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MICHAEL B. BEVER

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Composite Materials: Long-Term Degradation of Properties

Long-term degradation of the properties of polymer-matrix composite materials occurs primarily in two ways: hygrothermal effects and viscoelastic effects. In each case the effects are due primarily to the polymeric matrix, not the fibers, and therefore affect the matrix-dominated properties, rather than the fiber-dominated properties.

Hygrothermal effects are twofold in form. When a polymer-matrix composite is subjected to both heat and moisture, moisture is absorbed and the polymeric matrix swells, resulting in a dilatational moisture strain. This is totally analogous to a thermal strain, and therefore can be treated as mathematically analogous to a thermal strain, described as the product of a coefficient of moisture expansion and the percentage of moisture ingested by the composite matrix (see *Elastic Properties of Laminates*). Moisture absorption into the matrix is a diffusion process, analogous to temperature diffusion, and is adequately described by Fick's laws (Pipes et al. 1976, Flaggs and Vinson 1978, Sloan 1979, Wilson 1982, Vinson et al. 1977). The maximum that a polymeric composite can absorb is approximately 3 wt%, but the resulting dilatational strains can be as large as thermal strains, and therefore cannot be ignored in many structural analyses.

The second form of hygrothermal effects involves the glass-transition temperature (Vinson et al. 1977). Any dry polymer has a glass-transition temperature, above which the ultimate strength and elastic modulus decrease abruptly, significantly impairing its use as a structural material. When the polymeric matrix is subjected to both heat and humidity, the glass-transition temperature is significantly reduced, therefore significantly lowering the upper temperature limit at which a polymer-matrix composite can be used structurally. This second hygrothermal effect must be determined empirically, so that for many structural analyses a data bank of strength and stiffness at various temperatures and moisture contents is required.

Hence, for hygrothermal effects the phenomena are completely characterized and can be incorporated in any structural analysis involving polymer-matrix composite materials. Such effects do not exist in metal-matrix composites.

The second form of long-term degradation of composite materials is viscoelasticity, or creep; this can occur in both polymer-matrix and metal-matrix composites. In elasticity the mathematical model for the stiffness of material is that of a spring only, whose spring constant changes only with temperature but not time. However, almost all materials exhibit a

time-dependent behavior if the temperature of the material is raised sufficiently. In that case the material behavior is not that of a pure solid, but a mixture of solid and liquid phase, so that under load the material changes dimensions in either a reversible or an irreversible manner depending upon whether the material is unaging or aging in behavior. Mathematically, the viscoelastic material can be modelled by springs and dashpots, that is, elements whose resistance to displacement is proportional to the time rate of change of force, rather than force itself.

In the 1940s and 1950s these models led to the characterization of viscoelastic behavior by the Correspondence Principle, in which the viscoelastic structural analyses employed Laplace transforms, and, in the Laplace-transform plane, the mathematical equivalence enabled the use of any corresponding associated elasticity solution. The problem of such methods involved finding the proper inverse Laplace transforms to return to the physical plane.

More recently, much work has been done using other mathematical techniques, such as hereditary integral formulations for thermorheologically simple materials—that is, those in which time and temperature effects can be superposed. For those materials, an empirically determined temperature-dependent time-shift factor can be employed, so that the data from several simple short-time (i.e., minutes or hours) creep and relaxation tests at various temperatures can be used to develop a master curve for the material, describing its behavior adequately over years of real time. For materials that are thermorheologically complex (i.e., exhibiting aging), empirical temperature-shift factors for viscoelastic behavior must also be incorporated, resulting in less reliable mechanical property prediction. Fortunately, many polymer-matrix composite materials are thermorheologically simple, and so the superposition, Duhamel or hereditary integral methods of analysis can be employed.

It has been shown that for many polymer-matrix composites under conditions of quasi-static loading, the quasi-elastic methods of analysis can be employed to adequately describe the time-temperature effects. This simply utilizes an elastic analysis, employing the mechanical properties of the material for the particular time and temperature of interest. Empirically based power law or exponential series mathematical models are used to represent the viscoelastic properties, thus requiring experimental data over a wide range of temperature and times. Sims (1972) has shown that such a procedure describes the actual material properties to within 10%, sometimes quite accurate enough for engineering structural analysis.

The significance of viscoelastic effects on the struc-

tural response of polymeric fiber-reinforced laminates has been demonstrated by Wilson (1982). Using the quasi-elastic approximation, he shows that viscoelastic effects can reduce the critical buckling load by up to 80% of the elastic value for certain thin laminated plates under biaxial compressive loads. Hence, when calculating critical buckling loads, vibrational response and maximum deformations for thin-walled polymeric matrix composite material structures for long-time usage, viscoelastic effects cannot be ignored.

See also: Fatigue of Composites; Composite Materials: An Overview

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J. R. Vinson

Composite Materials: Nondestructive Evaluation

To reduce weight and increase durability, high-modulus fibers are being used to fabricate advanced composite structures for military and commercial products. The composites generally consist of fiber-reinforced plastics (FRPs) such as fiberglass, Kevlar, graphite-epoxy or boron-epoxy. The structures are made of fiber-epoxy tapes in multiple layers and in various angular orientations to obtain the desired thickness and strength. The laminate structure may range from 6 to 100 plies. Each tape ply represents a thickness of approximately 0.125 mm. More

recently, quasi-isotropic biwoven cloth, 0.33 mm thick, has been used.

For service temperatures up to 175 °C, epoxy resin systems have been the mainstay for laminating and molding such composite structures but polyimides and metal-matrix systems are now being developed for operation at temperatures up to 315 °C.

Composite structures come in a wide variety of shapes, sizes and configuration complexities. These structures may be laminates only, honeycomb assemblies with composite skins, laminates adhesively bonded to metal or combinations thereof.

1. Nondestructive Evaluation Policy

The major objectives of quality assurance non-destructive evaluation (NDE) are process control and structural integrity. Although existing non-destructive inspection (NDI) technology is not sufficient to ensure composite structural integrity directly, an NDE policy based on inspectable designs and in-process quality control can do so indirectly. Because composite materials are anisotropic and susceptible to various processing variables which may generate critical flaw types, an NDE policy should be established during the preliminary design phase.

Nondestructive evaluation of advanced composite structures, manufactured by the autoclave process, has revealed the following possible defects: interlaminar separations (delaminations), debonding, fiber misorientation, thickness variations, resin starved areas, honeycomb core fitup and splices, interlaminar porosity, cracks, inclusions, resin rich areas and adhesive voids.

2. In-Process Cure Monitoring

The dielectric test method is used to monitor the curing of a thermosetting resin. A capacitor is made with the composite as the dielectric. The properties measured are the dielectric constant and loss tangent. These properties are established by changes of the resin during the curing process. Both capacitance and dissipation vary due to, respectively, the variation of the resin dielectric constant and changes in the resin viscosity resulting from polymerization throughout the cure cycle. By monitoring the capacitance and loss tangent during the cure cycle, one may determine the optimum time to apply pressure and produce a dense, void-free composite.

3. In-Process Flaws

One of the most common flaws encountered in composite laminates is interlaminar porosity. Theory predicts and experiments show that mechanical properties decrease in relation to the severity of the porosity (Martin 1978).

The second most commonly occurring flaws are

adhesive voids and porosity (Hagemaier and Fassbender 1978a). These can occur at laminate-to-laminate, laminate-to-metal or laminate-to-honeycomb core bond joints. They also occur at honeycomb core splices and core-to-closure bond joints. When composite laminates are precured and inspected prior to bonding, it is easy to detect, identify and record flaws in the laminate. After bonding, the joints are inspected for voids, porosity or debonding, and the flaws are identified and recorded. However, if the laminate and bond joints are cured at the same time, it may become difficult to distinguish whether the defects are in the laminate or bond joint.

Debonding or delaminations, caused by improper cleaning, surface preparation or foreign materials, are the third most commonly occurring flaws (Hagemaier and Fassbender 1978a). Delaminations may also be caused by impact damage during handling or shipping. The remainder of the defects, listed in Sect. 1, occur with less frequency and severity and generally have little effect on the serviceability of the structure. However, because they may occur and be detected, criteria for acceptance or rejection must be established for fabrication inspection.

4. In-Service Flaws

When the structural parts are put into service, periodic inspections may be required to detect debonding (caused by moisture intrusion or poor adhesion), delaminations or cracks (caused by impact or excessive stress) and water intrusion into honeycomb structures. The probability of these defects occurring in service is fairly high, so their effect on the serviceability of the structure should be determined early in the program. Damage tolerance tests may be required and the appropriate NDE tests may need to be developed and specified periodically.

5. Nondestructive Inspection Methods

5.1 Ultrasonic Inspection

Very often, more than one NDE method is used to inspect composite structures because different conditions or defects are revealed by each method. The dielectric test method has proved useful in monitoring the cure of composites. Ultrasonic attenuation measurements (see *Ultrasonic Nondestructive Evaluation*) can be used to measure void content (in volume percent) and, subsequently, any loss in mechanical properties.

Ultrasonic C-scan inspection is primarily used to record automatically porosity, delaminations, foreign objects, voids and cracks. The ultrasonic C-scan method is useful also for inspecting adhesive-bonded composite structures for voids, porosity and debonds. The C-scan method is generally performed using focused search units which operate at 10.0 MHz for thin laminates decreasing, to 2.25 MHz for thicker

laminates. The part may be immersed in a tank filled with water which acts as an ultrasonic couplant between the search unit and the part. Alternatively, a squirter system may be used. (Honeycomb assemblies are generally inspected using the squirter method because of the difficulty of immersing a part which floats.) In either case, the search unit scans the part and the ultrasonic signals are fed through the pulser-receiver to a recorder to produce a facsimile of the part.

The C-scan method may be used in three different modes: through-transmission, pulse-echo or reflector plate. In the through-transmission technique, a sending search unit is placed on one side of the part and a receiving unit is placed on the other. Because the sound only passes through the part once, this technique is generally used for inspecting bonded honeycomb structures and thick or attenuating laminate materials. The pulse-echo technique uses one search unit as both sender and receiver. This technique is used generally to inspect laminates 5 mm or greater in thickness. The reflector-plate technique is similar to the pulse-echo technique except that the ultrasonic beam is transmitted through the laminate to a metal plate located about 10 mm behind the laminate back surface. Laminates 5 mm or less in thickness are generally inspected using this technique.

Some bonded and laminate structures have complicated shapes which do not lend themselves to inspection by the immersion C-scan method. In these cases, manual contact pulse-echo ultrasonic inspection is used. The contact method is performed with small diameter search units operating at 5 to 10 MHz. Manual contact scanning may be used in conjunction with a digital-readout ultrasonic thickness gauge to detect delaminations. If a composite laminate is not delaminated, the gauge will indicate the correct required thickness. When there is a delamination, the gauge reading indicates its presence and its depth below the test surface.

Ultrasonic bond testers are used to perform manual inspection of adhesive-bonded joints for voids, porosity and debonds. These instruments operate on the principle of resonance impedance and are calibrated to respond to a shift in frequency and signal amplitude between defective and nondefective standards. The part must be scanned manually and flaw locations marked on the part surface.

One instrument especially useful for determining the depth or defective bond line of a multiple-layered bond joint operates on the concept of ultrasonic impedance-plane analysis using a scope display. The scope serves as the ultrasonic impedance plane, where a "flying dot" display indicates the tip of the total ultrasonic impedance vector. Using the center of the scope screen as the origin (calibrated for properly bonded material), phase changes in impedance are displayed circumferentially, while amplitude

changes are shown radially. Thus, the position of the dot on the scope reveals the phase and amplitude of the material's ultrasonic impedance. Bond-line anomalies of different types or at different depths, produce characteristic dot locations on the scope display.

5.2 X-Ray Radiographic Inspection

Radiography (see *Radiographic Nondestructive Evaluation*) is useful for evaluating the porosity and void content of adhesively bonded joints provided the adhesive is opaque to x rays, and it is especially useful for inspecting honeycomb structures for core and adhesive filler defects. Composite structures are relatively low absorbers of x radiation. Therefore, low-kilovoltage machines having beryllium windows are used to make radiographs of these materials.

Laminates can be evaluated for interply porosity, foreign materials and impact damage. There are times when edge delaminations are obvious in laminated structures. The extent of the delamination may be determined by ultrasonic inspection. Radiography may also be used by brushing an x-ray opaque solution, such as 1,4-diiodobutane (99%), on the edge of the laminate and letting it seep into the defect as demonstrated by Hagemaiier and Fassbender (1978b). Diiodobutane is effective because it evaporates from flaws in a matter of hours and is not toxic.

5.3 Dye Penetrant Inspection

Experience has shown that liquid penetrants (see *Penetrant Nondestructive Evaluation*) are excellent for finding cracks, edge delaminations and porosity at the surface of a composite laminate. The major objection is the difficulty of removing the dye from the flaws; this interferes with repairs. In cases where repairs are to be made, a small amount of fluorescent dye may be added to alcohol or other solvent and used as a flaw indicator.

5.4 Infrared Inspection

Thermal or infrared tests (see *Infrared-Thermal Nondestructive Evaluation*) have been used to inspect composite honeycomb structures. Infrared tests are generally performed using infrared radiometers or heat-sensitive coatings applied to the surface of the part. The radiometer technique slaves the detector to a moving heat source and records variations in heat absorption or emission while scanning the part surface. The signal is amplified and serves to modulate the brightness of a lamp, which is focused onto a Polaroid film. The thermal pattern may also be observed on a cathode ray tube or storage (memory) tube display.

There are three basic types of heat-sensitive coatings which have had limited use for the NDE of composites: cholesteric liquid crystals, thermochromic paints and thermoluminescent paints.

When illuminated with white light, cholesteric liquid crystals selectively scatter certain wavelengths of the incident light, producing vivid colors easily visible to the naked eye. For a given compound, different wavelengths are scattered at different temperatures. Thus, the image produced changes color according to the surface temperature of the object.

Thermochromic paints are composed of a mixture of temperature-indicating materials that have the ability to change color when certain temperatures are reached. The paints are easy to apply and remove and provide visible isothermal patterns over the surface of the test object. The color change is a result of chemical reaction caused by heat which drives off gas. For some paints, the color change is caused by moisture evaporation from the paint. As the paint cools, it reabsorbs moisture from the atmosphere and returns to its original color.

The use of an ultraviolet-transmitting coating, containing a thermoluminescent phosphor that emits light under excitation by ultraviolet radiation, permits the direct visual detection of disbonds as dark regions in an otherwise bright (fluorescent) surface. As the disbond area cools, the dark spot will fade and become fluorescent.

There are two conditions that limit the sensitivity of infrared or thermal tests and, consequently, their usefulness for NDE: (a) the thickness of the facing sheet or laminate, and (b) the thermal conductivity of the composite structure materials. Flaws close to the surface of the part are more easily detected than deep-lying ones. Flaws in a bond line between graphite/epoxy skins and aluminum honeycomb core are more easily detected than in similar parts containing graphite/epoxy skins and nonmetallic core.

6. Engineering Laboratory Inspection Techniques

The NDE methods described in Sect. 5 may not completely characterize flaw parameters. Methods such as holographic interferometry (see *Acoustic Holography*), vibrothermography (see *Vibrothermography*), neutron radiography (see *Neutron Radiography*) and eddy current testing (see *Eddy-Current Nondestructive Evaluation: Pulsed Methods*; *Eddy-Current Nondestructive Evaluation: Sinusoidal Methods*) are therefore being investigated. In most cases, the specimen is subjected to uniaxial or biaxial loading conditions and the flaw growth is periodically monitored by one or more NDE methods.

Eddy current testing of aluminum/boron composite materials has shown a good relationship between volume fraction and eddy current conductivity in percent of the International Annealed Copper Standard (%IACS) for 6061 and 2219 aluminum alloy matrix materials.

Vibrothermography utilizes low-amplitude mechanical vibrations to induce localized heating in a

material. A real-time thermographic camera is used to monitor the temperature patterns established in the laminates by the vibration. The type of damage most readily observed is delamination or relatively large cracks or crazing in the matrix (Henneke and Jones 1979).

Thermal neutron radiography provides an image of the bond line or of the composite material in the presence of metal. Certain elements such as hydrogen and boron exhibit neutron attenuation coefficients which are two to three orders of magnitude greater than the average value for structural metals. The hydrogen content of organic materials such as epoxy adhesives typically ranges from 8 to 12%, which is adequate for good radiographic contrast. Flaws such as voids, porosity, cracks, resin-rich, resin-starved, bond-line thickness variations, and inclusions (more dense and less dense) have been detected using neutrons. Because of the high neutron absorption of boron, composites made from boron-epoxy cannot be inspected by this method.

Holographic interferometry can be used to disclose slight surface distortions as honeycomb specimens are stressed statically (by vacuum, pressure or heat) or dynamically (by variable frequency ultrasonics). Surface regions above subsurface discontinuities are deformed differently from the rest of the surface as a result of an applied stress, and hence produce anomalies in the fringe pattern. For example, Maddux and Sendekyj (1979) performed holographic studies of 16-ply graphite-epoxy specimens containing a center-drilled hole 5 mm in diameter. The initial specimens were evaluated by x-ray and holography methods. Then the specimens were alternately subjected to a loading program and NDE. The loading program consisted of an initial static tensile loading to 13 kN (3000 lb) followed by successive blocks of constant-load-amplitude fatigue loading using sinusoidal waveform. Images were obtained using real-time holographic techniques and heating to stress the specimens. Holograms were made of both the front and back faces of the specimens.

Damage in composite materials is very complex. It consists of matrix cracks, fiber fractures and delaminations. Moreover, the nature of the material tends to diffuse the effect of subsurface damage. In order to produce a surface deformation which results in a fringe anomaly, the effect of the damage has to be transmitted through the layers of intact fibers and matrix. The challenge to NDE of composites is very high; areas such as composite repair and heat damage have been neglected in the past and will require serious attention. However, new phenomena which have been observed in recent years, such as the Leaky Lamb waves (Bar-Cohen and Chimenti 1984), the effective use of signal processing techniques and the development of quantitative NDE techniques, can assist in overcoming obstacles that NDE of composites presently encounters.

See also: Composite Materials: An Overview; Non-destructive Evaluation: An Overview

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D. J. Hagemaier

Composite Materials: Nonmechanical Properties

The nonmechanical properties of composite materials (except some such as the magnetic properties of Alnico alloys) have not yet found wide commercial application, but their potentialities are intriguing.

Composite materials are novel materials in the sense that their properties may differ essentially from those of the constituent phases. They can exhibit a great variety of structures, resulting from specific fabrication techniques. One method is the artificial mixing of two or more (preshaped) substances, which may or may not be subjected to subsequent sintering processes or chemical reactions. Other methods are in situ growth by means of solidification of binary or polynary eutectic melts, or by disproportionation of crystalline or amorphous solids, and by isothermal reaction of a solid solution with a suitable ambient (see *In-Situ Composites*). The preparation methods to be used are dictated by the planned applications. An optimum property or combination of properties can be aimed for by a proper choice of the constituent phases and of the architecture of the composite material.

The nonmechanical physical properties of composite materials have been extensively reviewed by Hale (1976). They can be grouped as sum properties, product properties, and those based on structural

Table 1
Matrix classification of some physical properties or phenomena in materials according to the type of input and output parameters (after van Suchtelen 1972)

Output parameter (Y)		Input parameter (X)				
(1) Mechanical (force/deformation)	(2) Magnetic (field/polarization)	(3) Electrical (field/polarization, current)	(4) Optical and particle radiation (light or particle flux)	(5) Thermal (temperature, temperature gradient, heat current)	(6) Chemical (chemical composition, chemical composition gradient)	
(1) Mechanical (force/deformation)	Elasticity	Magnetostriction Magnetoviscosity (suspension)	Electrostriction Kirkendall effect Electroviscosity (suspension) Indirect: thermal expansion	Thermal expansion	Osmotic pressure	
(2) Magnetic (field/polarization)	Piezomagnetism	Magnetic susceptibility	Superconductors Galvanic deposition of ferromagnetic layer Direct generation of magnetic field	Photomagnetic effect	Thermomagnetism Ferromagnetic material at $T \approx T_c$ (+ magnetic field) ^a	Dependence of T_c on ferromagnetic composition
(3) Electrical (field/polarization, current)	Piezoelectricity Piezoresistivity	Magnetoresistance (+ electric current) ^a Hall effect (+ electric current) ^a Ac resonance	Dielectric constant, dielectric polarization Hall effect (+ magnetic field) ^a	Photoconductivity Photoemission Photoelectromagnetic effect (+ magnetic field) ^a	Thermoelectricity Ferroelectrics at $T \approx T_c$ (+ electric field) ^a Temperature-dependent resistivity (+ electric current) ^a	Dependence of T_c on ferroelectric composition
(4) Optical and particle radiation (light or particle flux)	Stress birefringence Triboluminescence	Induction of voltage Faraday effect Magnetooptic Kerr effect Deflection of charged particles	Electroluminescence Laser junctions Refractive index Kerr effect Absorption by galvanic deposits Cold emission of electrons	Ionization Refractive index Fluorescence Scintillation Color-center activation	Thermoluminescence	Chemoluminescence
(5) Thermal (temperature, temperature gradient, heat current)	Heat of transition of pressure-induced phase transition Piezoresistivity and Joule heating	Adiabatic demagnetization Nernst-Ettingshausen temperature gradient effect (+ electric current) ^a Magnetoresistance effect + Joule heating (+ electric field) ^a	Dissipation in resistance Peltier effect Nernst-Ettingshausen temperature gradient effect (+ magnetic field) ^a	Absorption	Thermal conductivity	Reaction heat
(6) Chemical (chemical composition, chemical composition gradient)	Pressure-induced phase transition		Electromigration Galvanic deposition	Light or particle stimulated reactions (photosensitive layers)	Soret effect (temperature gradient) ^a Phase transition Change of chemical equilibrium	

^a Indicates the parameter in parenthesis is essential as a second input

parameters such as anisotropy, periodicity, and size and interface effects.

1. Sum Properties

Physical properties of materials can be defined in terms of an X - Y effect, in which X is an input parameter and Y a corresponding output parameter. The behavior of the material is then given by $dY/dX = \alpha$, where α is a property such as thermal expansion, dielectricity, magnetic permeability, electrical conductivity or thermal conductivity.

Sum properties are those whereby the X - Y effect of the composite is a result of a combination of the same X - Y effects of the constituent submaterials. The simplest case is an isotropic composite material consisting of only two phases. If interface effects are negligible, then the value of the sum property lies somewhere between those of the constituent phases. It is determined by their volume fractions and, in a number of cases (e.g., for dielectricity and thermal conduction), also by the shape of the dispersed phase. Theoretical models have been designed and formulae have been derived to describe the properties for dispersed spheres, disks, lamellae and needles. In practice, for real composite materials there will be uncertainty about the degree of approximation involved in using the ideal theoretical models, but yet upper and lower bounds can be set up which enclose experimentally obtained values as a function of volume fraction (Hale 1976). If the X - Y effects are of opposite sign, they may then cancel each other out: for example, composite materials may have electrical resistance independent of temperature, owing to the fact that the one phase exhibits a positive temperature coefficient of resistance and the other a negative one (Boonstra and Mutsaers 1978).

If interface properties dominate, then the picture can change fundamentally. For example, the thermal and electrical conductivity of the composite may be lower than that of the constituent phases, due to thermal (acoustic mismatch) or electrical (depletion layers) contact resistances between the phases (Hale 1976).

Anisotropic composites can be obtained by alignment of at least one of the phases, even if the phases themselves are isotropic (see Sect. 3).

2. Product Properties

The concept of product properties (van Suchtelen 1972, 1980), is of great potential value when devising composite materials with novel properties. It is based on the supposition that the output from an X - Y effect in submaterial 1 can act as the input for a Y - Z effect in submaterial 2, resulting in an overall X - Z effect. The term product property is evident from the equation:

$$(dZ/dX)_{\text{comp}} = k(dY/dX)_1 \cdot (dZ/dY)_2$$

in which k is a coupling factor. A product property may be a completely new one or it may represent a known conversion, but with a higher yield. The handling of this concept is illustrated in Tables 1 and 2. Table 1 shows a 6×6 matrix exhibiting current X - Y (or Y - Z) effects. This table can be used to make many combinations giving a large number of product properties. A small selection is shown in Table 2. The coupling mechanism that achieves the transfer of the quantity Y from submaterial 1 to submaterial 2 may be of any nature—mechanical, optical, electrical, magnetic or thermal. The concept of product properties can also be applied to devices, such as integrated circuits, that also consist of microscopic arrangements of submaterials. However, with a composite material it is an intrinsic property of the material in the sense that any portion of it (provided that its size is large compared to the microstructural period) always has the same physical properties, which are not affected by minute damage or machining.

An example of mechanical coupling is the magnetoelectric effect produced in the cobalt ferrite-barium titanate eutectic composite. It yields 0.16 VA^{-1} and compares favorably with the value of only 0.025 VA^{-1} for Cr_2O_3 , the best single-phase transducer at room temperature. Application of a magnetic field (X) induces a change in the shape (Y) of the magnetostrictive cobalt ferrite phase, which, in turn, through mechanical coupling causes a strain in the piezoelectric phase in which an electric field (Z) is generated. An example of the occurrence of electronic coupling is the composite x-ray fluorescent material consisting of fine ($\sim 1 \mu\text{m}$) PbCl_2 particles in an anthracene matrix. Incident x rays (X) release secondary electrons (Y) in the PbCl_2 , and these electrons, having a range of a few micrometers, spend most of their time in the anthracene, which is a good scintillator (Z). This composite exhibits an x ray (X) to visible light (Z) conversion efficiency exceeding that of anthracene by at least one order of magnitude in a composite layer less than 0.05 cm thick (van Suchtelen 1972, 1980).

3. Properties Based on Structure and Phase Dimensions

3.1 Periodic Structures

(a) *Optical.* Periodic structures give rise to diffraction phenomena in electromagnetic and particle optics both in thin transparent composite layers and at etched composite surfaces (van Suchtelen 1980).

(b) *Electrical.* Electronic properties have been studied in composites with electronic superlattice structures, in which the electron mean free path in both phases is longer than the structure period. These properties have been discussed according to the Kronig-Penney model for moving electrons in a crys-

Table 2

Product properties of composite materials (after van Suchtelen 1972)

X-Y-Z (Table 1)	Property of phase 1 (X-Y)	Property of phase 2 (Y-Z)	Product property (X-Z)
1-2-3	Piezomagnetism	Magnetoresistance	Piezoresistance
1-2-4	Piezomagnetism	Faraday effect	Phonon drag
1-3-4	Piezoelectricity	Electroluminescence	Rotation of polarization by mechanical deformation
1-3-4	Piezoelectricity	Kerr effect	Piezoluminescence
2-1-3	Magnetostriction	Piezoelectricity	Rotation of polarization by mechanical deformation
2-1-3	Magnetostriction	Piezoresistance	Magnetoelectric effect
2-5-3	Nernst-Ettingshausen effect	Seebeck effect	Magnetoresistance
2-1-4	Magnetostriction	Stress-induced birefringence	Spin-wave interaction
3-1-2	Electrostriction	Piezomagnetism	Quasi-Hall effect
3-1-3	Electrostriction	Piezoresistivity	Magnetically induced birefringence
3-4-3	Electroluminescence	Photoconductivity	Electromagnetic effect
3-1-4	Electrostriction	Stress-induced birefringence	Coupling between resistivity and electric field (negative differential resistance, quasi-Gunn effect)
4-2-1	Photomagnetic effect	Magnetostriction	Electrically induced birefringence
4-3-1	Photoconductivity	Electrostriction	light modulation
4-3-4	Photoconductivity	Electroluminescence	Photostriction
4-4-3	Scintillation	Photoconductivity	Wavelength changer (e.g., infrared-visible)
4-4-4	Scintillation, fluorescence	Fluorescence	Radiation-induced conductivity (detectors)
			Radiation detectors, two-stage fluorescence

tal lattice. Oscillatory transport phenomena and negative differential resistances have been created in semiconducting superlattice composites (Hale 1976).

3.2 Anisotropic Structures

(a) *Optical*. Thin layers of 0.07 cm thickness of unidirectionally solidified InSb-NiSb eutectic act as polarizing filters which show at least 99% polarization when the diameter of the electrically conducting NiSb rods is small compared with the wavelength of the electromagnetic waves. This is due to the fact that electric vectors vibrating perpendicular to the axes of the conducting rods are not damped to any great extent and therefore traverse the composite layer, while those with electric vectors parallel to the rods will lose energy.

Composites containing aligned elongated transparent inclusions of an optically isotropic material in a transparent optically isotropic medium with a different refractive index exhibit birefringence if the periodicity of the composite is much less than the wavelength of the light (Hale 1976).

(b) *Electrical*. A very simple example is the electrical conduction anisotropy in a composite that consists of an insulating or semiconducting matrix with aligned metallic rods. The electrical conductivity in the direction of the rod axes can be orders of magnitude higher than in the transverse direction.

In composites of this kind, anisotropy also arises from the fact that a Hall voltage or a thermoelectric

force is short-circuited in the direction of the conducting rods, but not in a direction perpendicular to it. Outstanding magnetoresistive devices have been developed on the basis of the unidirectionally solidified InSb-NiSb eutectic composite, in which, on the application of a magnetic field, a Hall voltage is generated in the semiconducting InSb matrix and short-circuited by the metallic NiSb rods $\sim 1 \mu\text{m}$ diameter. The magnetoresistance effect is maximum when the axes of the rods, the input electric current and the applied magnetic field are all at right angles to one another. In this system a magnetic field of 1 T increases the electrical resistance by a factor of 20. The increase of homogeneous InSb is only 60% in 1 T. Applications include contactless variable potentiometers and resistors, and the measurement of magnetic fields (Hale 1976).

3.3 Size and Interface Effects

If the dimensions and the mean periodic parameter of one or more of the constituent phases in one or more directions become comparable with, or fall below, a characteristic physical length (e.g., the size of magnetic or ferroelectric domains or the thickness of a space charge layer at the interface) then novel properties come to the fore. Generally speaking, interface effects become more dominant as the degree of dispersion of the composite increases.

(a) *Magnetic*. High coercivity is required in permanent magnets and has been achieved by using

ferromagnetic materials built up of very fine particles, in which the possibility of magnetic domain boundary displacement is suppressed. Also, in the absence of magnetocrystalline anisotropy magnetic rods may exhibit a large demagnetization energy in the direction of the rod axes. In recent years, therefore, aligned magnetic rod-type eutectic composites have been investigated. High coercive forces have indeed been found, but the volume fractions of the magnetic rods were low and thus the energy products of the composites were too low and incompatible with the well-known commercially exploited Alnico alloys obtained by spinodal decomposition (Hale 1976).

(b) *Electrical* Multifilamentary superconducting composites are employed in the construction of powerful electromagnets in which no magnetic-flux jumping occurs (Hale 1976). They are used in high-energy physics including magnetohydrodynamics, particle beam transport, bending and focusing magnets in circular accelerators (e.g., the synchrotron), megawatt generators, and nuclear fusion reactors (Prodel 1979). These composite materials consist of multifilamentary type II superconducting wires (e.g., consisting of NbTi or Nb₃Sn) in a normally conducting ductile metal matrix (such as Cu) and can be produced by extrusion and wire-drawing. They are mechanically strong, exhibit a high critical temperature (above 15 K) and can carry very high overall critical electrical current densities and critical magnetic fields (above 12 T) (Roberge 1979).

When one phase of a composite material is *p*-type semiconducting and the other *n*-type semiconducting, the interface can have rectifying properties. The composite can behave as a field-effect transistor or can exhibit photovoltaic effects and act as a vertical multijunction solar cell. Such devices may exhibit a high spectral response over a wide spectral region. The photocurrent is high while the voltage output is less than or equal to that of a single junction if the junctions are connected in parallel. On the contrary, if the junctions are connected in series the photocurrent is low while the voltage output is high (i.e., equal to the sum of the voltages of each junction). The preparation of aligned lamellar eutectic composites exhibiting 10³–10⁴ heterojunctions per centimeter and showing diode characteristics and photovoltaic effects has been reported. Up till the early 1980s no commercially attractive solar cells have been fabricated using composite materials (van Suchtelen 1980, Anthony and Cline 1977).

See also: Composite Materials: An Overview

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W. Albers

Computer-Aided Materials Selection

Materials selection is an activity normally carried out by design and materials engineers. Its purpose is to identify materials which, after appropriate manufacturing operations, will have the dimensions, shape and properties necessary for the end product or component to perform its required function at the lowest total cost. As there are over 100 000 commercially available metals, plastics, elastomers and ceramics, which are significantly different when compared in terms of property combinations and cost, the use of a computer to store and manipulate this property information has obvious advantages over volumes of printed data sheets.

If the computer is fed with data on *m* properties for *n* different materials, then a program designed to operate on the *m* × *n* array can perform sorting and correlation operations. For example, the designer may set minimum limits on properties *n*₁, *n*₂, *n*₃ and ask the computer to print out the identification codes of all the materials which meet these criteria. Alternatively, with the aid of computer graphics a correlation plot between any two properties such as is shown in Fig. 1 may be obtained. In this case, the plot may be used, for example, to identify the material with the best combination of Young's modulus and impact strength at 23 °C. The searching of a 100 × 100 array takes about 45 s with a modern desk-top computer such as a Hewlett-Packard 9545T, for which the 9872A plotter takes 90 s to produce the plot shown in Fig. 1.

In practice, materials selection cannot be based

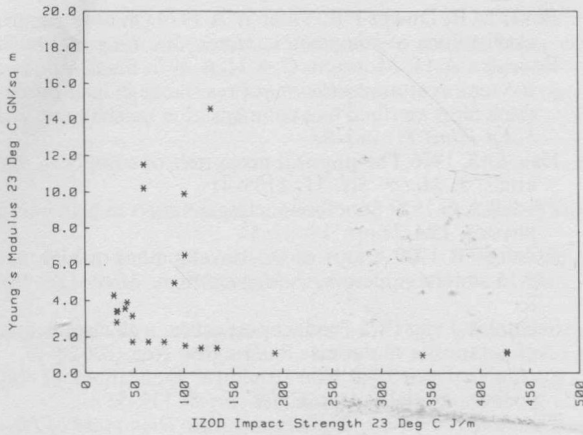


Figure 1
Computer plot of Young's modulus versus impact strength for a selection of engineering plastics

solely on single-point values of properties such as impact strength, Young's modulus and tensile strength for the following reasons:

- (a) Most materials properties are not intrinsic but depend on the method and circumstances of testing.
- (b) No two materials samples or set of testing conditions will ever be identical, and hence a spread of values is obtained rather than single-point data.
- (c) The conditions of the test may not simulate the intended environment in which the material is to be applied. Hence some extrapolation or interpretation of data may be necessary. This is particularly true for long-term properties such as creep and fatigue.
- (d) The structural integrity of products (e.g., stiffness) depends on the size, shape and location of supports as well as on the elastic modulus.
- (e) Materials selection for most applications is critically dependent on total cost, which in turn depends on variables such as raw-material cost, ease of manufacture and the necessary quality control.

However, computers are used to alleviate many of these problems and examples are given below.

1. Experimental Measurements and Processing of Raw-Materials Property Data

In a modern laboratory the measurement, analysis and presentation of most materials property data is computer assisted. This is particularly efficient in

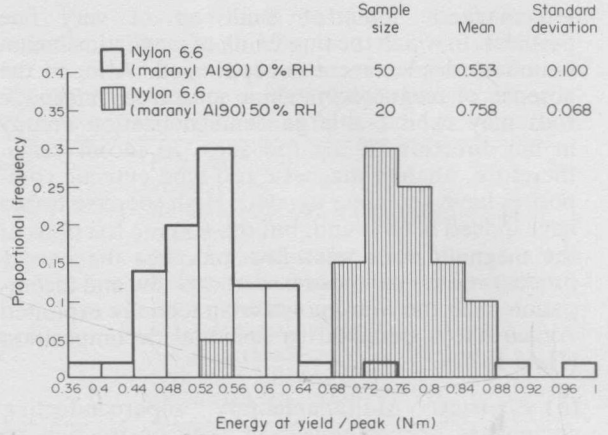


Figure 2
Distribution of impact yield energies of Nylon 6.6 at 0% relative humidity (RH) and 50% RH

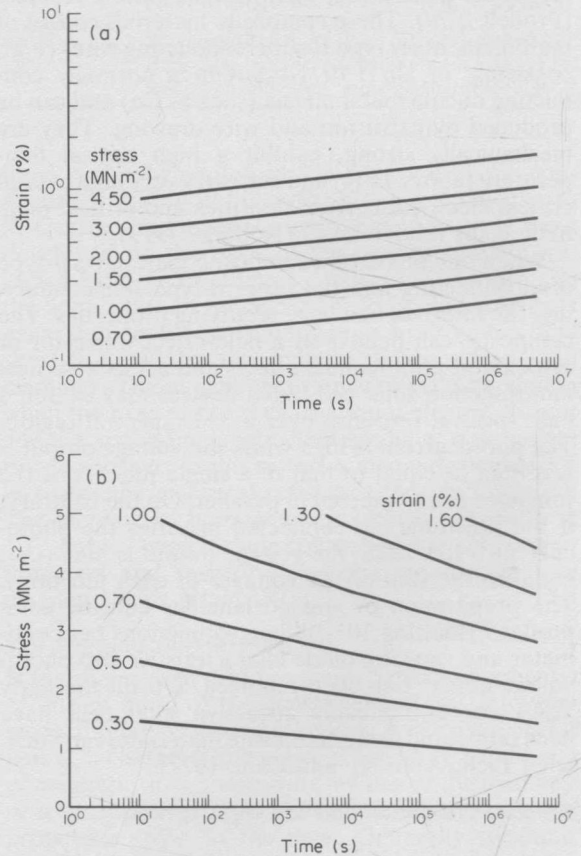


Figure 3
Computer-manipulated creep data (at 180°C) for an engineering plastic: (a) interpolated data; (b) isometric data