CHAPTER 4 MATRIX CHARACTERIZATION

4.1 INTRODUCTION

The function of the matrix in a composite is to hold the fibers in the desired position, and to provide a path for introducing external loads into the fibers. Since the strengths of matrix materials are generally lower than fiber strengths by an order of magnitude or more, it is desirable to orient the fibers within a composite structure so that they will carry the major external loads. Although the success of composites is largely due to this ability, the strength and other properties of matrix materials cannot be ignored. Matrix material properties can significantly affect how a composite will perform, particularly with respect to in-plane compression, in-plane shear, resistance to impact damage, and other interlaminar behavior, and especially when exposed to moisture and elevated temperatures.

A wide range of polymeric resin systems are used as the matrix portion of fiber reinforced composites. These systems generally fall into two broad categories: thermoplastic materials and thermosetting materials. The thermoplastics are non-reactive solids designed to soften, melt, and intimately infiltrate reinforcement fiber bundles at appropriate processing temperatures and pressures, and to solidify into a desired shape upon cooling. Thermosets are reactive materials comprised of organic resins and other constituents required for chemical “curing.” They may exist in various forms (liquid, solid, film, powder, pellets, etc.) in the uncured state, and may be partially reacted prior to combining with the reinforcing fibers. During composite processing they react irreversibly to form solids. In addition to the organic constituents, thermoset systems may also contain additives such as catalysts, fillers, and processing aids, which may be inorganic or contain metals. Thermoplastic or elastomeric fillers may also be incorporated. Due to their reactive nature, most uncured thermosets must be stored under refrigeration, although some multi-part systems designed for component mixing just prior to use may not require cold storage. Both thermoplastics and thermosets can be used to preimpregnate reinforcing fibers to produce prepreg, while processes like RTM (resin transfer molding) are generally more suited to thermosets.

This chapter focuses on methods of testing and characterizing matrix materials and their constituents. Chemical, physical, thermal, and mechanical properties are considered, as well as methods for test specimen preparation and environmental conditioning of test specimens. Tests of thermosets (in both the cured and uncured states), and thermoplastics are addressed.

The properties covered in this chapter will largely be of interest to resin formulators and material suppliers. The composite end user will also find some matrix properties useful, particularly for process cycle development and, to a lesser extent, for initial screening and material selection. A number of matrix properties and tests are also applicable to quality assurance, especially if resins are purchased separately from the reinforcement for use in RTM or similar processes.

4.2 MATRIX SPECIMEN PREPARATION

4.2.1 Introduction

Specimens of unreinforced (neat) matrix material are required for physical and/or mechanical characterization of these polymers in the solid (cured) state. Methods available for specimen preparation are strongly dictated by the type of matrix material being studied. Primary variables include thermoset vs thermoplastic, viscosity at various processing stages, processing temperature, amount of volatiles evolved, and degree of brittleness in the fabricated state. When working with uncured polymers, personal safety is always a concern, and the appropriate Material Safety Data Sheets (MSDS) should be consulted.

4.2.2 Thermoset polymers

Thermoset polymers of interest, i.e., those used as matrices in composites, are typically of sufficiently low viscosity at some point during the cure process to flow. Thus, they may be cast into plate forms to provide blanks from which finished specimens can be machined, or molded into even more complex geometries if necessary to create net- dimension specimens directly.

When casting neat (unreinforced) polymers for use as mechanical test specimens, it is critical that voids, inclusions, and similar defects be minimized, both in size and number. Most thermoset polymers used as matrices, even those considered to be toughened, tend to be relatively brittle, and thus their ultimate strengths are strongly dictated by critical flaw size.

Inclusions can be present in impure resin as obtained from the supplier, or introduced during the fabrication process (e.g., inadequately cleaned molds, airborne dirt particles, inadequate mixing of components, etc.). Caution also must be exercised when using release agents, to avoid contamination of the polymer.

Defects can be in the form of surface scratches, edge chips, and mold marks. Voids are typically caused by trapped volatiles which evolve during the initial stages of the curing process. The evolution of volatiles can be suppressed, or at least minimized, by subjecting the polymer to pressure during the curing process. However, it is more common to apply a vacuum during the initial stage of the cure cycle, either while the polymer is still in the mixing container or already in the mold. This is done at one or more points in time as the temperature is being elevated, and while the viscosity is at its lowest. Thus, a vacuum oven is useful.

The vacuum can evoke a strong evolution of volatiles, requiring that the container or mold have sufficient volume to contain the frothy polymer until the gas bubbles burst. If a single flat panel is to be fabricated, a simple box mold consisting of five steel plates, viz., a bottom and four sufficiently high sides, held together with screws, works well. This box can be disassembled after cure, for ease of polymer matrix plate removal, and easy clean-up. Individual strips of polymer can also be made in this manner, by placing thin steel strips of width equal to the desired polymer matrix specimen width upright on one long edge, spaced apart to the desired polymer specimen thickness.

Since volatiles are being evacuated, the vacuum pump itself should be protected, by the use of a cold trap to condense these vapors before they pass through the pump.

If a cavity mold is being used to produce individual specimens of net dimensions, an elastomeric funnel works well to contain the volume of volatiles; the polymer will flow back down into the mold as the bubbles collapse. The funnel can then be left in place during the remainder of the cure. During clean-up, the funnel can be flexed to easily remove the cured polymer residue on it.

The individual specimen cavity molds can be fabricated of metal, usually steel rather than aluminum because of its lower thermal expansion and higher surface hardness. These are typically two-piece split molds, to permit cured specimen removal. Elastomeric molds, themselves easily fabricated by casting around a permanent pattern, are an attractive alternative. The cured mold can be slit along its length to remove it from around the pattern, this slit also permitting it to be later pried open to easily remove the polymer specimen cast in it. In any case, the individual specimen molds are typically ganged together for efficiency. The as-molded specimens are ready for testing with little or no further preparation. At most, and primarily for aesthetic reasons, the mold seam(s) may be lightly sanded off.

If vacuum is not being subsequently used to remove volatiles, the molds can be filled from the bottom, to minimize trapped air, but this adds complication and is usually not necessary. Likewise, if the viscosity of the polymer is too high for gravity fill, pressure can be used to force it into the mold. Again, this is not usually necessary considering the composite processing requirements of these polymers as matrix materials anyway.

As an alternative to a box mold for fabricating flat neat matrix plates, the polymer can be cast between two vertically positioned flat plates, held the desired cast polymer plate thickness apart by spacers, and sealed around three edges. The polymer is then poured into the open top edge. The plates may be metal or glass. However, this technique is not always successful. Because of the constraint of the mold at both surfaces of the polymer, and the difficulty of achieving full release, the cast polymer plate may crack due to the stresses induced by differential thermal contraction during cooldown from the cure temperature. Also, the polymer, which typically has a higher coefficient of thermal expansion than the mold, may contract away from the mold surfaces, producing a mottled surface. These local depressions are typically very shallow and can be removed by subsequent surface grinding of the cast plate. However, thermal residual strains associated with the formation of these surface irregularities remain (as can be observed under polarized light), and are very difficult to anneal out. Also, the very long path length that any trapped air bubbles or volatiles must travel to reach the free surface makes the production of void-free polymer plates more difficult to achieve.

4.2.3 Thermoplastic polymers

Thermoplastic polymers used in composites are typically high processing temperature (620-840°F (325-450°C)) systems and higher temperature mold materials must be used. Matrix polymers for use in fabricating neat specimens tend to be available in film or granular forms. Pressure injection or compaction is typically necessary, which is complicated by the fact that the minimum viscosities achievable tend to be higher than for thermosets. Although volatile evolution is usually not an issue when molding thermoplastics since they are typically fully polymerized, trapped air can still be a problem. Thus, the use of vacuum during forming may still be desirable.

These high temperature thermoplastics tend to be less brittle than the thermoset polymer matrix materials. Thus, cracking of the polymer plate during the molding operation due to differential contraction of plate and mold is less of a problem, but it can still occur.

4.2.4 Specimen machining

For both thermosets and thermoplastics, if the neat matrix specimen has been molded to final shape, no additional preparation is needed. Dogbone cylindrical specimens, typically for use in solid-rod torsion testing, but sometimes used for tension and compression testing, are one such example.

Tension, compression, and Iosipescu shear specimens of thermoset polymers are typically machined from flat plates or strips rather than being molded to net dimensions. Although individual dogbone flat specimens of commodity thermoplastics are commonly (injection-) molded to final dimensions, high temperature thermoplastic matrix materials are usually not. Rather, flat rectangular blanks are molded, and dogbone specimens are machined from them.

The various polymers are relatively easy to machine using abrasive wheels. If desired, the surfaces of as-molded plates can be ground prior to cutting individual specimens from them. The plates are cut into strips and specimen blanks using thin abrasive blades, although sometimes diamond wheels, or even toothed band saw blades, are used. Dogbone specimens can then be ground to final dimensions. The notches in Iosipescu shear specimens can likewise be ground in, using shaped grinding wheels and multiple passes. Specimens can be stacked together for this operation, mutually supporting each other.

Most polymer matrix specimens will tolerate minor grinding-induced scratches and chipped edges, even though this is never desirable. However, some polymers are extremely sensitive to these surface defects. All surfaces and edges within the specimen gage length must then be carefully smoothed with fine (e.g., down to 600-grit) emery cloth. When working with a new polymer matrix, both as-ground and surface-polished tensile specimens should initially be tested, to determine the polymer's sensitivity to surface defects. Since final polishing adds additional labor cost, it is desirable to only do so when necessary.

4.3 CONDITIONING AND ENVIRONMENTAL EXPOSURE

These issues as applied to the matrix materials themselves (after cure or consolidation) are very similar to the same issues applied to the composite materials using these matrices. The latter case is discussed in detail in Volume 1, Section 6.3. Despite this there are several distinct differences that affect how the information in Section 6.3 is applied to unreinforced matrix material. These include the following:

1. Without reinforcement, most matrix materials are nearly isotropic. In such cases, conditioning restrictions or concerns based on consideration of anisotropy, such as specimen aspect ratio concerns due to moisture absorption through the edge of a specimen, need no longer apply.
2. The transport properties (thermal and moisture) of the unreinforced matrix materials are significantly different than those of the composite. For example, an unreinforced ("neat") epoxy has both a significantly higher diffusivity constant and a significantly higher equilibrium moisture content, as compared to a fiber reinforced composite containing the same resin system.
3. Additional test methods for properties of the matrix material are available that are not typically applied to the composite, such as the moisture content test methods for matrix materials discussed in Section 4.5.7.

4.4 CHEMICAL ANALYSIS TECHNIQUES

Chemical characterization techniques are listed in Table 4.4. Elemental analysis and functional group analysis provide basic and quantitative information relating to chemical composition. Spectroscopic analysis provides detailed information about molecular structure, conformation, morphology, and physical-chemical characteristics of polymers. Chromatographic techniques separate sample components from one another, and thereby simplify compositional characterization and make a more accurate analysis possible. Employing spectroscopic techniques to monitor components separated by gas or liquid chromatography greatly enhances characterization, providing a means to identify and quantitatively analyze even the most minor components.

4.4.1 Elemental analysis

Elemental analysis techniques such as ion chromatography, atomic absorption (AA), X-ray fluorescence, or emission spectroscopy can be applied to analyze specific elements, such as boron or fluorine. When necessary, X-ray diffraction may also be used to identify crystalline components, such as fillers, and to determine the relative percent crystallinity for certain resins.

4.4.2 Functional group and wet chemical analysis

The analysis of reactive functional groups is particularly important in determining equivalent weights of prepolymers. Titration and wet chemical analysis for specific functional groups are useful techniques for characterizing individual epoxy components but have limited application and may provide misleading results when complex resin formulations are analyzed.

4.4.3 Spectroscopic analysis

Infrared spectroscopy (IRS) provides more useful information for identifying polymers and polymer precursors than any other absorption or vibrational spectroscopy technique and is generally available in most laboratories. IR yields both qualitative and quantitative information concerning a polymer sample's chemical nature, i.e., structural repeat units, end groups and branch units, additives and impurities (Reference 4.4.3(a)). Computerized libraries of spectra for common polymeric materials exist for direct comparison and identification of unknowns. Computer software allows the spectrum of a standard polymer to be subtracted from an unknown to estimate its concentration and perhaps to determine whether another type of polymer is also present in the sample.

TABLE 4.4 *Techniques for chemical characterization.*

Elemental Analysis -	Conventional Analytical Techniques X-Ray Fluorescence Atomic Absorption (AA) ICAP EDAX Neutron Activation Analysis
Functional Group Analysis -	Conventional Wet Chemical Techniques Potentiometric Titration Coulometry Radiography
Spectroscopic Analysis -	Infrared (Pellet, Film, Dispersion, Reflectance), Fourier Transform IR (FTIR), Photoacoustic FTIR, Internal Reflection IR, IR Microscopy, Dichroism Laser Raman Nuclear Magnetic Resonance (NMR) 13C, 1H, 15N; Conventional (Soluble Sample), Solid State (Machined or Molded Sample) Fluorescence, Chemiluminescence, Phosphorescence Ultraviolet-Visible (UV-VIS) Mass Spectroscopy (MS), Election Impact MS, Field Desorption MS, Laser Desorption MS, Secondary Ion Mass Spectroscopy (SIMS), Chemical Ionization MS Electron Spin Resonance (ESR) ESCA (Electron Spectroscopy for Chemical Analysis) X-Ray Photoelectron X-Ray Emission X-Ray Scattering (Small Angle-Saxs) Small-Angle Neutron Scattering (SANS) Dynamic Light Scattering
Chromatographic Analysis -	Gas Chromatography (GC) or GC/MS (Low MW Compounds) Pyrolysis-GC and GC/MS (Pyrolysis Products) Headspace GC/MS (Volatiles) Inverse GC (Thermodynamic Interaction Parameters) Size-Exclusion Chromatography (SEC), SEC-IR Liquid Chromatography (LC or HPLC), HPLC-MS, Multi-Dimensional/ Orthogonal LC, Microbore LC Supercritical Fluid Chromatography (SFC) Thin-Layer Chromatography (TLC), 2-D TLC

Infrared (IR) spectroscopy is sensitive to changes in the dipole moments of vibrating groups in molecules and, accordingly, yields useful information for the identification of resin components. IR spectroscopy provides a fingerprint of the resin composition and is not limited by the solubility of resin components (References 4.4.3(b) - 4.4.3(d)). Indeed, gases, liquids and solids may be analyzed by IR spectroscopy. Advances in technology have led to the development of Fourier transform infrared spectroscopy (FTIR), a computer-supported IR technique for rapidly scanning and storing infrared spectra. Multiple scans and Fourier transformation of the infrared spectra enhance the signal-to-noise ratio and provide improved spectra for interpretation. In addition, the FTIR attenuated total reflection (ATR) and diffuse reflectance techniques may be applied for quality assurance of thermoset composite materials to assess their state of cure; i.e., residual epoxide concentration. (See Section 5.5.3)

Although not as popular as IR, laser Raman spectroscopy complements IR as an identification technique and is relatively simple to apply (Reference 4.4.3(a)). As long as the specimen is stable to the high intensity incident light and does not contain species that fluoresce, little or no sample preparation is necessary. Solid specimens need only be cut to fit into the sample holder. Transmission spectra are obtained directly with transparent specimens. For translucent specimens, a hole may be drilled into the specimen for passage of the incident light and a transmission spectra obtained by analyzing light scattered perpendicular to the incident beam. The spectrum of a turbid or highly scattering specimen is obtained by analyzing the light reflected from its front surface. Powdered samples are simply tamped into a transparent glass tube and fibers can be oriented in the path of the incident beam for direct analysis.

4.4.4 Chromatographic analysis

High performance liquid chromatography (HPLC) is the more versatile and economically viable quality assurance technique for soluble resin materials (References 4.4.4(a) - 4.4.4(g)). HPLC involves the liquid-phase separation and monitoring of separated resin components. Dilute solutions of resin samples are prepared and injected into a liquid mobile phase which is pumped through column(s) packed with a stationary phase to facilitate separation and then into a detector. The detector monitors concentrations of the separated components, and its signal response, recorded as a function of time after injection, provides a "fingerprint" of the sample's chemical composition. Quantitative information may be obtained if the sample components are known and sufficiently well-resolved, and if standards for the components are available. Size exclusion chromatography (SEC), an HPLC technique, is particularly useful in determining the average molecular weights and molecular weight distributions of thermoplastic resins (Reference 4.4.4(g)). Recent advances have resulted in improved and automated HPLC instrumentation that is relatively low cost and simple to operate and maintain.

A powerful, but technically more demanding, technique for directly analyzing polymers is pyrolysis GC/MS (gas chromatography/mass spectroscopy). In this case, the sample only needs to be rendered sufficiently small to fit onto the pyrolysis probe. Not only can the polymer type be identified by comparing the resulting spectrum with standards, but volatiles and additives can be identified rapidly and quantitatively, and polymer branching and crosslink density can sometimes be measured.

Other chromatographic and spectroscopic techniques have also been considered (References 4.4.3(a), 4.4.4(h) - 4.4.4(l)). Gas chromatography (GC), GC head-space analysis, and GC-mass spectroscopy are useful for analyzing residual solvents and some of the more volatile resin components. Combined thermal analysis - GC-mass spectroscopy can be used to identify volatile reaction products during cure (References 4.4.4(m) and 4.4.4(n)).

4.4.5 Molecular weight and molecular weight distribution analysis

Techniques for evaluating polymer molecular weight (MW), molecular weight distribution (MWD), and chain structure are listed in Table 4.4.5. Size-exclusion chromatography (SEC) is the most versatile and widely used method for analyzing polymer MW and MWD. Once the solubility characteristics of a polymer are known, a suitable solvent can be selected for dilute solution characterization. THF is most often the solvent of choice for SEC, however, toluene, chloroform, TCB, DMF (or DMP) and m-cresol are also used. If the polymer's Mark-Houwink constants, K and a, in the solvent are known, size-exclusion chromatography (SEC) can be applied to determine the polymer's average MW and MWD (Reference 4.4.5(a)). If the constants are unknown or the polymer has a complex structure (e.g., branched, a copolymer, or mixture of polymers), SEC still may be used to estimate the MWD and other parameters relating to the structure and composition of the polymer. Although SEC indicates the presence of soluble nonpolymeric components, high performance liquid chromatography (HPLC) is the better technique for characterizing residual monomers, oligomers, and other soluble, low MW sample components.

Light scattering, osmometry, and viscometry are also used to analyze polymer MW. Although seldom applied to synthetic polymers, sedimentation is an excellent technique for characterizing the MW of polymers having very large MW. The "special" techniques tend to be somewhat empirical or have limited utility and therefore are used less often.

New techniques which show great promise for characterizing polymer chain structure also are listed in Table 4.4.5. One of the most promising new techniques is dynamic laser light scattering. Unlike SEC, dynamic light scattering can be applied to any soluble polymer, regardless of temperature or solvent, and does not require polymer standards for calibration. Figure 4.4.5 illustrates the MWD of poly (1,4-phenyleneterephthalamide) (i.e., Kevlar™) measured by the laser light scattering (Reference 4.4.5(b)).

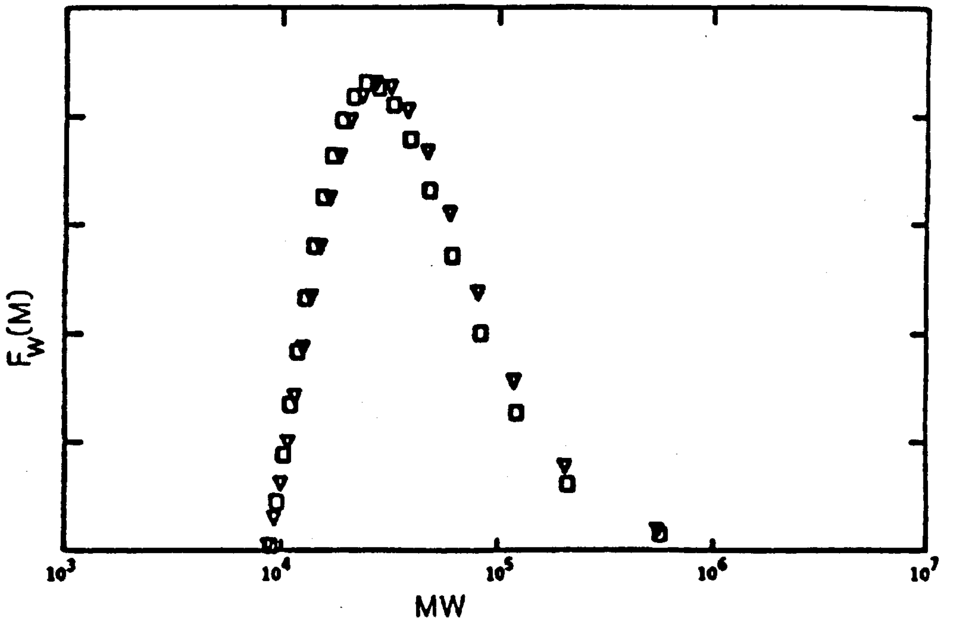

FIGURE 4.4.5 *Molecular weight distribution (MWD) of Kevlar™ in concentrated sulfuric acid, using dynamic laser light scattering.*

As indicated, the polymer's MWD can be fully characterized using very little sample and a single solution with concentrated sulfuric acid as the solvent.

Dilute solution viscometry is a simple technique for determining the limiting viscosity number or intrinsic viscosity [η] of soluble polymers (Reference 4.4.5(a)). The apparatus is inexpensive and simple to assemble and operate. The [η] of a polymer depends upon its hydrodynamic volume in the solvent and is related to the MW of the polymer.

4.4.6 General scheme for resin material characterization

The following questions deserve careful consideration when developing procedures for preparing and characterizing polymer and polymer precursor (thermosetting resins and resin formulations) samples -

What are the inherent characteristics of the polymer or prepolymer?

Will certain operations cause irreversible changes in the sample?

TABLE 4.4.5 *Polymer molecular weights, molecular*

Standard Techniques	Parameters Measured
Size-Exclusion Chromatography	Mol. wgt. averages and MWD, also provides (SEC) information relating to polymer chain branching, copolymer composition, and polymer shape.
Light Scattering (Rayleigh)	Weight-average mol. wgt. M_w (g/mol), virial coefficient A_2 (mol. cc/g^2), radius of gyration $<R_g>_z(A)$, polymer structure, anisotropy, polydispersity.
Membrane Osmometry	Number-average mol. wgt. M_n (g/mol), virial coefficient A_2 (mol cc/g^2). Good for polymers with MW's in the range $5000 < MW < 10^6$, lower MW species must be removed.
Vapor Phase Osmometry	Same as membrane osmometry except that the technique is best suited for polymers with MW < 20,000 g/mol.
Viscometry (dilute solution)	Viscosity-average mol. wgt. M_η (g/mol) as determined by intrinsic viscosity [η] (ml/g) relationship $[\eta] = KM_v$ where K and a are constants.
Ultracentrifugation or Sedimentation	Sedimentation-diffusion average mol. wgt. M_{sd} as defined by the relationship $M_{sd} = S_w/D_w$. Number- and z-average mol. wgt., M_n and M_z. MWD determined by the relation $S = kM^a$ where k and a are constants. Also provides information on the size and shape of polymer molecules.

Special Techniques	Parameters Measured
Ebulliometry	Number-average mol. wgt. M_n (g/mol) for $M_n < 20{,}000$ g/mol.
Cryoscopy	Number-average mol. wgt. M_n (g/mol) for $M_n < 20{,}000$ g/mol.
End Group Analysis	Number-average mol. wgt. M_n (g/mol generally for $M_n < 10{,}000$. Upper limit depends on the sensitivity of the analytical method used.
Turbidimetry	Weight-average mol. wgt. M_w (g/mol) and MWD based upon solubility considerations and fractional precipitation of polymers in very dilute solutions

weight distribution and chain structure.

	Principle
	Liquid chromatography technique. Separates molecules according to their size in solution and employs various detectors to monitor concentrations and identify sample components. Requires calibration with standard polymers.
	Measurement of scattered light intensities from dilute polymer solutions dependent upon solute concentration and scattering angle. Requires solubility, isolation, and in some cases fractionation of polymer molecules.
	Measurement of pressure differential between dilute polymer solution and solvent separated by a semi-permeable membrane. Colligative property method based upon thermodynamic chemical potential for polymer mixing.
	Involves isothermal transfer of solvent from a saturated vapor phase to a polymer solution and measurement of energy required to maintain thermal equilibrium. A colligative property.
	Employs capillary or rotational viscometer to measure increase in viscosity of solvent caused by the presence of polymer molecules. Not an absolute method, requires standards.
	Strong centrifugal field is employed with optical detection to measure sedimentation velocity and diffusion equilibrium coefficients S_w and D_w. Sedimentation transport measurements of dilute polymer solutions corrected for pressure and diffusion provides the sedimentation coefficient S. Permits analysis of gel containing solutions.

	Principle
	Measures boiling point elevation by polymer in dilute solution. A colligative property.
	Measures freezing point depression by polymer in dilute solution. A colligative property.
	The number or concentration of polymer chain end groups per weight or concentration of polymer are determined by specific chemical or instrumental techniques.
	Optical techniques are applied to measure the extent of precipitation as polymer solution is titrated with a non-solvent under isothermal conditions or as the solution prepared with a poor solvent is slowly cooled.

TABLE 4.4.5 *Polymer molecular weights, molecular*

Special Techniques	Parameters Measured
Chromatographic Fractionation	Molecular weight distribution. An absolute MW technique is needed to analyze fractions.
Melt Rheometry	Weight-average mol. wgt. M_w (g/mol) and weight-fraction differential molecular weight distribution semi-empirical method.
Gel-Sol Analysis of Crosslinked Polymers	Gel fraction, Crosslink density
Swelling Equilibrium	Network structure, crosslink density, number- average mol. wgt. of chains between crosslinks M_c.

Promising Techniques	Parameters Measured
Laser Light Scattering (quasi-elastic, line-broadening or dynamic)	Same as Rayleigh light scattering plus trans-diffusion coefficient, molecular weight distribution, and information relating to gel structure.
Field Flow Fractionation (FFF)	Mol. wgt. averages and MWD. Requires calibration.
Non-Aqueous Reverse-Phase High Performance Liquid Chromatography HPLC and Thin-Layer Chromatography TLC	Mol. wgt. averages and MWD. Requires calibration.
Supercritical Fluid Chromatography (SFC)	Mol. wgt. averages and MWD. Requires calibration.
Neutron Scattering Small Angle (SANS)	Weight-average mol. wgt. M_w (g/mol), Virial coefficient A_2 (mol-cc/g^2), Radius of gyration $<R_g>_z$ (A)

weight distribution and chain structure.

	Principle
	Polymer is coated onto silica particles packed in thermostated column and separated according using solvent gradient elution. Polymer solubility decreases with increasing MW.
	Dynamic melt rheological method involving measurement of spectrum of diffusional relaxation times for polymer during oscillatory deformation.
	Extraction, filtration, and centrifugation are employed to isolate soluble polymer from gel. MW of soluble polymer is determined separately.
	Molar volume of crosslinked polymer immersed in swelling liquid and density of the swollen polymer are determined. Theory of partial molar free energy of mixing is applied.

	Principle
	Same as above but also involves measurement of the low-frequency line broadening of the central Rayleigh line of the scattered light. The structure of polymers in both dilute and concentrated solutions can be analyzed.
	Separates polymers according to their size and shape in solution. An elution technique, like chromatography, except that a field/gradient (thermal, gravitational, flow, electrical, etc.) is applied perpendicular to the axis of solution flow through a capillary or ribbon-shaped channel and a single phase is employed.
	Liquid chromatography technique based upon equilibrium distribution of polymer molecules between a non-aqueous binary solvent mobile phase and a nonpolar stationary (packing) phase.
	Liquid chromatography technique involving the use of a mobile phase under supercritical conditions (100 bars, 250°C).
	Measurement of amplitude of neutron scattering momentum vector for polymer in dilute solution or blend with another polymer. Scattering angle and polymer concentration are varied. Deuterated solvents are used. Dilute solid solutions and polymer blends have been studied.

What requirements does the characterization technique impose upon the sample?

Is it necessary to isolate the polymer or prepolymer from other sample components?

It should be recognized that the properties of polymer compounds and prepolymer formulations are often quite different from those of the pure polymers and polymer precursors. Polymer properties are greatly influenced by the presence of other components, e.g., fillers, additives, processing aids, dyes, residual catalysts, impurities, solvents and other polymers, low MW oligomers and monomers.

One must decide whether the specimen needs to be modified or specially treated for a particular analysis. Chemical structure, thermal transition behavior and solubility determine what can be done with a specimen. Operations, such as heating or extraction, may alter morphology or change the chemical composition of a specimen and thereby affect its properties and compromise the validity of certain tests. Many characterization techniques require polymer specimens to be modified or have a particular shape or form. If a specimen does not conform precisely to test criteria, the test may be invalid. On the other hand, in order to apply certain techniques (e.g., light scattering and membrane osmometry for MW analysis), it is essential that the polymer be totally isolated from nonpolymeric components.

Knowledge of the type of polymer or prepolymer is important in developing characterization procedures. If the material is unidentified, a simple series of tests (Level I in Figure 4.4.6(a)) may be applied, first to answer the question of whether the sample actually contains polymer, and then to determine its characteristics and identify the polymer or prepolymer.

Specimen modification for Level I merely involves breaking or cutting a small section from the sample and, if possible, further reducing the specimen size by grinding. To facilitate thermal and spectroscopic analysis and solubility testing, the specimen should have a large surface area. Liquid and heterogeneous specimens should be thoroughly mixed before removing an aliquot for analysis. Each test can be run using as little as 10 mg sample.

Structural and compositional information obtained by the tests in Level I is used to help develop more sophisticated specimen preparation schemes and support the application of more detailed or specialized characterization techniques. The major concern of Level II is representative sampling and insuring that specimen modification procedures (cutting, grinding, molding, etc.) do not compromise polymer characteristics to be evaluated. Level II also addresses the "quantitative" aspects of sample composition (percent polymer, additives, volatiles, and inorganic and other organic residues) and, if necessary, deals with the identification of nonpolymeric components.

A general scheme for polymer analysis is illustrated in Figure 4.4.6(b). The polymer sample should be uniform and have a large surface area. Once volatile components are removed, the polymer can be directly analyzed, or a variety of techniques (e.g., extraction, precipitation, filtration, liquid chromatography) may be applied to isolate the polymer. If required, special procedures are applied to prepare the polymer sample for chemical characterization - molecular weight, molecular weight distribution, and chain structure evaluation, and bulk characterization (Level III in Figure 4.4.6(a)).

Whenever possible, complementary techniques should be used for the chemical quality assurance of resin materials. Techniques, such as HPLC and IR spectroscopy, are fundamentally different from one another and provide direct, but different, information about a resin's composition. If appropriate test methods are applied, HPLC and IR spectroscopy are usually powerful enough to detect differences or changes in the chemical compositions of resins. DTA and DSC complement HPLC and IR spectroscopy by providing information relating to the handleability (i.e., the T_g and extent of reaction of the resin)and the processability of the prepreg. TGA and GC head-space analysis techniques for volatile components are secondary, but important, techniques. Special techniques for analyzing specific components or elements should be used if knowledge of the concentrations of the components is critical for processing the resin or if their presence could adversely effect the performance and durability of the cured composite. The information provided by mechanical, rheological, and dielectric analysis techniques is related to the chemical composition of the prepreg resin and thereby complements the more direct chemical techniques.

However, caution is recommended in applying non-chemical techniques since the information obtained is complex and frequently ambiguous when attempts are made to relate measured parameters to chemical composition. (See Section 5.5)

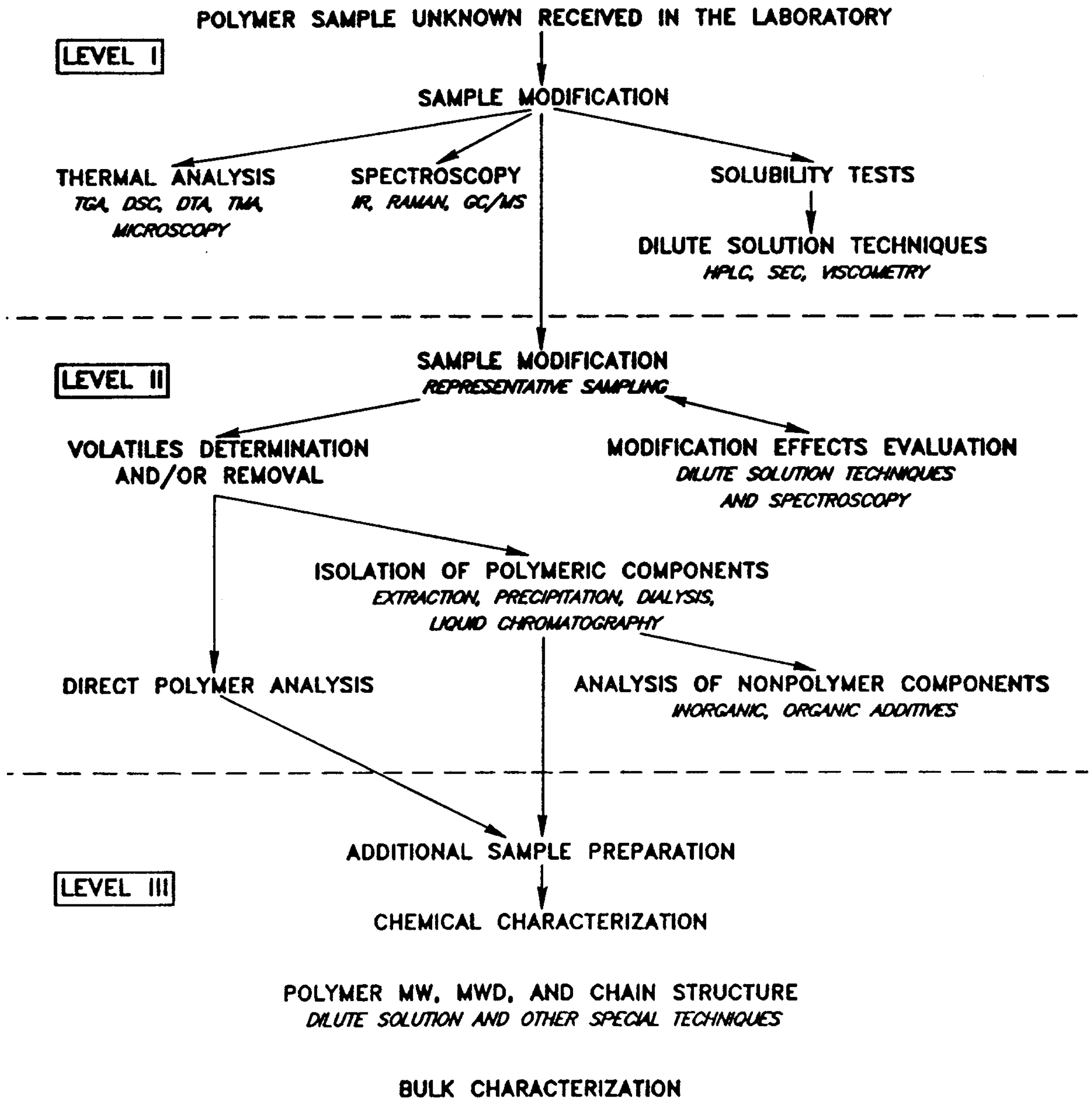

FIGURE 4.4.6(a) *Polymer/prepolymer characterization scheme.*

Polymer Sample (fine powder or thin film)

Volatiles Removal and/or Determination

- Weight loss on drying
- TGA (Thermal Gravimetric Analysis)
- Head-Space analysis (GC/MS)
- Moisture analyzer

Isolation of Polymeric Component(s)

- Extraction
- Dissolution
- Filtration
- Precipitation
- Centrifugation

Chemical Characterization Techniques

- Elemental analysis
- Functional group analysis
- Spectroscopic analysis
- Chromatographic analysis

Polymer Molecular Weight, Molecular Weight Distribution, and Chain Structure

- Dilute solution techniques
- Other special techniques

Bulk Characterization Techniques

- Thermal analysis
- Microscopy
- Morphology
- Mechanical testing
- Miscellaneous

FIGURE 4.4.6(b) *General scheme for polymer analysis.*

4.5 THERMAL/PHYSICAL ANALYSIS AND PROPERTY TESTS

The physical properties of the matrix material will influence the processing method as well as determine the type of application appropriate for the fabricated composite. Thermal analysis methods are used to determine glass transition and crystalline melt temperatures, thermal expansion, thermal decomposition, heat of reaction, and other thermal events in matrix materials. Rheological methods provide information on the temperature-dependent flow behavior. In addition, the cure-dependent characteristics of thermosetting resins can also be evaluated. Other methods can be employed to determine the morphology and density of the matrix material. The analysis techniques discussed in the following sections are used to determine the physical properties of thermoplastic and thermosetting materials.

4.5.1 Introduction

This section is reserved for future work.

4.5.2 Thermal analysis

Thermal analytical techniques, such as thermal gravimetrical analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermal mechanical analysis (TMA), dynamic mechanical analysis (DMA), and torsional braid analysis (TBA) provide useful information relating to the composition and processability of resins.

Thermal gravimetric analysis (TGA) monitors the weight changes in a sample as a function of temperature. Although primarily used for studying the degradation processes, TGA can also be applied as a quality assurance technique to provide information about the volatiles, resin, fiber, and inorganic residue content of prepreg materials (Reference 4.5.2(a)). Since dissimilar materials often degrade and volatilize at different temperature and rates, compositional differences may be reflected by differences in their TGA thermograms. Thermal oxidative degradation rates determined by TGA are useful for estimating the life cycles of resin materials (Reference 4.5.2(b)).

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) techniques are frequently employed for characterizing resins and composite materials (References 4.4.4(g), 4.4.3(b), 4.5.2(c), and 4.5.2(d)). Both DSC and DTA monitor enthalpy changes in materials as a function of temperature (DSC directly and DTA indirectly) and thereby provide similar information useful for quality assurance of prepreg materials. DTA measures the temperature difference (ΔT) between the epoxy resin specimen and a reference material; whereas DSC measures the rate of heat evolution (dH/dt) or enthalpy absorption of the specimen relative to a reference. DTA and DSC measure thermal changes (1) as a function of time with both the specimen and reference material held at the same temperature (isothermal), or (2) as a function of temperature with both the specimen and reference material heated at the same heating rate (dynamic).

For quality assurance applications, DTA and DSC are usually run in the dynamic mode with the weighed specimen in an aluminum specimen holder and an empty holder used as the reference. Dynamic DTA and DSC measure the glass transition temperature T_g and heat of reaction ΔH of the prepreg resin but do not provide information about chemical composition directly. By monitoring the fraction of heat evolved as a function of temperature or time, information relating to the extent of cure and curing kinetics can be obtained. DSC and DTA may also be applied to evaluate the melting temperature T and to estimate the degree of crystallinity of thermoplastic resins and composites. Since the average specimen size used in DSC is only about 10 mg (0.00002 lb), special care must be taken in obtaining representative materials. Multiple specimens runs are advisable.

Thermal mechanical analysis (TMA) is used in conjunction with DTA and DSC to study the thermal transition behavior (e.g., T_g) of prepreg resins and cured laminates. TMA simulates a linear dilatometer to measure the thermal expansion and contraction of specimens under dynamic or isothermal heating conditions. Adjustable loads are applied via a specially designed probe resting upon the specimen surface. Sensitive displacement devices are employed to monitor the "nominal" thermal response of a material. Since thermal transition behavior is related to the chemical composition and extent of cure of a prepreg resin, TMA can be applied as a quality assurance technique.

As previously discussed, TGA provides an indication of a sample's thermal decomposition temperature T_d and is used to estimate the relative amounts of volatiles, polymer, nonpolymeric additives, and inorganic residues. DSC or DTA is applied to evaluate the extent of cure and curing characteristics of thermoset resins, to determine a polymer's T_g, and, if the polymer is semi-crystalline, to determine its crystalline melting temperature T_m. Suggested procedures for measuring T_g and T_m are given in ASTM Standards D 3417 and D 3418 (References 4.5.2(e) and 4.5.2(f)). TMA can also be used to determine the T_g and to obtain further information about a polymer's heat distortion temperature and thermal expansion coefficient. For pelletized or molded samples, a razor blade or microtome can be used to cut samples to approximately fit the dimensions (thickness and diameter) of the sample holder. If the sample has been cut or is already in film or sheet form with a thickness no greater than 0.015 in (0.04mm), a punch or cork borer may be used to cut disks of an appropriate size.

Alternatively, a hot stage microscope may be used to observe the heat distortion temperature and onset of flow of powdered samples. Initially the powder particles have sharp, rough edges. As the sample is heated and the heat distortion temperature is approached, the edges first become blurred and then the particles start to agglomerate. Finally, at T_m, for semi-crystalline polymers, or T_g, in the case of glassy polymers, flow occurs and a clear melt or liquid forms. Microscopes equipped with cross polarizers are useful for defining crystal-crystal transitions and the onset of melting of semi-crystalline polymers.

4.5.3 Rheological analysis

The processing characteristics of a thermoplastic or thermosetting resin are dependent upon flow behavior, which is characterized by rheological analysis. Methods which measure the temperature-dependent viscosity under constant shear conditions are used to obtain information on flow behavior. These methods include the use of viscometers or capillary rheometers. Since the viscosity of thermosetting materials also depends on the degree of cure, other methods may be used to obtain rheological information during cure.

Dynamic mechanical analysis (DMA), torsional braid analysis (TBA), and various mechanical spectrometers may be used to measure the rheological response of resins as a function of frequency, temperature, and/or state of cure. Both DMA and TBA can provide information relating to the storage modulus, loss modulus, complex viscosity, and tan delta of polymers. In addition, information relating to gelation, vitrification, and the T_g of cured thermosetting resins can be obtained (References 4.3.1(c) and 4.5.3(a) - (c)). Rheological techniques are most often used to optimize processing parameters. However, since rheological properties are related to resin composition and morphology, rheological techniques may also be applied for the quality assurance of resins.

Dynamic dielectric analysis (DDA) techniques can provide information on the flow behavior and curing characteristics of matrix materials. DDA involves the use of electrical measurements to monitor changes in the dielectric constant, the dissipation factor, capacitance, and/or conductance of the resin during processing as a function of frequency, time, and temperature. Measured electrical parameters are highly responsive to changes in resin viscosity and are often employed to investigate and optimize prepreg processing parameters such as resin flow and gelation time/temperature. Since chemical composition affects the electrical properties and curing behavior of thermosetting resins, DDA techniques may also be applied for their quality assurance (References 4.5.3(c) - 4.5.3(j)).

ASTM test methods which are applicable for rheological analysis (References 4.5.3(k) - (o)) include:

ASTM D 2393 "Viscosity of Epoxy Resins and Related Components". Method for measuring the viscosity of the liquid components of an epoxy resin system and/or the mixed formulation.

ASTM D 3835 "Rheological Properties of Thermoplastics with a Capillary Rheometer". Method describes the measurement of the rheological characteristics of thermoplastics at temperatures and shear conditions common to processing equipment.

ASTM D 4065 "Determining and Reporting Dynamic Mechanical Properties of Plastics". Practice for obtaining rheological information by free vibration and resonant or nonresonant forced vibration techniques.

ASTM D 4440 "Rheological Measurement of Polymer Melts Using Dynamic Mechanical Procedures". Practice for determining the rheological properties of thermoplastics over a range of temperatures by nonresonant forced-vibration techniques.

ASTM D 4473 "Measuring the Cure Behavior of Thermosetting Resins Using Dynamic Mechanical Procedures". Practice is intended to provide means for determining the cure behavior of supported and unsupported thermosetting resins over a range of temperatures by free vibration and resonant and nonresonant forced-vibration techniques.

Definitions of terms related to dynamic mechanical analysis are provided in ASTM D 4092 (Reference 4.5.3(p)).

4.5.4 Morphology

The morphology of the matrix material will be dependent upon the type of polymer. The formation of a highly cross-linked network in thermosetting materials is controlled by the degree of conversion and the functionality of the components involved in the cure. Their degree of cross-linking is described in terms of the degree of cure which can be determined by thermal analysis and spectroscopic methods.

On a microscopic scale, the semi-crystalline thermoplastics contain regions of three-dimensional order (crystalline) and regions which lack long-range order (amorphous). Typically the crystalline regions consist of spherulites, which are aggregates of lamellar crystals that radiate from a nucleation site. The thermal history of the material, as well as the presence of fibers and/or fillers will affect the size and number of spherulites and the degree of crystallinity (References 4.5.4(a) - 4.5.4(b)). Differences in the crystalline region may also have an effect on mechanical properties (References 4.5.4(c) - 4.5.4(d)).

The analysis of the crystalline region is achieved by a variety of techniques. The size and degree of orientation of crystals can be studied by X-ray diffraction, electron microscopy, and birefringence methods, while a polarizing microscope is typically used for the analysis of spherulites. The degree of crystallinity can be determined by X-ray diffraction, specific volume, and heat of fusion. The specific volume method requires determining the specific volume of the sample as well as completely amorphous and crystalline samples of the material. The heat of fusion method involves ratioing the heat of fusion of the sample and a completely crystallized sample of the material. The heats of fusion can be determined using ASTM D 3417 (Reference 4.5.2(e)).

The noncrystalline thermoplastics may exhibit different levels of molecular orientation. The liquid crystal polymers may have regions of one- and/or two-dimensional order which can be evaluated by thermal analysis. The amorphous thermoplastics, typically lacking any long-range order, can undergo orientation depending upon the processing technique. In general, molecular orientation can produce anisotropic properties in the material. However, the morphological characteristics of a neat resin sample may be quite different from those found in a fabricated composite.

4.5.5 Density/specific gravity

4.5.5.1 Overview

The matrix density is required when determining the approximate void content of the composite as described in ASTM D 2734 "Void Content of Reinforced Plastics" (Reference 4.5.5.1(a)). Density is also used to identify or characterize matrix material within a given class of polymers. For example, in semi-crystalline thermoplastic matrices, the degree of crystallinity of a particular polymer will change the density of that polymer.

The density of the composite matrix is almost always assumed to be the same whether it is in the composite or is a cast neat resin plate and the neat resin value is always used in practice. It is important to point out that the composite matrix density and the cast neat resin density may not be identical due to differences in their processing history. In the composite the matrix experiences a different thermal, pressure, and spatial environment, including surface conditions in the fiber/matrix interphase. Theoretical thought has led many to believe that the bulk matrix density value is lower than that found in the composite (Reference 4.5.5.1(a)). However, there is no known experimental verification of this assumption. Further, if a density difference does exist, the question arises as to whether it is significant enough to be of consequence.

With few exceptions, the determination of density is accomplished indirectly by measuring the volume and weight of a representative sample of the cured matrix resin, and then combining these values to calculate density. The weight measurement is most easily obtained by using a quality analytical balance. To determine volume, however, there are several approaches used. The most common approach uses simple Archemedes methods involving displacement of liquids of known density.[1] Direct measurement of density can be made by observation of the level to which the test material sinks in a density-graded liquid (Reference 4.5.5.1(b)).

Liquids are used almost exclusively in displacement techniques. However, there are advantages to using a gas medium in place of liquid to determine specimen volume. One advantage is minimization of errors associated with liquid surface tension. The gas displacement approach is often referred to as helium pycnometry. When helium pycnometry is used the test specimen volume is determined by measuring pressure changes of a confined amount of helium. Helium pycnometry is not yet a standardized test method for measuring the volume and density of cured matrix resins, yet it has been demonstrated to be a viable technique (References 4.5.5.1(c) and (d)). As no test standard or guidelines exist for this method as applied to resins, a test procedure has been developed within the MIL-HDBK-17 Testing Working Group (see Section 6.6.4.4.1).

At present there are two ASTM standards which deal specifically with obtaining the density of cured matrix resins. These are test methods D 792 (Reference 4.5.5.1(e)), covering the liquid displacement method, and D 1505 (Reference 4.5.5.1(b)), covering the density gradient method.

For detailed guidance on how to experimentally obtain the density of cured matrix resins the reader is referred to Sections 6.6.4.7 through 6.6.4.6 of this volume of the Handbook. Note that Section 6.4.4 refers specifically to composites, but the methods discussed are fully applicable to cured matrix resins except as noted in Section 4.5.5.2 below.

4.5.5.2 Recommended procedure changes to Sections 6.6.4.2, 6.6.4.3 and 6.6.4.4 (D 792, D 1505 and helium pycnometry) for use in measuring cured resin density

Differences between measuring composite density as opposed to the density of a neat resin sample are slight and occur in the area of specimen preparation. The neat resin specimen will typically be more fragile and may crack during machining operations. Due to the relative softness (compared to a composite) and isotropic nature of the resin, good edge quality is easier to obtain using fine grit sandpaper.

4.5.5.3 Density test methods for MIL-HDBK-17 data submittal

Data produced by the following test methods (Table 4.5.5.3) are currently being accepted by MIL-HDBK-17 for consideration for inclusion in Volume 2.

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[1] For a quick and convenient, but less accurate density determination method, the reader is referred to the micrometer technique as specified in ASTM D 2734, Test Method C. This method obtains specimen volume by simple dimensional measurement and is only appropriate for precision work in limited specific cases.

TABLE 4.5.5.3 *Resin density test method for MIL-HDBK-17 data submittal.*

Property	Symbol	Fully Approved, Interim, and Screening Data	Screening Data Only
Density	ρ	D 792, D 1505, 4.5.5.2*	D 2734C

*When this method is used to generate data for subsequent determination of composite void volume, the test specimen must occupy at least 30% of the test cell volume.

4.5.6 Volatiles content

The volatiles content of resin materials is of interest to prepreg manufacturers, RTM fabricators, and manufacturers using wet lay-up techniques. Inadequate control of volatiles may effect handling of prepregs and final laminate quality. The property is most relevant where materials have a solvent incorporated into the formulation. The volatile content represents the solvent(s), resin components, and other constituents that volatilize at the test temperature. The remainder is commonly known as resin solids and filler. The resin solids include the materials that can be dissolved in an organic solvent (usually polymer constituents) and the filler is generally insoluble inorganic material. The test for volatiles is commonly performed as a quality control check.

Specific methods are material dependent, but they generally involve placing the materials in an air circulating or vacuum oven at a specified temperature for a specified time. Weight loss is measured gravimetrically. The time and temperature are selected such that volatiles completely evaporate and resin solids do not volatilize or degrade. ASTM D 3530 "Volatiles Content of Carbon-Fiber Prepreg" (Reference 4.5.6.a) represents the standard oven exposure test method intended for carbon/epoxy fiber prepregs. The procedure may also be used as a guideline for most thermosetting resins, though the user is cautioned that the temperature may not be appropriate for other resin systems. In the ASTM standard, the time is fixed but the temperature is selected to represent the part process cycle.

Thermogravimetric analysis (TGA) is sometimes used instead of an oven exposure method. TGA is an instrumented procedure where a small specimen is placed on a microbalance. The instrument is automated to gradually increase the temperature while continuously monitoring the specimen weight. A TGA procedure for volatiles content should specify heating rate, gas and flow rate, specimen size, and the temperature range used to define volatile content. While there is no established ASTM procedure for TGA to determine volatiles in resins, ASTM E 1131 “Compositional Analysis by Thermogravimetry” (Reference 4.5.6.b) gives general guidance. Other techniques such as TGA-FTIR and Headspace Gas Chromatography (Reference 4.5.6.c) may be used in a research or problem-solving environment for qualitative/quantitative determination of volatiles.

4.5.7 Moisture content

Depending on the resin system, moisture may retard cure, create volatiles or cause other undesirable reactions during processing. For those resin systems affected, control and measurement of the moisture content is required. Automated moisture meters based on the Karl Fischer titration method are commonly used to determine moisture content in most types of resins. A small sample, typically 5 grams of liquid resin, is introduced to a cell containing the Karl Fischer Reagent and a solvent, typically methanol. A current is passed between two electrodes, creating iodine in a quantitative series of reactions with water and the Karl Fischer Reagent. The reaction and test are described in ASTM D 4672 “Polyurethane Raw Materials: Determination of Water Content in Polyols” (Reference 4.5.7.a).

An alternate method for determining moisture content uses an instrument that heats a small specimen, typically 10 grams of solid. The moisture is volatilized and transported to an electrolytic cell by a nitrogen carrier gas. The water reacts to form phosphoric acid, which is then quantitatively measured by passing current through the cell. A standard for this test is ASTM D 4019, “Method for Moisture in Plastics by Coulometric Regeneration of Phosphorous Pentoxide" (Reference 4.5.7.b).

4.6 STATIC MECHANICAL PROPERTY TESTS

4.6.1 Introduction

Knowing the static mechanical properties of the matrix material can be very useful when choosing among various candidate systems for use in a composite material. If a particular composite property must be enhanced, the proper selection of an alternate matrix material may be sufficient to meet the need. For example, substituting a matrix with only a slightly higher modulus of elasticity may reduce a fiber microbuckling problem to an acceptable level. A matrix with an enhanced shear strength, or shear strain to failure, will enhance the corresponding composite property.

Likewise, detailed knowledge of the static mechanical properties of the matrix material is mandatory if a micromechanics analysis is to be used to predict composite properties from constituent properties. Even those polymers that are termed “brittle” often exhibit nonlinear tensile and compressive stress-strain responses, the nonlinear nature of which is non-negligible. Even more important is the very significant nonlinear shear stress-strain response exhibited by most polymers. Thus, not only must the initial stiffness properties (E^m, ν^m, G^m) be determined, but also the complete stress-strain curves to failure. This can present special strain instrumentation challenges, as discussed in the following sections.

In general, the polymers used as matrix materials in composites are not formulated to be used in the neat (unreinforced) form. Thus, their viscosities and volatile contents may not be particularly amenable to casting into the void-free neat resin sheets, plates, and other forms required for mechanical test specimen preparation, as discussed in Section 4.2. Nevertheless, obtaining the quality specimens required for the mechanical tests described in the following sections is particularly critical, and must be given special attention.

4.6.2 Tension

F_m^{tu}, F_m^{ty}, E_m^t, ν_m^t, ε_m^{tu}

4.6.2.1 Introduction

Neat (unreinforced) matrix tensile testing is typically performed per ASTM D 638 (Reference 4.6.2.1(a)). Although this standard was originally written (in 1941) for commodity thermoplastics, it can be followed directly for the testing of high performance thermosets and high temperature thermoplastics used as matrices in composites. Another standard, ASTM D 882 (Reference 4.6.2.1(b)), intended for testing thin plastic sheeting, is also available. It is stated in this standard that the "tensile properties of plastics 1.0 mm (0.04 in.) or greater in thickness should be determined according to Test Method D 638." That is, ASTM D 882 typically does not apply to neat matrix testing.

4.6.2.2 Specimen preparation

Most commonly, flat dogbone (i.e., dumbbell-shaped, per the terminology of ASTM D 638) specimens are used. As discussed in Section 4.2, these specimens are typically machined from cast flat plate material rather than being individually molded to final dimensions. It is important to observe the plate fabrication precautions discussed in Section 4.2, to help ensure that adequate material quality will be maintained. Likewise, the quality of specimen machining must be controlled. As discussed in Section 4.2, some matrix polymers, being relatively brittle, are very sensitive to surface scratches and edge chips accidentally induced during machining. In fact, some matrix polymers are very sensitive to roughness of machined surfaces in general, and require polishing as a final preparation step. Neat polymer tensile specimens are not usually tabbed, the dog-boning making this unnecessary.

As recommended in ASTM D 638, the Type I specimen geometry, or something very similar, is preferred, and most commonly used, when testing the high performance composite matrix materials. This geometry is recommended for testing specimens 0.28 in. (7.0 mm) or less in thickness, which is usually the case. As shown in Figure 4.6.2.2, this 6.50 in. (165 mm) long specimen is 0.75 in. (19 mm) wide, reduced to 0.50 in. (13 mm) in the 2.25 in. (57.0 mm) long gage length region, with an ample 3.0 in. (76 mm) transition radius. Should this specimen not fail in the gage section, the Type II specimen is recommended. It is of similar geometry, but with a gage section width of only 0.25 in. (6.0 mm) rather than 0.50 in. (13 mm). That is, it has a more severely reduced gage cross section than the Type I specimen. Three other specimen types are also defined in ASTM D 638, but these are not normally applicable to matrix polymer testing.

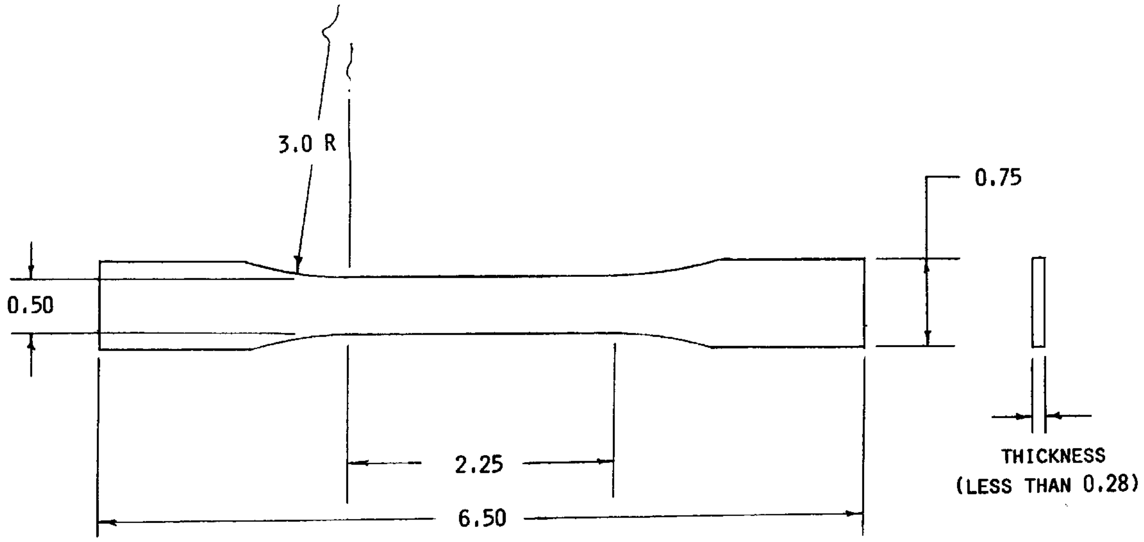

FIGURE 4.6.2.2 *ASTM D 638 type I flat dogbone tensile specimen geometry (all dimensions in inches).*

Occasionally, dogbone solid circular cylindrical specimens are used for tensile testing, as discussed in ASTM D 638, but such specimens tend to be more difficult to fabricate, and to grip, than flat specimens. A detailed experimental investigation of the influence of solid circular cylindrical specimen size and geometry is presented in References 4.6.2.2(a) and 4.6.2.2(b). Thin-walled tubes can also be tensile tested. However, this specimen geometry is even more difficult to fabricate and grip than a solid cylindrical specimen. Details of thin-walled tube specimen geometry and gripping are included in ASTM D 638.

4.6.2.3 Test apparatus and instrumentation

The flat dogbone specimens are usually tested using wedge grips. Mechanical and hydraulically-actuated grips usually function equally well. Although not as frequently used, screw-actuated grips can also perform satisfactorily since the tensile strength of neat polymer specimens is not very high and thus only moderate grip forces are required. Correspondingly, slipping in the fixed-position screw- actuated grips due to Poisson contraction is usually not a serious problem.

Screw-actuated grips often incorporate smooth metal or rubber gripping surfaces, while most wedge grip inserts have aggressive serrations. Thus, it is common to use some type of padding material between the specimen and these wedge grip faces. One or two layers of emery cloth works well. ASTM D 638 also discusses the use of abrasive wire mesh and plastic sheet.

The so-called flame-sprayed grip faces that are finding increasing use in test laboratories, although not yet referred to in the ASTM D 638 standard, are proving to be particularly effective. These grip faces are typically coated with tungsten carbide particles in a nickel (or cobalt) matrix. These grip faces are usually very smooth and nonaggressive, having a surface roughness similar to that of about 150 grit emery cloth. However, they have excellent holding power, equivalent to that of serrated grips. Such grip faces would be a good choice for screw-actuated grips as well.

Although extensometers are recommended in ASTM D 638 for measuring strains, strain gages have been shown to perform at least as well (References 4.6.2.2(a) and 4.6.2.2(b)), even on relatively brittle polymers. If Poisson's ratio is to be determined, a biaxial extensometer (or two linear extensometers) must be used. Correspondingly, a biaxial strain gage is convenient for this purpose.

4.6.2.4 Tensile test methods for MIL-HDBK-17 data submittal

Data produced by the following test method are currently being accepted by MIL-HDBK-17 for consideration for inclusion in Volume 2:

TABLE 4.6.2.4 *Resin tensile test methods for MIL-HDBK-17 data submittal.*

Tensile Property	Symbol	Fully Approved, Interim, and Screening Data	Screening Data Only
Ultimate Strength	F_m^{tu}	ASTM D 638	
Yield Strength	F_m^{ty}	"	
Modulus	E_m^t	"	
Poisson's Ratio	ν_m^t	"	
Strain to Failure	ε_m^{tu}	"	

4.6.3 Compression

F_m^{cu}, F_m^{cy}, E_m^c, ν_m^c, ε_m^{cu}

4.6.3.1 Introduction

Compressive testing of neat polymer matrix materials tends to be performed much less frequently than tensile and shear testing, although there does not appear to be any intrinsic reason. Compressive testing is usually no more difficult. The elastic response of most polymer matrices does tend to be similar in tension and compression (References 4.6.3.1(a) and 4.6.3.1(b)), although the ultimate strength in compression is typically much higher since "critical flaw size" does not influence failure as severely.

ASTM D 695 (Reference 4.6.3.1(c)) governs the compressive testing of rigid plastics, and is the test method commonly used. It defines the axial compressive loading of a short prism (or tube), or a dogbone flat specimen laterally restrained against column buckling.

The short prism specimen is commonly used. This specimen for measuring compressive strength may be square or circular in cross section, having a length twice the transverse dimension (i.e., a specimen with an aspect ratio of 2). A recommended specimen size for strength determination is 0.50 in. (12.7 mm) in cross-sectional dimensions and 1.0 in. (25.4 mm) long. A specimen of the same cross-sectional dimensions but twice as long is recommended for modulus and offset yield stress measurement.

4.6.3.2 Specimen preparation

Circular rather than square cross section short prism specimens are commonly used. Particularly for thermoset polymers, it can be difficult to cast a void-free 0.50 in. (12.7 mm) thick plate (as discussed in Section 4.2) from which to cut square specimens. Also, excessive heat-up due to exothermic reactions during cure can be a problem when casting such thick plates. As a secondary consideration, any remaining material from this thick casting is not particularly useful for other neat matrix testing, e.g., tensile, shear, thermal, or moisture expansion testing.

It is often more practical to cast 0.50 in. (12.7 mm) diameter cylinders to net diameter and then simply cut them to the desired length. Of course square specimens could be cast, but a mold with a circular cavity is usually easier to fabricate.

Since specimens machined from neat polymer plates typically 0.12 in. (3.2 mm) thick or less are commonly used for both tensile and Iosipescu shear testing, it is often convenient to fabricate compression specimens from these same cast plates. In this case, ASTM D 695 suggests the use of dogbone flat specimens similar to those used for tensile testing (per ASTM D 638), but only about half as long.

Whether short prism or flat dogbone specimens are being prepared, particular attention must be given to the parallelism of the specimen ends, and their perpendicularity to the specimen longitudinal (loading) axis. Recommended tolerances are given in ASTM D 695 (Reference 4.6.3.1(c)). The influence on compressive strength of roughness of the specimen surfaces, whether as-cast or machined, must also be evaluated. Some polymers are much more sensitive to surface imperfections than others. ASTM D 695 simply states, "All machining operations should be done carefully so that smooth surfaces result."

4.6.3.3 Test apparatus and instrumentation

The short prism specimens are simply loaded in compression between two flat platens. If testing machine platens are used, it is important that they be flat and parallel, and well-aligned perpendicular to the loading axis of the testing machine. ASTM D 695 describes a compression subpress which is a very convenient alternative. This self-contained unit includes a rigid frame with linear ball bushings guiding a hardened steel loading plunger free to move axially but carefully aligned with a hardened steel specimen support anvil.

When testing the flat dogbone compression specimens in axial compression, lateral support must be provided to prevent gross column buckling. A support jig is defined for this purpose in ASTM D 695. SACMA Recommended Method SRM 1 (Reference 4.6.3.3) describes an improved fixture which serves the same purpose but is much easier to use.

Although extensometers are recommended in ASTM D 695 for measuring strains, strain gages have been shown to perform at least as well (References 4.6.3.1(a) and 4.6.3.1(b)), even on relatively brittle polymers. If Poisson's ratio is to be determined, a biaxial extensometer (or two linear extensometers) must be used. Correspondingly, a biaxial strain gage is convenient for this purpose.

4.6.3.4 Limitations

Short Prism Compression Specimens: Either a special 0.50 in. (12.7 mm) thick plate must be molded from which to cut 0.50 in. x 0.50 in. (12.7 mm x 12.7 mm) square cross section specimens, or a special 0.50 in. (12.7 mm) square or circular cross section mold must be available. If ASTM D 695 is adhered to, specimens of two different lengths must be tested, to measure compression strength and modulus, respectively. Also, either special care must be taken to align the testing machine, or a compression subpress must be used.

Laterally Supported Flat Dogbone Specimens: Specimen preparation is slightly more time consuming since the specimen must be dogbone. Also, a special lateral support fixture is required.

4.6.3.5 Compressive test methods for MIL-HDBK-17 data submittal

Data produced by the following test method are currently being accepted by MIL-HDBK-17 for consideration for inclusion in Volume 2:

TABLE 4.6.3.5 *Resin compressive test methods for MIL-HDBK-17 data submittal.*

Compression Property	Symbol	Fully Approved, Interim, and Screening Data	Screening Data Only
Ultimate Strength	F_m^{cu}	ASTM D 695*	
Yield Strength	F_m^{cy}	"	
Modulus	E_m^c	"	
Poisson’s Ratio	ν_m^c	"	
Strain to Failure	ε_m^{cu}	"	

* The SACMA SRM 1 test fixture is also an acceptable supporting jig.

4.6.4 Shear

F^{su}, F^{sy}, G^m

4.6.4.1 Test methods available

The shear properties of resin matrix materials are typically determined by testing either a solid circular cylinder rod in torsion or a standard Iosipescu (V-Notched Beam) specimen in a standard test fixture. In the former case, ASTM E 143 is applicable (Reference 4.6.4.1(a)). In the latter case, ASTM D 5379 applies (Reference 4.6.4.1(b)). Dynamic mechanical analysis (DMA) (Reference 4.5.3(m)) is also available, but is not commonly utilized.

4.6.4.2 Torsion specimen preparation

Originally, solid rods were cast as rods of uniform diameter, either in a glass tube which could then be broken away after cure, or in a plunger-in-cavity steel mold and pushed out the end after cure. Currently, dog-boned cylindrical specimens are usually used. These solid rods are typically cast in either steel or silicon rubber molds, although other mold materials can be used also. The metal mold is typically split along its diameter, to permit removal of the cured specimen. The silicon rubber mold is typically split along a radius, so that it can be spread open to remove the cured specimen (and to remove the pattern it itself was originally molded from). The lower end of the mold is closed off and the resin poured in from the top (or sometimes injected from the bottom, under pressure if necessary for low viscosity systems). Cored specimens have also been infrequently utilized, using a silicon rubber core of constant diameter which can then be pulled out one end after cure to form a tubular specimen.

4.6.4.3 Iosipescu shear specimen preparation

Iosipescu specimens are typically machined from flat plates either cast in an open mold or injection molded in the case of low viscosity resins, e.g., the high temperature thermoplastics. Specimens could also be molded to net dimensions but this is not known to have been done to date.

4.6.4.4 Test apparatus and instrumentation

A torsion testing device of relatively low torque capacity is used to test solid rod specimens, while a standard Iosipescu shear test fixture is used with the Iosipescu specimen. Strain gages, typically ±45° biaxial rosettes, bonded to the surface of either the solid rod or the Iosipescu specimen, are utilized to determine shear modulus, and the complete shear stress-shear strain curve to failure.

4.6.4.5 Limitations

Solid Rod Torsion Test (ASTM E 143): The shear strain varies from zero at the specimen axis of twist to a maximum at the specimen surface. Almost all resin materials, even those generally considered to be brittle, exhibit significant nonlinearity in shear beyond the elastic limit, and thus the strain variation is not linear. The shear strain being measured by the strain gages is the surface strain. Correspondingly, the calculation of shear stress in the nonlinear range must account for this nonlinearity. (The shear strain is uniform in the gage section of the Iosipescu specimen and thus no special consideration is required when testing nonlinear materials.)

Solid (or hollow) rod specimens must be specially prepared rather than being cut from the same plate material as tensile and compression specimens.

A torsion testing machine in the required torque range is not available in many laboratories.

Iosipescu Shear Test (ASTM D 5379): A standard Iosipescu shear test fixture must be available. For very ductile resins, the fixture may bottom out (very large shear strains) before the specimen fails. For very brittle resins, crushing of the specimen at the loading points may require the use of tabs.

4.6.4.6 Shear testing methods for MIL-HDBK-17 data submittal

Data produced by the following test methods are currently being accepted by MIL-HDBK-17 for consideration for inclusion in Volume 2:

TABLE 4.6.4.6 *Shear testing methods for MIL-HDBK-17 data submittal.*

Shear Property	Symbol	Fully Approved, Interim, and Screening Data	Screening Data Only
Ultimate Strength	F^{su}	ASTM E 143 & D 5379	
Yield Strength	F^{sy}		
Modulus	G^{m}		

4.6.5 Flexure

F_m^{fu}, F_m^{fy}, E_m^f

4.6.5.1 Introduction

As previously noted in Section 4.6.3, the measured ultimate tensile strength of a neat polymer is typically much less than the ultimate compressive strength, because of the greater critical flaw size sensitivity in tension. Therefore, polymer flexure specimens tend to fail at or near the tensile surface (depending on where a critical flaw is located). Thus, it is usually more logical to test for tensile strength directly, by performing a polymer matrix tensile test as described in Section 4.6.2.

Because of this, flexural testing of neat polymers is not commonly performed, even though flexural testing of composite materials is. For composites, flexural testing tends to persist because of the simplicity of the test specimen and test apparatus, not because of the general value of the data obtained, which is often limited. One exception is when the composite material is to be actually used in service in a similar geometric configuration and loading.

If flexural testing of a neat polymer is to be performed, ASTM Standard D 790 (Reference 4.6.5.1) is available for general guidance.

4.6.5.2 Specimen preparation

The flexure test specimen is a simple rectangular strip of polymer matrix, of constant width and thickness. Thus, it can be readily machined from a molded plate of the appropriate thickness, using the techniques and precautions described in Section 4.2. The ASTM D 790 recommendation of a span length to specimen thickness ratio of 16 for polymers dictates the length of the specimen, allowing for at least 10 percent overhang (but not less than 0.25 in., 6.4 mm) at each end. Specimen width should not exceed one-fourth of the support span, except that the minimum width should not be less than 0.50 in. (12.7 mm). For example when testing a 0.10 in. (2.5 mm) thick polymer matrix material, the test span would be 1.6 in. (41 mm), and thus the overall specimen length about 2.1 in. (53 mm) and the specimen width 0.50 in. (12.7 mm).

4.6.5.3 Test apparatus and instrumentation

ASTM D 790 permits either three-point or four-point loading, with no preference indicated. It will be noted that for three-point loading the maximum tensile stress occurs locally at the surface opposite the loading point. For four-point loading the maximum tensile stress occurs over the entire surface between the loading points, again at the surface opposite that where the loading points are applied. Thus, based upon the higher probability of a critical flaw being present, statistically it can be expected that four-point flexure will result in lower measured flexural strengths. However, very often this difference is less than the normal data scatter, particularly for less brittle polymer matrix materials.

ASTM D 790 does suggest that the specimen be supported and loaded via circular cylinders of diameters which may be up to three times the specimen thickness, but not less than 0.25 in. (6.4 mm). Thus, for the 0.10 in. (2.5 mm) thick polymer specimen used as an example in Section 4.6.5.2, the cylinders should be between 0.25 in. (6.4 mm) and 0.30 in. (7.6 mm) in diameter. Since fixtures are typically supplied with cylinders of standard sizes, e.g., likely 0.25 in. (6.4 mm) or 0.50 in. (12.7 mm) in the present case, the 0.25 in. (6.4 mm) diameter cylinders would be appropriate. In all cases, the goal is to use cylinders of sufficient diameter so as to minimize excessive indentation of the specimen, or local failures due to stress concentrations directly under the cylinders.

ASTM Standard D 790 suggests the use of either testing machine crosshead displacement or specimen midlength deflection to determine flexural strain and/or modulus. A strain gage bonded to the tensile surface of the specimen at midlength can also be used.

4.6.5.4 Flexural test methods for MIL-HDBK-17 data submittal

Data produced by the following test method (Table 4.6.5.4) are currently being accepted by MIL-HDBK-17 for consideration for inclusion in Volume 2:

TABLE 4.6.5.4 *Resin flexural test methods for MIL-HDBK-17 data submittal.*

Flexural Property	Symbol	Fully Approved, Interim, and Screening Data	Screening Data Only
Ultimate Strength	F_m^{fu}	ASTM D 790	
Yield Strength	F_m^{fy}	"	
Modulus	E_m^f	"	

4.6.6 Impact

This section is reserved for future work.

4.6.7 Hardness

This section is reserved for future work.

4.7 FATIGUE TESTING

Fatigue testing of unreinforced resins is performed by cyclic loading of a test specimen below failure load to determine time or number of cycles to failure. A wide variety of loading conditions may be employed, including bending, crack opening, tension, compression, or tension-compression reverse loading. The loading is often characterized by the ratio of the minimum to maximum load, for example, tension-tension fatigue, R=0.1. A series of tests are usually conducted at a loading frequency chosen to be low enough to avoid heating of the specimen. This heating can lead to thermally-induced failure. Load or deformation is cycled between selected values until failure, and maximum load or some other indication of load intensity is plotted against the log of the number of cycles to failure. Multiple tests are performed at each of several load levels, and the plot of the results of these tests is referred to as an S-N curve.

Since the fatigue resistance of a fiber-reinforced composite does not depend in a predictable way on the fatigue resistance of the unreinforced matrix, detailed recommendations for such tests are not included in this handbook. A discussion of fatigue testing of composite materials may be found in Section 6.9.

4.8 TESTING OF VISCOELASTIC PROPERTIES

Testing of viscoelastic, as opposed to elastic, properties involves characterization of the time dependence of these properties . This time dependence arises from the viscoelastic nature of polymeric resins. These tests may be conducted by measuring deformation as a function of time at constant load (creep testing), by measuring load as a function of time at constant deformation (stress relaxation), or by subjecting the material to some more complex load or deformation history to determine the elastic and viscous components of the material response. Dynamic mechanical analysis is an example of cyclic loading for viscoelastic material characterization. A discussion of dynamic mechanical analysis may be found in Section 6.6.3.

Since the viscoelastic or time-dependent properties of a fiber-reinforced composite do not depend in a predictable way on the viscoelastic response of the unreinforced matrix, detailed recommendations for such tests are not included in this handbook. A discussion of viscoelastic testing of composite materials may be found in Section 6.11.

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