymeric system can be considered as a “novel” material at each degree of cure as different thermo-mechanical properties are identified. Therefore, coefficients of thermal expansion are necessarily varying with
the degree of cure. A traditional technique which can be used to evaluate the coefficient of thermal expansion at various degrees of conversion is thermomechanical analysis (TMA). Two problems arise when using the TMA procedure:

1. no test can be performed if the specimen is not solid, and
2. post-cure reactions will affect the result above the glass-transition temperature.

Since the equipment to measure the temperature-induced dimension variation employs an LVDT displacement sensor, the requirement of a solid sample is mandatory. The effects of post-cure reaction on the measurement, instead, need much more detail and discussion. For a partially cured thermosetting resin, a post-cure reaction is expected when the actual temperature rises above the corresponding glass-transition temperature, $T_g$. Above this temperature, the volume variation due to post-cure reactions is superimposed upon thermal expansion (18). For this reason, TMA is a technique for measuring the CTE of the partially cured sample that is suitable only within the glassy region ($T < T_g$), while for a fully cured sample useful information can also be obtained for the CTE in the rubbery
Fig. 7. Thermomechanical curve of data obtained for partially cured samples: — sample A; —sample B; — sample C; • sample E.

region. Figure 7 shows TMA curves for partially cured samples A, B, C, and E. In the case of sample A, when the resin approaches the glass-transition region (110°C) it softens and the measured linear dimensional change drops owing to the static holding force applied by the probe to the specimen during the test. To verify that the characteristic inflections shown by the thermomechanical curves for the partially cured samples are respectively due to the glass transition and the simultaneous effects of temperature and post-cure reaction, it seems appropriate to compare DSC and TMA curves for the same sample (see Fig. 8).

Above the glass transition, the material starts to undergo post-cure reactions, so that the linear thermal expansion is attenuated by the contemporaneous chemical shrinkage effect until the post-cure reaction is completed. At the end of the post-cure reaction, the now fully-cured system expands, only because of temperature changes. Penetration of the probe into the top of the resin specimens cannot be excluded. This further condition will be limiting for any further possible analysis of the curves at $T \geq T_g$.

The glassy coefficients of thermal expansion can then be evaluated as the slopes of the thermal volumetric strain vs. temperature curves below the glass-transition temperature (see Fig. 9), defined at the onset of the first step for each curve. For these curves, in fact, the following relationship can be written:

$$\varepsilon_V(T, \alpha) = \frac{(l - l_0)}{l} = \gamma_{CTE}(\alpha) \Delta T$$  \hspace{1cm} (10)

where $\varepsilon_V$ is the thermal volumetric strain, $l$ and $l_0$ are respectively the final and initial sample length; $\gamma_{CTE}(\alpha)$ and $\Delta T$ are the coefficient of thermal expansion and the temperature variation. Experimental value determined for the partially cured
Fig. 8. DSC and TMA thermogram comparison for post-cure effects on dimensional variation: — sample A (TMA); ○, sample A (DSC).

Fig. 9. Glassy CTE values vs. conversion: □, sample A; ○, sample B; △, sample C; ○, sample D; ×, sample E.
Chemical Shrinkage. Chemical shrinkage is the result of a progressive matter densification due to the advancement of the reaction. For the resin matrix, volume variations are measured during cure for different isothermal temperatures. The results compared with experimentally determined degree-of-cure profile allow to evaluate the chemical shrinkage coefficient of the matrix system.

Thermal shrinkage is the most obvious source of the residual stresses generated during the manufacturing process of composite laminates or component parts with a polymeric matrix (19). However, other important factors contribute to setting up of residual stresses, or the warpage or poor quality of the manufactured composite part and so need to be investigated. With special reference to composites with a thermosetting matrix, chemical shrinkage comes up as one of the most important factors that need to be taken into account. In fact, organic thermosetting polymers, of the type currently used as a matrix for polymer composites, undergo volumetric changes as a result of the polymerization reaction. Typical values of volumetric shrinkage during cure are 1–5% for epoxy (20) resin and 7–10% for polyester resins (21); however, some thermoplastic polymers may exhibit some degree of crystallization as the matrix cools down from the forming temperature to room temperature, resulting in a volumetric shrinkage of 2 to 36% (22).

Table 3 reports reproducible data for volumetric shrinkage obtained from dilatometric experiments (21,22,24). Modelling of chemical shrinkage, therefore, is of particular relevance for a correct analysis. The absolute volumetric change in a cubic element can be modeled as follows: Considering the dimensions of the cube to be \( l_1, l_2, l_3 \) and their relative finite changes as \( \Delta l_1, \Delta l_2, \Delta l_3 \), the absolute...
Table 3. Shrinkage Measurements on Epon 828 Cured with Different Curing Agents, TETA and DTA

<table>
<thead>
<tr>
<th>System</th>
<th>Gel time, min</th>
<th>Volume shrinkage after gelation %</th>
<th>Total volume shrinkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 phr Triethylenetetramine (TETA), cure at 65°C</td>
<td>116</td>
<td>2.31</td>
<td>5.72%/24 hr.</td>
</tr>
<tr>
<td></td>
<td>112</td>
<td>2.29</td>
<td>5.72%/24 hr.</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>2.34</td>
<td>5.79%/24 hr.</td>
</tr>
<tr>
<td>Diethylenetriamine</td>
<td>130</td>
<td>2.08</td>
<td>4.33%/48 hr.</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>2.00</td>
<td>4.33%/48 hr.</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>1.96</td>
<td>4.21%/48 hr.</td>
</tr>
</tbody>
</table>

*From Ref. 23.

volume change is

\[ |\Delta V^r| = V_{\text{final}} - V_{\text{initial}} = [(l_1 + \Delta l_1)(l_2 + \Delta l_2)(l_3 + \Delta l_3)] - (l_1l_2l_3) \]  

(11)

On dividing by the total unit volume of the element, equation 11 can be expressed in terms of the strain components as follows:

\[
\frac{\Delta V^r}{V^r} = \epsilon_1 + \epsilon_2 + \epsilon_3 + \epsilon_1\epsilon_2 + \epsilon_2\epsilon_3 + \epsilon_1\epsilon_3 + \epsilon_1\epsilon_2\epsilon_3
\]

(12)

where \( \epsilon_i \) for \( i = 1, 2, 3 \) represents the general strain component in the principal direction.

Assuming that the volumetric shrinkage is isotropic, and neglecting all higher order terms, the strain, \( \Delta \epsilon^r \) corresponding to volume resin shrinkage, \( |\Delta V^r| \), can be written as

\[
\Delta \epsilon^r = \frac{1}{2} \left( -1 + \sqrt{1 + \frac{3}{4} \Delta V^r} \right)
\]

(13)

Although dimensional changes are important in such operations as designing tooling for processing plastics or achieving the tolerances required in electronic and computing applications, and in encapsulating and laminating processes, these dimensional changes are not as important in themselves as they are in determining the stresses set up in the cured resin as a result of chemical shrinkage. When these aspects of polymerization shrinkage are considered, it becomes apparent that from the practical point of view the most important phase of the shrinkage to predict (and, hopefully, to control) is that occurring after gelation. If it is possible to locate on the shrinkage/time curve the point of gelation, then data on shrinkage after gelation become directly available. Shrinkage after gelation is minimized when gelation occurs late in the curing reaction, since constrained conditions arise just at the end of the curing process, thereby reducing the length of the crucial stage during which residual stresses can be set up. Lascoe (25) has reported a very comprehensive study on the volume and linear shrinkage of an epoxy resin system.

Interpolated dilatometric curves obtained during isothermal cure at different temperatures, \( T = 120, 130, 140, 150, \) and 160°C, are reported in Figure 11. Results
Fig. 11. Linear interpolation of acquired data of specific volume variation during cure at different isothermal temperatures.

have shown that the densification due to polymerization reaction (see Fig. 12) is a linearly dependent phenomena, by a factor of 0.054.

Thermomechanical Properties

The evolution of conversion, $\alpha$, gives rise to a progressively stiffer material. The passage from a liquid-like to a solid-like material can be suitably described by relaxation modulus as a function of the degree of conversion and temperature.

Fig. 12. Linear profile of specific volume change vs. degree of cure.
Mapping the relaxation modulus in each body point then requires the experimental evaluation of such quantity.

The data can be obtained from dynamic mechanical analysis (DMA) tests used to construct the stress relaxation master curves at different levels of conversion, within the frame of time-temperature superposition principle. Curves of stress relaxation modulus can be modeled using the stretched Kohlrausch–William–Watts (KWW) exponential function at each level of conversion, as follows:

\[ E(t, T, \alpha) = E_{\infty}(\alpha) \exp \left[ -\left( \frac{\xi(t, T, \alpha)}{\tau_p(\alpha)} \right)^{\beta(\alpha)} \right] \]  

(14)

where \( E_{\infty} \) indicates the fully relaxed modulus and \( \tau_p \) and \( \beta \) are the KWW model parameters. The functionality of the ultimate modulus and the KWW parameters over the degree of conversion is related to the physical assumption to consider as a “new material” the system at each level of conversion. A linear function was found satisfactory to model the nonexponential parameter \( \beta \) vs. conversion; Mijovic and co-workers (26) established the same linear dependency applied to dielectric constant decay function. Assuming that the molecular mobility influences the glass transition through the same mechanism that controls the stress relaxation function, then the behavior of the glass-transition temperature at a fixed degree of cure can be normalized with respect of its value for a given conversion. This normalization will lead to the definition of a potential function, which is identical to that obtained by normalizing in the same way the characteristic relaxation times with respect to the relaxation time at the same fixed conversion. From the mathematical point of view, it can be stated that

\[ \frac{T_g(\alpha)}{T_g(\alpha_{\text{ref}})} = g_{T_g}(\alpha) \]  

(15)

where \( T_g(\alpha) \) is the glass-transition temperature as a function of the degree of cure, and \( T_g(\alpha_{\text{ref}}) \) is the particular value for the fixed conversion. If the same mechanism drives the change in normalized relaxation time, then it follows that

\[ \frac{\tau_p(\alpha)}{\tau_p(\alpha_{\text{ref}})} = g_{\tau_p}(\alpha) \]  

(16)

and therefore,

\[ g_{T_g}(\alpha) = g_{\tau_p}(\alpha) \]  

(17)

where \( \tau_p(\alpha) \) is the relaxation time expressed as a function of the degree of cure, and \( \tau_p(\alpha_{\text{ref}}) \) is the value for the fixed conversion \( \alpha_{\text{ref}} \). Figure 13 shows good correlation between the normalized principal stress relaxation time and the normalized value of the glass-transition temperature. Using the transformed KWW model, stress relaxation modulus can be predicted over the whole range of conversion according to the kinetics model at each material point. Figure 14 reports the KWW model prediction for different levels of conversion.
Fig. 13. Normalized values of single relaxation time vs. conversion, compared with normalized values of glass-transition temperature obtained experimentally by thermal analysis as well as torsional rheometry. Predictions of DiBenedetto-type model are also shown (solid line): ——— DiBenedetto model; •, log [tau]/log [tau (0.96)]; ⋄, DSC \( T_g \) measurements.

Structural Relaxation

When a material is cooled from above to below \( T_g \), the resulting glass is unstable and its density will gradually increase with time. This process toward thermodynamic equilibrium (called structural relaxation or generally physical aging)

Fig. 14. KWW model prediction for the whole range of conversion: ■ 0.1; ▲ 0.2; ×, 0.3; —— 0.4; •, 0.5; +, 0.6; –, 0.7; —, 0.8; ◦, 0.9; □, fully cured.
occurs more rapidly at temperatures close to $T_g$, being an activated phenomenon, and manifests itself through a continuous change of a large number of properties including but not restricted to density, enthalpy, entropy, and consequently all the related viscoelastic functions. The structural relaxation cannot be avoided; it occurs in all glasses even when cooling is performed such that the temperature gradients over the material are small and the resulting thermal stresses are negligible.

The structural relaxation is a direct consequence of the considerably longer time scale of molecular relaxations within and below the glass-transition region compared to the experimental time scale of the applied signal. In other words, even the slowest experimentally attainable cooling rate is much too fast for the polymer chains to relax to equilibrium. The nonequilibrium structure first experiences an abrupt contraction and then undergoes a time-dependent rearrangement toward the equilibrium state. Monitoring the kinetics of any structure-sensitive property changes such as enthalpy or specific volume can follow the gradual rearrangement of the non-equilibrium structure. The multi-parameter phenomenological model for structural relaxation based on the Tool–Narayanaswamy–Mohinyan (TNM) theory was largely utilized in the literature for a number of organic and inorganic glasses.

In principle, the knowledge of TNM model parameters allows the prediction of volume as well as enthalpy relaxation under arbitrary thermal histories. As such, the volume as well as enthalpy fluctuations, which arise when polymers are cooled from the molten rubbery state, can be calculated at each body point provided the local thermal history is known.

Typical experimental volumetric and calorimetric data obtained under different thermal histories are shown in Figures 15 and 16 for given thermal histories (details of the numerical procedure are given in Reference 27). The key parameter of the modeling procedure based on TNM phenomenological approach, is the fictive temperature, $T_f$. As discussed in the above-cited references, $T_f$ can be conveniently

![Figure 15](image_url)

**Fig. 15.** Experimental specific volume ($V$) vs. Temperature ($T$) data during a cooling scan at $1^\circ$C/min (open circles) and the corresponding model predictions (full lines) at different cooling rates: $\circ$, 10000°C/min; $\square$, 1000°C/min; $\diamond$, 100°C/min; $\times$, 10°C/min; $+$, 1°C/min.
regarded as a measure of the actual structural state. Mathematically it is defined as

\[ \int_{T}^{T_{f}} \frac{\partial(P - P_{g})}{\partial T} \, dT = \int_{T_l}^{T_{f}} \frac{\partial(P_{e} - P_{g})}{\partial T} \, dT \]  

(18)

If \( P \) represents the specific volume \( V \), then taking the derivatives of both sides of equation 8 it can be written,

\[ \frac{dT_{f}}{dT} = \frac{\alpha_{v} - \alpha_{v_{g}}}{\alpha_{l} - \alpha_{g}} = \frac{dV^{N}}{dT} \]  

(19)

where subscripts \( l \) and \( g \) stand for liquid and glassy state, respectively and \( \alpha_{v} \) represents the temperature derivative of specific volume. The variation of the normalized functions are described by a relaxation function \( \phi(t) \). The most widely used relaxation function is the so-called stretched exponential equation, which is related to the structural sensitive property \( P \) according to the following equation

\[ \phi(t) = \frac{P - P_{e}}{P_{o} - P_{e}} = \exp \left[ - \left( \int_{t_{o}}^{t} \frac{dt'}{\tau} \right)^{\beta} \right] \]  

(20)

In equation 16, \( t' \) is the time when the change in temperature occurs, \( \beta \) is the exponent, and \( \tau \) is the characteristic relaxation time. Nonexponentiality (memory effect) is reflected in the value of \( \beta < 1 \). When treating nonisothermal situations (arbitrary thermal history) the relaxation function can be represented by the superposition of responses to a series of temperature jumps constituting the actual thermal history. The fictive temperature is defined as the actual
non-equilibrium parameter and takes on the following form:

\[ T_f(T) = T_0 + \int_{T_0}^{T} \left\{ 1 - \exp \left[ -\left( \int_{t(T)}^{t(T)} \frac{dt}{\tau} \right) \right] \right\} dT' \]  

(21)

with \( T_0 \) being the initial temperature. The next input needed by the model is an expression for the structural relaxation time \( \tau \), which appears in equation 6. Following Tool’s original work, various expressions for the structural relaxation time have been proposed, all in exponential form and containing temperature and fictive temperature as variables.

The Narayanaswamy–Moynihan (NM) expression has the following form:

\[ \tau = A \exp \left[ \frac{x}{\Delta h^*} (1 - x) \frac{\Delta h^*}{RT} \right] \]  

(22)

where \( \tau \) is the structural relaxation time, \( A \) is a constant (preexponential factor), \( \Delta h^* \) is the characteristic activation energy, and \( x \) the partitioning parameter (0 < \( x < 1 \)) that defines the degree of nonlinearity.

The experimental data of Figures 15 and 16 can be utilized to find the optimum set of parameters (\( A, \Delta h^*, x, \beta \)) that best describes the behavior of the material functions in the glass-transition region. From Figure 17 the coefficient of thermal expansions for a given temperature history (and, therefore, for a given body point during the cooling process) can be obtained.

![Fig. 17. Model prediction of coefficient of thermal expansion (CTE) as a function of temperature (T) at different cooling rates: ◦, α-10000 C/min; □, 1000 C/min; ▼, 100 C/min; ⋄, 10 C/min; ×, 1 C/min.](image)
**Submodels**

**Resin Flow Submodel.** Resin flow analysis in a manufacturing process provides estimates of resin flow, and fiber and resin distribution and compaction. In the early stage of the autoclave process, after the prepregs are staked and vacuum bagged, the system is pressurized while the temperature is increased in order to minimize the resin viscosity. In this way the resin flow removes the excess resin from adjacent plies and makes uniform the fiber distribution. In the RTM process the dry fibers inside the mold can be considered as a porous medium through which the resin is injected from a single or multiple inlets: Darcy’s law can be used to perform a two-dimensional flow analysis. Darcy’s law can be written as

$$
\begin{bmatrix}
u(x, y) \\ u(x, y) 
\end{bmatrix} = - \frac{1}{\mu} \begin{bmatrix}
k_{xx} & k_{xy} \\ k_{yx} & k_{yy}
\end{bmatrix} \begin{bmatrix}
\frac{\partial P(x, y)}{\partial x} \\ \frac{\partial P(x, y)}{\partial y}
\end{bmatrix}
$$

where \(k_{ij}\) is the generic component of the permeability tensor, \(\mu\) is the viscosity, \(P\) is the pressure, and \(v\) and \(u\) are the components of the velocity in the \(x\)- and the \(y\)-directions, respectively. If the resin is considered to be an incompressible fluid then the continuity equation can be reduced to the following form:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad (24)$$

and the mass balance in an RTM process assumes the following form, provided the directions \(x\) and \(y\) coincide with the principal directions of the fiber perform/matt (28).

$$\frac{\partial}{\partial x} \left( \frac{k_{xx}}{\mu} \frac{\partial P}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{k_{yy}}{\mu} \frac{\partial P}{\partial y} \right) = 0 \quad (25)$$

In autoclave forming the main resin flow is normal to the tool surface and Darcy’s law is again used but in its one-dimensional form:

$$V = - \frac{S}{\mu} \frac{dP}{dz} \quad (26)$$

where \(S\) is the apparent permeability and \(z\) is the direction normal to the tool.

Resin flow parallel to the tool plate takes place along the parallel and perpendicular fiber directions. Between the two mechanisms, the resin flow along the fibers is the most prominent as, in fact, the flow perpendicular to the fibers is small because of the resistance created by the fibers.

The flow along the fiber direction can be modeled as a channel flow (the viscous flow between two parallel plates). Loss and Springer (29) validated thermomechanical models, including the chemorheological behavior of resin and resin flow models.
**Void Growth Model.** The resin flow during composite processing inevitably leads to the formation and growth of voids. Although all the manufacturing processes of composite materials are based on solid engineering principles, current technologies cannot assure a part-by-part reliability required by the production and assembly of the parts for a complex and larger composite structure. For thick composite parts (30) the occurrence of voids has been widely verified and their detrimental effects proved. The void formation necessarily occurs during the fabrication process and involves the different concurrent phenomenology of heat, mass, and momentum transfer. An even more complex scenario comes out considering that polymerization reaction occurs for the matrix while thermomechanical properties are varying with time, temperature, and degree of conversion. In some cases the system can be considered multiphase.

The correct mechanism of void formation is related to the system being used and to the specific manufacturing process. Even when a part appears to be fully impregnated by the resin and the resin matrix has been previously degassed at the prescribed temperature, in order to eliminate mechanically entrapped air bubbles, void formation still occurs. During a general manufacturing process the voids can be formed either by the mechanical entrapping of air or by a nucleation process. In the first case, it can be related to gas bubbles associated with the mixing operation of the resin bulk, by bridging of particles of additives, by air and wrinkles when the lay-up sequence is built, or by the resin flow during tow impregnation. Particularly important for injection type processes (like RTM, injection molding, or resin film infusion) this latter mechanism leads to the formation of microvoids and consequently dry spots within the low-permeability area of the perform. Schematically, the voids formation associated with the resin flow can be divided in to four stages, as follows:

1. the flow reaches the tow to be impregnated,
2. the flow front comes around the tow or bundle and it passes,
3. still the resin has to penetrate and fill the space inside the tow among the different fibers, and
4. air voids remain inside the tow and eventually move in the resin between tows owing to the high pressure acting on the tow.

Modeling of void formation is intimately related with cure kinetics and viscosity profiles of the resin system. For modeling purposes it can be conveniently divided into three different phases:

1. formation and stability of the forming voids,
2. void growth and/or dissolution by diffusion, and
3. void transport process.

A nucleation process is generally described assuming the initial formation of the voids to be in accordance with the classical nucleation theory. It can be assumed that nucleation occurs between resin and fiber or resin and added particle (heterogeneous nucleation) or within the resin itself (homogeneous nucleation).
Application of classical nucleation theory (31) leads to favorable results, especially for the case of homogeneous nucleation, for which critical size nuclei can be formed at rate $N$, given by the following equation:

$$
N = \left[ \frac{P^*}{\sqrt{2\pi M kT}} \right] 4\pi^2 \exp\left( -\frac{\Delta F}{kT} \right)
$$

(27)

where $P$ stands for the total water plus air pressure, $M$ is the molecular weight of the vapor phase, $n$ the molecular density in the formed nuclei, $\Delta F$ the maximum free energy for the nucleation process, and $k$ and $T$ are respectively the Boltzmann constant and the absolute temperature. When the nuclei are formed, several factors determine the stability and the growth of the voids. Changes in temperature and pressure cause an increase in the solubility in the resin leading to the dissolution of the voids. Generally, a void becomes stable when its inner pressure equals or exceeds the surrounding resin hydrostatic pressure plus the surface tension forces. This condition can be stated as follows:

$$
P_v - P_{sr} = \frac{\gamma_{r-v}}{R_{v-a}}
$$

(28)

where $P_v$ and $P_{sr}$ are respectively the void and resin pressure, $\gamma_{r-v}$ is the resin–void surface tension, and $R_{v-a}$ is the ratio of the volume and surface of the voids. As the temperature and pressure change with time, from a product-quality point of view it is most important to model the time-dependent growth process.

This phenomenon, however, would require the solution of many time-dependent and coupled partial differential equations, which would result in too difficult an approach. To overcome the intrinsic difficulties related to changes physical properties and the excessive computational time of the equation solver, two “equivalent” physical schemes are generally studied assuming that the void growth perpendicular to the ply (critical capillary scheme) or through an isotropic pseudo-homogeneous medium where the growth occurs not preferentially perpendicular to the plies. This latter approach seems to be more realistic considering the physical possibility of pure water vapor growing for diffusion into the surrounding resin or into a void initially consisted of entrapped air and it become equivalent to bubble growth in a liquid medium.

The main assumptions in building a general void growth model are

(1) the voids remain between two plies and move with respect to the fixed coordinates system in the laminate;
(2) the voids are considered spherical and their characteristic dimension is calculated based on an equivalent sphere;
(3) no interactions between two voids are considered;
(4) during the lay-up process and at the beginning of the cure process, void nucleation occurs almost instantaneously;
(5) temperature and moisture concentration are time independent; and
(6) the void growth is limited by the flow rate of arrival of the diffusing species.
Structural Analysis

The complex interactions between material property evolution and the manufacturing stages represent a critical issue for correct part design and for controlling the entire production process. In order to evaluate the integrity of the manufactured part, a structural analysis needs to be performed to simulate the effects of mechanical, nonmechanical, and geometric part constraints due to the manufacturing tools utilized during the specific process.

Modeling of the coupled transfer phenomena (mass, heat, and momentum) need to be solved considering appropriate constitutive equations for the evolving properties in order to optimize the integrity of the final material system and at the same time to control the final shape of produced composite element.

If, as we can recognize, the curing process involves thermal variations from room temperature to cure temperature, then thermal expansion is a necessary part of that process. A common hypothesis has been proposed in past papers (32–36) to simplify the complex phenomenology, that is, no stresses develop prior to completion of the curing process.

Even if it is possible to obtain good results using a simulation model, in which it is assumed that the crucial stage for formation of residual stresses is the period of cooling from cure to ambient temperature, recent work has demonstrated that the residual stress formation mechanism is strongly influenced by the overall curing process (37–43). Moreover, using this approach, the phenomenon of structural relaxation, which occurs near the glass-transition region of the developing structure, is not considered at all. The above phenomena needs much more effort in order to be well quantified and eventually taken into account. In fact, these chemical/physical changes cause more deformation in the transverse directions than in the longitudinal direction since resin-dominant properties are experienced within the ply in that direction.

Mechanical Tests: Review

Mechanical tests for advanced composite materials conform in many respects to the conventional test typology used for traditional isotropic materials. Despite the complication associated with the heterogeneity of composite systems, the interface between fiber and matrix, and the anisotropy at the micro- and macroscopic levels, the same characteristic property definitions generally used for conventional materials can be identified for these novel materials. In some cases additional constants are required and some differences in nomenclature are introduced especially when no isotropic counterpart exists.

Mechanical characterization of composite materials is a complex scenario to deal with, either because of the infinite number of combinations of fiber and matrix that can be used, or because of the enormous variety of spatial arrangements of the fibers and their volume content. The foundation of the testing methods for the measurement of mechanical properties is the classical lamination theory; this theory was developed during the nineteenth century for homogeneous isotropic materials and only later extended to accommodate features enhanced by
fiber-reinforced material, such as inhomogeneity, anisotropy, and anelasticity. Two basic approaches are proposed to determine the mechanical properties of composite materials: constituent testing and composite sample testing.

Academically, composite constituents could be tested separately and then composite properties evaluated by simple or more complex mixture rules according to the wanted level of accuracy. Many references can be found in the literature for this approach. Mechanical properties of composites are generally assumed to be dependent on the following variables:

1. properties of the fiber,
2. properties of the matrix,
3. properties of any other additive or phase constituting the composite,
4. volume fraction of the fiber,
5. spatial distribution of the fiber (or a third phase), and
6. nature of interface.

From a strictly theoretical point of view, the so-called constituent testing approach or micromechanics approach is the most valuable. Tests performed on composite constituents supply the required material constants of each phase of the composite material—namely for long-fiber-reinforced composite—for the fiber and the matrix, to use in appropriate mixture rules. These rules obtained by physical and mechanical considerations are the basic relationships between the composite constituents, and they leads to a complete characterization of the final composite.

Fibers can be tested in the form of single fiber, tow, or fabric; all tests can be grouped into three main categories:

1. Chemical Tests. They are generally used for elemental analysis and surface investigation. Following is a list of the most important chemical tests:
   a. X-ray photoelectron spectroscopy (XPS)
   b. Low-energy electron diffraction (LEED)
   c. Scanning Electron Microscopy (SEM)
   d. Carbon assay (CA)
   e. Fourier transform infrared spectroscopy (FTIS)
   f. Sizing Content (SC)
   g. Thermal desorption mass spectrometry (TDMS)
   h. Auger electron spectroscopy (AES)
2. Physical tests. They are generally performed to measure different physical properties for fiber and for fabric. Properties of interest required for specific application design are
   a. Density (ASTM D792 using displacement, ASTM D3800 based on Archimedes principle and ASTM D1505 by means of density gradient column)
   b. Weight per length, typically in g/µm
   c. Weight per unit area or aerial weight, reported in g/m²
d. Filament diameter measured by microscopy image according to the standard ASTM D578

e. Electrical conductivity

f. Thermal expansion

g. Number of twists

h. Tensile strength (ASTM D579)

(3) Mechanical test. It is important to point out that these mechanical tests are chosen based on whether the fiber sample is single fiber, tow, or fabric. For this reason, it is extremely important to define the specific fiber sample typology used during the tests when a mechanical test campaign is started. The main mechanical tests generally performed are

a. Single-filament tensile test [ASTM D3379 (44)]
b. Tensile test for tow [ASTM D4018 (45)]
c. Tensile test for dry fabric [ASTM D579 (46)]

For resin matrix, several tests (chemical, physical, and mechanical) are generally performed by the supplier; their results are used not only for design but also for processing control and optimization. Along with traditional tests, some specific procedures, such as stress relaxation or creep, are considered if viscoelastic effects are investigated. The experimental setup for the stress relaxation test is shown in Figure 18; while stress relaxation raw data, for an epoxy-toughened resin matrix used for aerospace structural composite materials, are reported in Figure 19. Despite the fact that testing of a single constituent could eliminate inherent difficulties related with material handling, this approach is not representative of composite performance; in fact, many factors associated with the manufacturing process and the realistic arrangement of the fiber into the composite system are not taken into account as modeling assumptions are necessary even in the case of more complex schematization.

The second approach, which determines the mechanical properties of the composites by directly testing a composite laminate, is a much more straightforward procedure, widely implemented to determine composite properties required for analysis and design. The whole philosophy of testing a laminate of composite material is essentially based on the classical laminate theory. CLT employs elasticity theory to derive the basic relationships between stress and strain and, therefore, to identify material properties. These relationships are quite simple for traditional homogeneous and isotropic materials, however, for composites they can be either extremely complex or, in some case, these equations are imperfect “tools” for modeling (ie it is not possible to estimate the stress state at the tip of a crack by classical laminate theory). Static and fatigue tests are generally performed on composite laminates as well as on traditional systems; for these novel materials, however, some new test typologies need to be introduced to evaluate specific properties or to describe particular failure modes not shown by traditional materials. Despite inherent imperfections and simplifications, the existing formal framework contains justification for the various constraints and stipulations that have been imposed on test configurations and procedures for long-fiber composites.
The principal features and precautions arising from the testing of long-fiber composites are in relation to

(1) generation of uniform stress in the critical reference volume,
(2) avoidance of overwhelming “end-effects,”
(3) tension-shear coupling effects,
(4) adequate loading levels to avoid failure or damage at loading points, and
(5) appropriate sample dimensions compared to the scale of structural inhomogeneity.

Even though the inhomogeneity and anisotropy of composite materials give rise to various additional configurations, the above precautions apply similarly to the testing of homogeneous isotropic materials.
Specimens for mechanical tests on composites are usually taken in three different forms: pultrusion, filament-wound tubes, and flat sheet. For each form, tests can be performed on the entire sample or on coupons of given fixed dimensions. It is extremely important to notice that the first two forms are generally considered for their convenience of fabrication and also because for composite materials, the specific manufacturing process employed strongly influences the final performance of the material in its final application. Therefore, testing on the “realistic” configuration leads to more reliable results in terms of mechanical characterization. Commercially available flat sheets are in the form of randomly oriented fiber, various sequences of UD or woven laminate and sandwich structures. The mechanical properties of these items as well as of the extracted coupons vary with the stacking sequence, the alignment of the specimen’s axis in relation to the pattern of the fiber and with the in-plane position of the specimen.

To evaluate the performance of a composite or for a general characterization of a composite system, the following mechanical properties are generally investigated:

1. Uniaxial tensile modulus
2. Tensile strength
3. Uniaxial compression modulus
4. Compressive strength
5. Flexural modulus
6. Flexural strength
7. In-plane shear modulus
8. Lateral contraction ratios
Table 4. Mechanical Testing Plan for Mechanical Characterization of Composite for Aeronautical Applications

- Tensile strength at room temperature
- Uniaxial compression at room temperature
- Interlaminar shear at room temperature
- Open hole tension at room temperature (see Fig. 19)
- Open hole compression at 93 °C
- Hot/wet compression strength
- Edge-plate compression strength after impact, at room temperature

(9) Apparent interlaminar shear strength
(10) Facture toughness

With time, an extensive variety of test methods and procedures have been introduced to develop new applications of composite materials and more in general to sustain the diffusion in various fields of these novel materials. However, the complexity of the properties, the great variety of their applications, and the diversity of their features compared with traditional materials have resulted in the developments, often arbitrary and in some cases more specific, to satisfy particular sectors of the industry.

No single organization or industry is likely to carry out a general investigation program to identify a general routine procedure for mechanical characterization of composite materials, supported by solid theoretical considerations. In order to satisfy the various downstream requirements, which vary from company to company, different test programs have been stipulated. In USA, a large commercial airplane has proposed the test program reported in Table 4 as fundamental for the “initial” evaluation phase of composites, which differs from the test plan identified by U.S. automotive industries, whose test plan is reported in Table 5.

For composite materials, the exposure to critical environment is also an important issue; therefore while selecting an appropriate test method for evaluating composite mechanical properties the extreme conditions experienced during service for a particular application must be taken into account. Environmental exposure can be “accidental” during the specimen preparation and instrumentation, or “planned” to investigate the moisture effect, chemical attack, or cycling

Table 5. Mechanical Test Program Agreed by Important Automotive Manufacturers

- Elastic and strength properties at temperature in the range 40–150 °C
- Effect of loading rate on tensile and compressive properties in the range 0.00167–16.7 s⁻¹
- Creep
- Creep and stress relaxation
- Residual strength after fatigue
- Fatigue
- Effects of notches and holes
- Energy absorption after impact
- Manufacturing effects
- Joints and fastener characterization
temperature. In both cases, extensive and very expensive tests are performed to assess the performances of the composite material during service at these extreme conditions.

In 1987, a survey (47) of currently available mechanical standardized tests concluded that the existing standardized, semistandardized, or available procedure were deficient in respect to three main aspects:

1. too many variants were used for a single test and there was no evidence of the effects of the variation of generated data on reliability,
2. some tests were not fit for their intended purpose, and
3. some important phenomena were neglected either because they were not properly understood or because they were too time-consuming to assess.

The above-mentioned report has attributed this state of the art to poor interactions between academy and industry and to the failure to establish an adequate common infrastructure among composite experts and manufacturers. In the last few years, many laboratories in the area of composite materials have launched inter-laboratory testing programs to establish common procedures for investigation of mechanical properties by various techniques. Many round-robin test programs (48–54) are still running in the area of interlaminar fracture mechanism on composite laminate fracture toughness of new 3-D-reinforced-fiber materials, dynamic mechanical analysis, through thickness crack propagation test, and fatigue tests. These research programs aim either to harmonize or to build a common framework for parameters acquisition to be used for the analysis and design of high quality composite structure.

Following is a list of the main testing mode adopted to characterize advanced composite materials along with reference standards:

1. Tension: ASTM D3039, BS 2782-320, CRAG 300-301, CRAG 302, and ISO 572
2. Compression: ASTM D695M, ASTM 3400, and CRAG 400
3. Shear: ±45° tension test, 10° off-axis test, rail shear test, V-notched beam test, plane-twist test, and torsion of thin-walled sample
4. Flexure: ASTM D790M-93, CRAG report 88012, BS2782-1005, and ISO 14125
5. Through-thickness testing: BS EN ISO 14 and 130, ASTM D3846, and ASTM D 5379
6. Interlaminar fracture toughness
8. Fatigue

Structural tests on real-scale elements are also performed to validate the design criteria and manufacturing settings as a final verification of the desired components. In Figure 20, a typical test is shown for a real-scale composite panel for aeronautical applications. The panel is loaded in shear mode under both static and dynamic conditions.
Fig. 20. Structural mechanical test on real scale composite panel for aeronautical application.

**BIBLIOGRAPHY**


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