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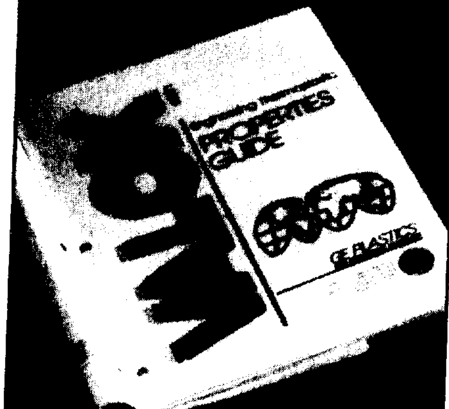

nonfilled parts n[illegible] from phenolics a[illegible] should be avoided.

Applications

Alkyd and polyester molding compounds are used in applications that require the combination of good electrical, mechanical, and dimensional stability properties.

Applications for electrical distribution and control include circuit breakers, motor [illegible] housings. Elec-[illegible] grades [illegible] also available which are capable of withstanding the temperature extremes of vapor phase soldering. Automotive applications include distributor caps, coil tops, and rotors.

Colored alkyd polyester molding compounds are used for decorative effect on appliances. Polyester molding compounds have been developed that are transparent to microwave radiation.

Unsaturated polyester

By T.K. Sprow

The versatile chemistry of unsaturated polyester resins allows them to be used in a variety of molding processes for numerous end-use applications. They are made by reacting one or more difunctional acids with one or more glycols. This reaction normally takes place at 180 to 200° C. The reaction is of the condensation type; hence water is distilled off. The resulting polymer is then dissolved in an unsaturated monomer, most commonly styrene.

Because these resins contain an unsaturated acid, maleic anhydride or fumaric acid, they are capable of further crosslinking during a molding process.

The selection of saturated acids and the glycols allows the manufacturer to formulate for a broad range of properties. Typical properties of interest include mechanical properties, chemical resistance, electrical properties, and weatherability.

The most common saturated acids include phthalic anhydride, isophthalic acid, and adipic acid. The most common glycols are propylene glycol, ethylene glycol, diethylene glycol, neopentyl glycol, and dipropylene glycol. The unsaturated polyester manufacturer generally controls the molecular weight by monitoring the acid value and the viscosity. Once the proper end point is achieved the molten polyester is transferred into a thinning tank containing the crosslinking monomer and selected inhibitors. The hot solution is cooled and is then ready for blending with appropriate additives. The blended product always contains one or more inhibitors to maintain adequate shelf life and to control gel and cure rates during the crosslinking process. Crosslinking can take place at room or elevated temperature.

For a room temperature cure system the resin manufacturer normally adds a cobalt promoter and a tertiary amine accelerator. This blended resin is then cured by the molder by adding a free radical initiator, most commonly an organic peroxide. If the molder employs an elevated temperature curing process, an initiator such as benzoyl peroxide or tertiary butyl perbenzoate is commonly employed.

Processing and applications

Unsaturated polyesters are used in unreinforced and reinforced applications. Approximately 80% of unsaturated polyesters are used in combination with reinforcing materials, generally fibrous glass. Reinforced polyester molded parts have good physical properties and dimensional stability and better strength-to-weight ratios than many metals. They also can be processed to perform well in corrosive environments and can be designed for improved fire and smoke performance.

A variety of molding techniques is employed that can generally be classified as either closed (press molding) or open (contact molding). Press molding processes include compression, injection, continuous pultrusion, and resin transfer. Open mold processes include hand layup, sprayup, filament winding, and centrifugal casting.

Compression and injection molding processes typically use a sheet molding compound (SMC) or a bulk molding compound (BMC). These processes employ elevated temperature, relatively high pressure, and metal dies. The dies are generally very smooth and usually chrome plated. Matched metal die processes permit very short cycle times, often less than 2 min., and are adaptable to high-volume production.

In the pultrusion process, the reinforcing medium is pulled through a resin bath and then through a heated metal die. Pultrusion is a continuous process for the manufacture of parts having a constant cross section. Molding conditions are typical of that for compression and injection molding.

The hand layup and sprayup processes are common for the molding of large reinforced polyester parts such as boats and recreational vehicle structures. In this process a pigmented polyester resin known as a gel coat is applied to the mold first and allowed to cure before applying subsequent layers of reinforcement and resin. Because molding takes place at room temperature with minimal pressure, lower-cost tools normally are employed. These molds usually are made with a glass fiber-reinforced polyester or epoxy resin. The finished parts are smooth on one surface only. Because hand rolling is required for air removal, hand layup/sprayup processes are more labor intensive. Capital investment, however, is quite low compared to that of press molding equipment.

In filament winding, fibrous glass is typically pulled through a resin bath and wound onto a rotating mandrel. Cure normally takes place at room temperature or slightly elevated temperature and the sur-

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T. K. Sprow is Technical Manager—Resins & Coatings Div., Owens-Corning Fiberglas Corp., Fiberglas Tower, Toledo, OH 43659.

ace is smooth on the interior only. The filament winding process typically is employed for the manufacture of reinforced plastic pipe and tanks.

The selection of a press molding or contact molding process is dependent on the size and volume of part to be manufactured as well as upon the surface aesthetics desired. Currently, approximately 70% of unsaturated polyesters used in reinforced plastics are molded via a contact molding process. It should be recognized that cycle times are considerably longer than with press molding. The molding times range from a minimum of 45 min. to as long as 8 hr. Contact molding processes are adaptable to very large parts including extremely large boat hulls and barge covers.

Nonreinforced applications include simulated marble castings, buttons, bowling balls, and numerous coatings. Coatings are applied by spray or dip coating.

Reinforced applications cover a broad range. Typical applications include boats, tub/shower stalls, recreational vehicle components, above- and underground storage tanks, and Class A automotive parts. Applications in the appliance, electrical, and microwave cookware fields are showing substantial growth.

Recent applications include an RP minesweeper for the U.S. Navy, sucker rods for oil drilling, high-performance structural parts for automotive, and cookware for microwave and conventional ovens.

Recent advances

The incorporation of dicyclopentadiene (DCPD) into the polyester backbone has become common. These resins have good electrical properties and perform well at high temperature. Because they wet out very well, they have proven beneficial in applications wherein fillers such as aluminum trihydrate are employed. Proper control of the resin manufacturing process is crucial for unsaturated polyesters employing DCPD. These resins have proven to be beneficial for improved surfaces in the marine industry, but the boat molder must carefully monitor the process to achieve the desired results including good interlaminar adhesion.

The formulation of other polymers into the unsaturated polyester is becoming increasingly important. Such systems known as *interpenetrating networks*, or IPN, include low-profile and low-shrink systems in which thermoplastic additives are employed. The thermoplastic is soluble in the uncured resin but becomes insoluble as the polyester crosslinks. This results in the formation of microvoids, compensating for the shrinkage during polymerization. The degree of shrinkage that takes place and the pigmentability of the final molding compound depends on the choice of unsaturated polyester and thermoplastic.

Another example of an IPN includes a combination of polyurethane and unsaturated polyester resin. Diisocyanates or polyisocyanates are blended with the unsaturated polyester and are designed to crosslink together.

The incorporation of tougher, more resilient materials together with the fine tuning of molecular weight is allowing the molder to incorporate increasingly higher levels of reinforcement, thus enhancing static and dynamic end-use performance.

Polyetherimide

By J.R. Bartolomucci

Polyetherimide is an amorphous high-performance thermoplastic introduced under the Ultem[1] trade name. The material is characterized by high strength, rigidity, heat resistance, dimensional stability, and electrical properties, combined with broad chemical resistance and processibility. Unmodified polyetherimide is amber-transparent in color and exhibits inherent flame resistance and low smoke evolution without the use of additives.

Chemistry and properties

Polyetherimide has a chemical structure based on repeating aromatic imide and ether units. High performance strength characteristics at elevated temperatures are provided by rigid imide units while the ether linkages confer the chain flexibility necessary for good melt processibility and flow.

Polyetherimide is resistant to a wide range of chemicals including most hydrocarbons, alcohols, and fully halogenated solvents. It is resistant to mineral acids and tolerates short-term exposure to mild bases. Partially halogenated solvents can be good solvents for polyetherimide.

Hydrolytic stability is good with greater than 85% tensile strength retention after 10,000 hr. boiling water immersion and 100% tensile strength retention after steam autoclaving 2000 cycles at 270° F. Polyetherimide's resistance to UV is very good, as is resistance to gamma radiation, the latter evidenced by a 94% retention of tensile strength after 400 megarads of CO_{60} irradiation.

Polyetherimide resins are rated for 170° C. and 180° C. continuous use temperatures by Underwriters Laboratories and are UL 94 V-0 listed down to 10 mils thickness depending on grade. Oxygen index is 47%. Glass transition temperatures of 215° C. and greater allow intermittent use at 200° C. and short-term excursions to higher temperatures. At 180° C., the tensile strength and flexural modulus remain in excess of 6000 and 300,000 p.s.i., respectively. Electrical insulating qualities of polyetherimide resin are largely maintained in elevated temperature and humidity environments. The resin is microwave transparent.

Grades

Resins are available in unreinforced, and in 10, 20, 30, and 40% glass fiber-reinforced grades for general-purpose molding and extrusion. Also available are easy-flow and release grades, wear-resistant grades, carbon fiber-reinforced grades for high strength and static dissipation, along with a family of high-heat grades offering 25° F. plus higher HDTs and 200° C. service.

Grades for structural foam molding along with a new family of polyetherimide blends tailored for use in vapor phase soldering environments and high-impact applications are among new grade offerings.

Processing

Polyetherimide can be readily processed on most conventional thermoplastic process equipment. The resin must be dried thoroughly prior to melt processing.

Melt temperatures of 640 to 800° F. and mold temperatures of 150 to 350° F. are used for injection molding. Film thickness of 0.25 mil can be obtained using solvent casting techniques. Components can be conventionally and laser machined and bonded together or to other materials using solvent, ultrasonic, hot platen, and adhesive assembly methods.

Applications

Principal markets for polyetherimides are transportation, electrical/electronic, medical, computer and business equipment, appliance, packaging, and specialty including military.

Electrical/electronic applications include high-strength and dimensionally stable connectors and circuit boards that are vapor and wave solderable, microwave transparent radomes, IC chip carriers and burn-in sockets; conventional, miniature, and infrared switches; coil bobbins, low-flame and low-smoke plenum connectors, explosion-proof enclosures, flexible circuitry, lamp reflectors, relay sockets, and high-precision fiber optic components.

Medical components can undergo repeated steam autoclave, hot air, ethylene oxide, gamma radiation, and cold chemical sterilization. Surgical instrument handles and enclosures, trays, non-implant prostheses, staplers, and nebulizer components are among several medical applications.

Transportation applications include under-the-hood temperature sensors, fuel system components, lamp sockets and metallized reflectors, high-strength transmission and jet engine components; and flame-resistant/low-smoke sheeting for aircraft interior applications.

Dual-ovenable cookware and coextruded food packaging requiring NSF and FDA resin compliance are other applications.

Specialty uses include computer rigid disks, printer wheels, and heads; high-strength, heat, and corrosion-resistant fluid and air handling components; fasteners, extruded profiles, bearings, advanced composites, and direct metal replacement.

[1] — Registered trademark of General Electric Co.

J.R. Bartolomucci is Manager-Ultem Technical Marketing, Plastics Group, General Electric Co., One Plastics Ave., Pittsfield, MA 01201.

Fibrous reinforcements

Aramid

By L.H. Miner

Introduced commercially in 1972, Kevlar[1] aramid fiber is finding broad application where light weight, high strength and stiffness, resistance to stretch, vibration damping, and resistance to damage are important. The fiber originally was developed to replace steel in radial tires and is finding increasing use in the belts of radial car tires and carcasses of radial truck tires where it saves weight and increases strength and durability. Kevlar 29 is the low density, high-strength aramid fiber designed for ballistic protection, slash and cut resistance, ropes, cables, and coated fabrics for inflatables and architectural fabrics. It is also used in friction products, such as brakes and clutches, and in gaskets to replace asbestos.

Kevlar 49 aramid fiber is characterized by low density and high tensile strength and modulus. These properties are key to its successful use as reinforcement for plastics composites in aircraft, aerospace, marine, automotive, and other industrial applications, and in various kinds of sports equipment.

Du Pont Co. manufactures and sells continuous-filament yarns and rovings, chopped fiber (staple), and pulp of Kevlar 29 and Kevlar 49. Kevlar 49 yarns in 195, 380, 1140, 1420, 2130, and 2840 denier sizes are supplied to commercial weavers who make broadwoven fabrics, woven rovings, and narrow woven tapes for plastic reinforcement applications. Commercial prepreggers supply fabrics and tapes preimpregnated with thermoset resins. Chopped fibers can be combined with thermosets or thermoplastics to make chopped fiber molding compounds.

Kevlar 49 aramid is used in high-performance composite applications where light weight, high strength and stiffness, damage resistance, resistance to fatigue and stress rupture, and vibration damping are key properties. Reinforced composites can save up to 40% of the weight of glass fiber composites at greater stiffness. The aramid composites resist shattering upon impact and the presence of the fiber inhibits propagation of cracks. Depending upon selection of resin systems, aramid composites have a useful temperature range from −320 to +400° F. They are nonconductive and exhibit no galvanic reaction when in contact with metals. While the tensile behavior is linear and failure occurs at high stress, aramid composites exhibit ductile behavior when subjected to compressive or flexural loads and the ultimate strength is lower than that of either glass or carbon composites. Aramid can be combined with glass or carbon in hybrid composites (see articles, p. 138). Hybrids allow the design engineer to achieve a balance of properties not available from a single reinforcing fiber.

Resins and processing

In the aircraft industry, Kevlar 49 most often is used to reinforce epoxy composites, while the marine industry uses orthophthalic and isophthalic polyesters and vinyl ester resin systems. Polyimide, phenolic, and other resins also can be reinforced.

Aramid fibers can be processed in essentially the same ways as glass and carbon to produce composites. Vacuum bag molding of fabric prepregs is most often used in the aircraft industry. High-performance pressure vessels and missile engine cases are filament wound with rovings. Rovings also can be used in pultrusion, allowing continuous manufacture of parts of constant cross-sectional area. Rovings of Kevlar 49 are available in 4560 and 7100 denier sizes. In the marine industry, fabrics and woven rovings of aramid are used in the wet, or hand layup, method. Fabrics, chopped fiber, and continuous fibers (such as XMC, PPG Industries Inc.'s trademark for continuous cross-plied fiber reinforcement) can be compression molded. Technology is being developed to use Kevlar 49 more efficiently in chopper gun sprayup, chopped fiber mat, preform, and injection molding.

Because of the inherent toughness of the fiber, special tools are required to cut fabrics and woven rovings and to efficiently machine composites. Scissors and power cutters are available to cut fabrics and woven rovings, as are tools for cutting and machining composites.

Applications

In the aircraft industry, composites of Kevlar 49 are used in components of aircraft such as the Lockheed L-1011, Boeing 757 and 767, McDonnell-Douglas DC-9-80, DeHavilland DHC-7 and DHC-8, Airbus 310, Cessna Citation and Conquest, Canadair Challenger, and Sikorsky Blackhawk and S-76 helicopters to save weight over incumbent metal or glass fiber components. Filament wound structures are used on the Space Shuttle Orbiter, the interim upper stage of the Orbiter, the Trident C-4 missile, the Pershing II missile, and the Boeing 747SP aircraft.

In the marine market, composites are used in the hulls of canoes, kayaks, sailboats, and large and small power boats.

Aramid fiber now is used in a variety of sports equipment—surfboards, sailboards, fishing rods, and skis—for light weight, stiffness, strength, and vibration damping.

Development programs are well under way in the automotive industry to identify and manufacture prototype components where plastic composites can contribute to fuel economy in future automobiles.

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[1] —Trademark of Du Pont Co.

L.H. Miner is Research Associate, E.I. du Pont de Nemours & Co. Inc., Wilmington, DE 19898.

Carbon

By Roger Prescott

Carbon fibers possess a range of stiffness unequaled by any other family of materials. The Young's modulus varies from about 5 million p.s.i., which is half that of aluminum or glass fiber, up to 100 million p.s.i., or more than three times that of steel. With current manufacturing technology the highest fiber strengths are obtained for fibers in the intermediate stiffness range, from 30 to 40 million p.s.i. Fibers of this type possess the most useful balance of mechanical properties and are by far the most widely used variety. They are notably effective as reinforcing elements in composite materials and are employed in many structural end uses, particularly in the aerospace field.

These fibers also, of course, possess the electrical, thermal, and chemical properties characteristic of carbon.

Manufacture

Many techniques have been tried for producing carbon fibers. All of them involve the heat treatment of a carbon-containing raw material, usually in the form of a polymer fiber. However, just three raw materials have been employed to date for production of commercial products. These are rayon, acrylic or PAN (polyacrylonitrile) fibers, and fibers spun from pitch.

The first high-stiffness, structural fibers were made from rayon. However, these materials did not compete with PAN-based carbon fibers which later became available as commercial products.

A third manufacturing technology has been developed based on pitch raw materials in the expectation that this approach would lead to lower-cost fibers. Today, fibers of this type are available with stiffnesses in the lowest and highest ranges, but not in the intermediate range. Evidently it has not yet been possible to produce pitch-based fibers with mechanical properties competitive with the most commonly used PAN-based types.

Available types

The wide variety of carbon fibers creates a challenge for the potential user. A useful way of categorizing available fibers can be based on the Young's modulus, as shown in Table I. Typically, the intermediate modulus types possess the highest strengths, while the lowest and highest modulus varieties exhibit the lowest strengths.

The highest composite mechanical properties are obtained in materials containing at least 60% by volume of unidirectional, continuous fiber in a matrix such as a high-strength epoxy. In such cases composite moduli and strengths measured parallel to the fiber direction reach levels of 50% or more of the fiber properties.

Composites containing continuous fibers laid in two or more directions possess lower mechanical properties in any one direction, but are more balanced overall. Lower, but still useful, mechanical properties are obtained when short-length carbon fibers are used as the reinforcement of molding compounds. In a typical case, nylon containing short-length intermediate modulus fibers, as a more or less random dispension, possesses a modulus of about 2.5 million p.s.i. and tensile strength of approximately 35,000 p.s.i.

The forms in which carbon fibers are supplied depend to some extent on the category. Low-modulus types are available as short-length fibers and in a variety of textile forms, including twisted yarns, fabrics, and felts. Intermediate- and high-modulus fibers are most commonly supplied as continuous filament, nontwisted yarns, and tows with various filament counts from 1000 to 320,000. They are also available in various short lengths from 0.3 to 2 in., as woven and nonwoven fabrics, and as preimpregnated tapes and fabrics. The highest modulus fibers are available in a limited range of forms, typically as fine continuous filament yarns containing 400 to 2000 filaments and as preimpregnated tapes.

Fabrication techniques

Carbon fibers are combined with resins and formed into composite structures using techniques essentially identical to those used for glass fiber. These include autoclave and die molding, filament winding, injection molding, and pultrusion. To attain the best mechanical performance it is necessary to form well-collimated fiber structures in an essentially void-free matrix. These factors therefore tend to be emphasized and have resulted in a number of specialized fabrication techniques such as automated tape layup.

Applications

Substantial weight savings are possible when carbon fiber composites are substituted for more conventional materials. Carbon fibers therefore are applied in areas where weight reductions are valuable. For this reason they are widely employed in aerospace components. Relatively recently the Army has started development of mobile field equipment using composites, including carbon fibers, with the objective of decreasing weights and increasing mobility. Personal equipment which has to be carried can also be lightened with carbon composites. Such items include orthopedic braces, wheelchairs, and backpack equipment.

Carbon fibers and their composites possess a number of useful characteristics in addition to their basic mechanical properties and weight-saving potential.

Their electrical conductivity, for example, is coupled with good mechanical properties in thermoplastic molding compounds for use in components where dissipation of static charge is needed, such as the support structures in electronic equipment.

Their good corrosion resistance is proving useful in chemical plants, oil fields and the marine environment. Their chemical inertness has also resulted in use of these fibers as reinforcements in the plastic components of artificial joints. In this case the fibers also provide creep and wear improvements.

The friction and wear characteristics and the high-temperature properties of carbon fibers are being put to use in pump packings, bearings, and brakes. Carbon fibers bonded with carbon of a different type to form "carbon-carbon" composites have proven to be very effective as a brake disk material for aircraft, resulting in substantial weight savings and increased braking effectiveness.

Sports equipment items now include skis and ski poles, golf clubs, racquets of various types, fishing rods, and racing cycles. These benefit not only from the increased strength, stiffness, and low density of the material, but also from its good damping properties. Carbon fiber-reinforced tennis racquets, for example, are reported to be easier on a player's wrist and elbow joints. The good fatigue and damping characteristics and low inertia of these materials are employed in high-speed rotating and reciprocating components in machine tools, business machines, and computer memory devices.

Automobile and truck components containing carbon fibers have been relatively slow in developing to date, although carbon fiber-reinforced parts have been used in racing cars for some time. However, one component which appears to be close to commercialization is a drive shaft. A variety of designs have been tested and found to be effective. In this case the structure is usually a hybrid with glass and carbon fibers, the latter being employed to provide the stiffness and damping capacity required.

Table I: Available carbon fibers

Fiber types	Young's modulus range, 10^6 p.s.i.	Tensile strength range, 10^3 p.s.i.	Raw material employed
Low modulus	5-10	50-150	Rayon, pitch
Intermediate modulus	30-40	450-800	PAN
High modulus	50-60	300-400	PAN, pitch
Very high modulus	70-100	250-350	PAN, pitch

Roger Prescott is Operations and Technical Director, Great Lakes Carbon Corp., P.O. Box 810, Rockwood, TN 37854

Glass

By P.F. Moore

Glass-reinforced products are noted for high strength-to-weight ratios, dimensional stability, resistance to heat and corrosion, and ease of fabrication. An extensive selection of fiber types offers a wide range of cost/performance benefits.

Glass fiber is the most widely used reinforcement for plastics products. They also position glass fiber composite as one of the most popular solutions to a variety of structural problems.

To form basic glass reinforcement, filaments of glass are drawn from a furnace of molten glass. Large numbers are formed simultaneously and gathered into strands or bundles. Surface treatments ease processing, protect fiber integrity, and establish compatibility with specific resin systems.

The strands can be wound into intermediate forming packages and later processed into the various types of reinforcement, or they can be directly processed into reinforcement products.

Most reinforced products are made with "E"-type glass, a designation growing from the original use in electrical applications.

E glass provides good electrical characteristics, good mechanical properties, and high-heat resistance. Also resistant to water and corrosion, E glass has applications in nearly every major industry.

E glass has a virgin tensile strength of 500,000 p.s.i. Its modulus of elasticity is 10.5 million p.s.i. The fibers range from 0.0001 to 0.001 in. in diameter and will stretch 4.8% before breaking.

Design keys to evaluating fiber reinforcement in a composite are the amount, length, and orientation of the fibers. Strength of a composite product increases proportionately to the percentage of glass fibers added. Orientation of the fibers determines the level and direction of strength. There are three fiber orientations: unidirectional, bidirectional, and multidirectional. Unidirectional orientation provides the greatest strength in the one direction of the fiber. It is possible to achieve up to 80% reinforcement loading by weight with unidirectional orientation.

Bidirectional, like woven fabric with some fibers at an angle to the others, provides strength in each direction of fiber orientation. Up to 60% glass loadings by weight can be obtained with woven roving and up to 75% with woven fabric. Multidirectional orientation provides essentially equal strength in all directions in the finished part. Up to 50% loading by weight can be obtained.

There are several basic forms of glass fiber reinforcement.

Continuous roving is supplied as bundles of gathered filaments wound onto a spool. Various lengths can be cut from the spool, allowing this standard package to be used in a variety of processes. Typical end uses include tub shower units, boat hulls, low- to medium-volume custom-fabricated products and corrosion resistant structures.

Woven roving, appearing as a heavy, drapable fabric is made from continuous roving strands woven at 90-deg angles to each other. It is available in various widths, thicknesses, weights, and strength orientations. Typical applications are large molded parts like boat hulls, process tanks, containers, shrouds, etc.

Woven fabrics made from glass fiber yarns and rovings are available in a wide range of styles, widths, lengths, and properties. Weights vary from 2.5 to 40 oz./sq. yd.; thicknesses from 0.035 to 0.048 in. Various strength orientations are possible.

Reinforcing mats are made from either chopped strands in a random pattern or continuous strands of glass fiber laid down in a swirl pattern. Resinous binders are generally used to hold the strands together. Chopped strand mats generally are used for the hand layup molding process. Continuous strand mats are used in compression molding, resin transfer molding, pultrusion, and stampable thermoplastics. Both types are available in weights ranging from 0.75 to 3 oz./sq. ft. and in various widths.

The many uses for mats include truck parts, tanks and ducts, agricultural components, and electrical parts. Reinforcing mat also is used to add additional reinforcement at key design points where strength is critical, such as corners.

Combination mats are one ply of woven roving bonded to a chopped strand mat. The combination mats form a strong drapable reinforcement that combines the bidirectional fiber orientation of woven roving with the multidirectional fiber orientation of the chopped strand mat. This saves time in hand layup since two layers can be placed in the mold in a single operation. Other combinations are available for surface finish improvement as well as for multilayer reinforcement.

Surfacing mat, or veil, is used in conjunction with reinforcing mats and fabrics to provide good surface finish. It is effective in blocking out the fiber pattern of the underlying mat or fabric. Surfacing mats are also used as inside layers of corrosion-resistant reinforced plastic products, providing a smooth, impermeable resin-rich surface.

Chopped fibers come in lengths from $\frac{1}{8}$ to 2 in. They are blended with resins and other additives to prepare molding compounds for compression, transfer, and injection molding and for encapsulation. Chopped strand glass fiber reinforcement is available with many surface treatments to ensure compatibility with most thermosets and thermoplastics.

Milled fibers, usually produced in $\frac{1}{32}$ to $\frac{1}{8}$ in. lengths, are used as reinforcing fillers for casting compounds and in adhesives to improve dimensional stability. They are also used by molders for thermal stability in thermoplastic applications with low to moderate strength requirements.

Specialized glass fiber compositions, in many of the eight basic design forms, are available when particularly demanding chemical, thermal, and mechanical properties are needed in the finished product.

Type 30[1] continuous strand rovings, for example, are specifically intended for such high-volume processes as filament winding, continuous pultrusion, and the weaving of glass fiber-reinforcing fabrics. Type 30 offers the advantages of fast wetout sizing and high strand integrity. It is also used in woven rovings.

S-2 Glass[1] reinforcements offer high strength-to-weight performance for critical military, aerospace, and other high-performance applications. It has a virgin tensile strength rating of about 650,000 p.s.i. and a modulus of elasticity of 12.4 million p.s.i. Its strength-to-weight ratios exceed those of most metals.

In the past few years, S-2 Glass has evolved in such significant applications as filament-wound pressure bottles, protective vests and helmets, helicopter blades, and aircraft flooring.

Leached glass is another special glass fiber reinforcement for extremely high-temperature applications. It is specially processed to achieve high silica content and usually is sold as woven fabric under various trade names.

Applications

Aircraft, aerospace, and military applications, where weight-to-strength ratios are often crucial design factors, are the fastest growing market for reinforced composites. In the next decade, reinforced composites are expected to account for 65% of materials used in commercial aircraft. Applications include aircraft access doors and flooring and ballistics protection. New composites are being used to simplify electrical appliance construction and design—improving compressor plate stability and heat retention seals in water heaters, etc.

The material is being used now for refrigerator compressor bases, room air-conditioner parts, inner doors on dishwashers, and to construct copiers and office machinery.

Glass fiber is playing a major role in design and production of tension support cables for fiber optics. It is still the dominant material in the electrical market where it is used for coverboards, light poles, electrical conduit, bus bar insulation, and third-rail insulators and covers.

Among the most successful applications of recent years has been in land transportation as more and more automobile manufacturers are turning to glass fiber composites. By 1990, glass fiber composites use

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P.F. Moore is Manager-Consumer & Construction Marketing Div., Owens-Corning Fiberglas Corp., Fiberglas Tower, Toledo, OH 43659

[1] —Registered trademark of Owens-Corning Fiberglas Corp.

is expected to jump to 61 lb. per vehicle, compared to 42 lb. this year. Glass fiber composites are not just used for body parts, but for leaf springs, bumper components, and even in hybrid glass/carbon fiber drive shafts. By the next decade, glass fiber composite could be used in load-bearing applications such as floors, space panels and even the entire underbody.

The noncorrosive properties of composites lead to wide use in such products as storage tanks, pollution control equipment, piping, pulp and paper processing equipment, and oil field equipment.

Thermoplastic fibers

By D.S. Cordova and H.H. Rowan

Thermoplastic fibers, such as polyester and nylon, have been the reinforcements of choice in rubber composites. With the introduction of Compet fibers by Allied-Signal Corp., nylon and polyester fibers specifically designed for use in plastics composites have become available commercially.

These high-strength fibers are characterized by dimensional stability over the range of composite processing temperatures. They utilize sizing systems that enhance fiber-matrix adhesion, resin wetout, and fiber dispersion in typical resin formulations. These engineered thermoplastic fibers are available with two different types of interface agents, creating either low- or high-integrity fibers. Both enhance adhesion and wetout but high-integrity also results in a stiffer and more cohesive bundle that is easily handled as cut fiber in BMC mixing systems or as a roving feed to SMC or TMC systems.

Highly oriented polyethylene fibers were also introduced by Allied-Signal Corp. under the trade name of Spectra fibers. Combining ultra-high strength with unusually low weight, these fibers can serve a wide roster of specialized uses in the high performance composite markets. Applications and research are well under way in the ballistic market area as a result of this fiber's high energy-absorbency qualities. Advanced technology applications where properties such as ultra-high strength, high impact, and low specific gravity are needed are perfectly suitable for this kind of fiber.

Partial replacement of brittle fibers with less dense, more flexible, and tougher thermoplastic fibers combines the benefits of both systems. These include enhanced impact, higher fatigue life, and lower surface porosity. Abrasion, resin demand, and part weight are also reduced.

Applications

Thermoplastic fibers are particularly effective in areas where high-shear processing causes traditional glass reinforcements to fracture, thereby compromising composite performance. Nonetheless, significantly improved impact has been achieved when substituting thermoplastic fabrics for their glass fiber counterparts.

Polyester-based fibers have significantly enhanced the performance of polyester, epoxy, vinyl ester, and phenolic thermosetting resins. Some applications are high-impact housings for power tools, shatter-resistant cookware, high torsion automotive grille opening panels, fatigue-resistant canoe bodies, and flexible antennas. These fibers are also being used in cement pier encasements to achieve corrosion resistance to chemical spills during the unloading of ships. These applications cover BMC, SMC, TMC, layup, pultrusion, and filament winding.

Nylon-based fibers have been used in rigid urethane systems to improve their poor impact and abrasion resistance. Current uses for nylon cut fiber and fabric are pump housings, canoe tips, and other sporting goods. Both nylon and polyester fibers are being used in cut, fabric, and mat forms in processes such as RTM, structural RRIM, TERTM, and layup. Dramatic impact improvements without catastrophic failure have been demonstrated in these processes with various resin systems.

Processing

There are no special limitations in processing thermoplastic fibers. They can be used in BMC, TMC, SMC, pultrusion, filament winding, RTM, hand layup, and sprayup processes. SMC and TMC systems generally require a high-integrity product and a method to cut fibers in a continuous fashion. Glass fiber choppers, however, have not been successful in cutting these tough thermoplastic fibers and hence an in-line cutter has been developed. Other auxiliary equipment, such as part deflashing tools, is also available.

Compression and injection molding of thermoplastic/fiber composites are virtually identical to glass-reinforced composites methods. No changes in equipment or cycle times are required.

D.S. Cordova is Research Engineer and H.H. Rowan is Technical Manager-Polyester, Tire & Industrial, Allied Corp., Fibers Div., P.O. Box 31, Petersburg, VA 23804

Hybrids

ARAMID/CARBON

By L.H. Miner

Hybrid composites reinforced with fibers or fabrics of Kevlar[1] aramid and carbon are finding use as structural members in various aircraft, aerospace, marine, and sporting goods applications. The two fibers have an almost identical low thermal coefficient of linear expansion (slightly negative), and therefore can be co-cured in a resin matrix without residual thermal stresses.

Epoxy matrixes are the most common, but aramid and carbon can be combined with other resins, such as polyimide, polysulfone, phenolic, polyester, and vinylester.

A comparison of fiber properties (Table I) shows that both the aramid and carbon are significantly lighter than glass fiber. The modulus of elasticity of aramid is nearly twice that of glass, while a typical high-tensile-strength grade of carbon fiber is more than three times as stiff as glass. However, aramid fiber has a lower compressive strength than either carbon or glass, while carbon is not as impact resistant as aramid. Therefore, a hybrid of the two materials results in a composite that is 1) lighter than a comparable glass fiber-reinforced plastic; 2) higher in modulus, compressive strength, and flexural strength than an all-aramid composite (see Table II, p. 140); and 3) higher in impact resistance and fracture toughness than an all-carbon composite (Table III, p. 140).

Aramid and carbon fibers can be hybridized in numerous forms. For example, balanced fabrics or unidirectional tapes of aramid or carbon can be combined as discrete plies in a hybrid laminate. Angular orientation and placement of these plies can be adjusted to tailor a composite structure to a predetermined balance of properties. Fabrics can be woven which arrange

Table I: Comparative yarn properties

Property	Aramid[a]	Type HT carbon	E-HTS glass
Tensile strength, 10^3 p.s.i.	525	450	350
Modulus, 10^6 p.s.i.	18	32	10
Elongation to break, %	2.5	1.40	3.5
Density, lb./in.^{3}	0.052	0.063	0.092

[a] Kevlar 49.

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[1] Trademark of Du Pont Co.

L.H. Miner is Research Associate, E.I. du Pont de Nemours & Co. Inc., Wilmington, DE 19898

CARBON/GLASS

By S J. Walling

When two or more reinforcing materials such as carbon and glass are combined in a common matrix, the resulting composite is called a hybrid. The major advantage is the ability to tailor the laminate for maximum performance and minimum cost.

Hybridization allows the strengths of one material to offset the weakness of another. A carbon fiber laminate, for example, may be used on an aircraft to reduce weight, but the poor impact resistance of the carbon fiber can be greatly improved by combining it with glass fiber reinforcement or by using a glass fiber composite outer skin.

Glass/carbon hybrids can increase impact strength, improve fracture toughness, prevent galvanic corrosion, and reduce costs of the finished laminate over an all-carbon composite.

The three basic methods of hybridization are interply, intraply, and selective placement. Interply is the combining of two or more reinforcements in discrete layers (sandwich-like) without mixing within the layers. Intraply is the combining of two reinforcements within a layer, such as alternating strands in a fabric or chopping two reinforcements together in a molding compound. In selective placement, a small amount of one reinforcement is added in selected areas, such as in corners or in a rib, while the laminate contains predominately another reinforcement.

Hybrid reinforcements can be combined in almost any material form, such as prepregs, fabrics, woven roving, and chopped fibers. They also can be utilized in most fabrication processes, such as hand layup, filament winding, pultrusion, compression molding, injection molding, and resin transfer molding.

Applications

The need for lightweight structural materials has prompted the increased use of composite materials that meet strength, stiffness, and other mechanical property requirements for high-performance applications. The aircraft, aerospace, marine, land transportation, industrial, and sports equipment markets will benefit from recent development work.

The sports equipment market has led the way in hybridization of carbon and glass to get the proper stiffness and weight in skis, ski poles, tennis racquets, fishing rods, and golf club shafts.

In the marine market, carbon/glass hybrids have allowed hull redesign from a solid laminate to a core/skin construction for lighter weight. Carbon provides the stiffness while glass provides the necessary impact strength.

The land transportation market is experimenting with the materials in structural applications, such as drive shafts and leaf springs.

The aircraft market is using carbon and aramid composites to save weight; however, glass is needed in certain areas to prevent galvanic corrosion and to improve impact strength.

High-volume processing

The need for a simple, economical process to form loadbearing structural materials is being met with the use of compression molded sheet molding compounds (SMC) composed of glass fibers in polyester or vinyl ester resin systems. A glass/glass hybrid structural grade SMC can be formed from combinations of continuous and chopped random glass fibers that comprise up to 70% by weight of the composite, resulting in the ability to produce composites with a wide range of mechanical properties.

Glass/carbon hybrids are easily compounded using conventional SMC machines, and can be molded using today's high-throughput compression molding presses.

Design considerations

The key to cost-effective hybrid design lies first in choosing the right fibers. Glass has a tensile strength higher than carbon or aramid. Glass fiber can add high impact strength and good compressive and flexural strength and is the most economical of the high-performance reinforcements.

S J. Walling is Marketing Communications Manager-Transportation, Equipment, Composites Div., Owens-Corning Fiberglas Corp., Fiberglas Tower 7, Toledo, OH 43659.

Nonfibrous property enhancers

By V.A. Stayner

Nonfibrous property enhancers are a hybrid class of materials, both filler and reinforcement in form and function. They include such disparate materials as high-density silica sands, low-density hollow microspheres of glass or phenolic, solid spheres, flakes of glass or mica, and a great many more—which are used singly or in combination.

Sometimes the materials supplement fiber reinforcements, displacing resin. Sometimes they displace a part or all of the fibers. Always they affect the properties, processing, and economics of the end product.

Property enhancement may include a wide variety of mechanical properties. Some add thermal insulation. Some improve electrical properties, either insulation or closely controlled conductivity. Some provide fire retardance and smoke suppression. Product designers sometimes achieve both property enhancement and cost reduction.

In most cases, basic material costs can be reduced by high loadings of relatively low-priced fillers. Often, more sophisticated use of filler systems achieves economic gains further downstream through improved processing, reduced molding cycles, lower reject rate, etc.

Glass flake serves as an economical reinforcement for reaction injection molded parts on the Pontiac Fiero and other models. Glass flake has been used with polyurethane RIM and with polyurea RIM for car fenders and other body parts. Mica flakes cut costs displacing glass fiber in polypropylene (PP) battery trays, glove compartments, and similar automotive parts.

Blends of varying shapes and densities produce a filler/reinforcement that speeds the casting of tubs and vanities, maintaining strength while reducing weight.

Carbon, metal powder and flake, and silver-coated glass spheres are used as cost-effective conductive fillers in plastics. Recently, nickel-coated mica flakes have been added to the list.

Panels and molded products of these materials are used to carry off static electricity in hospital operating rooms and at work stations for assembly and testing of delicate electronic equipment, and for storage and transport boxes. They also provide electromagnetic interference (EMI) shielding.

A multiwall hollow glass sphere cluster, available at low cost, offers greater compressive strength with less breakage in processing than most single hollow sphere particles. Also of note is a very lightweight polyvinylidene chloride hollow sphere that is extremely flexible for good distribution of impact energy.

Attention is being given to coupling agents for fillers and to engineering thermoplastics. Combining silane-treated phlogopite mica with glass fiber in nylons and in thermoplastic polyesters has reduced warpage greatly with only moderate decline in impact strength. A water-ground muscovite mica with high-aspect-ratio delaminated flakes treated with organosilane improves physicals substantially in PP and HDPE.

Shape and density

In evaluating nonfibrous materials their shape and density will determine their ultimate value in handling, loading, processing, and end-product properties. Each filler is unique and often a combination is

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V.A. Stayner is President, Patentech Corp., P.O. Box 63, Sugar Grove, IL 60554.

required to give the desired properties.

Shapes include fiber, flake, spheres, and a broad miscellaneous category including cubes, blocks, and irregulars. Except for the fiber and spheres, irregularity is more common than neat geometric shapes.

Densities can range from 0.07 to 2.42 and above. Density and shape will determine the volume of material able to be added to a processible composite.

Size and packing

With reinforcement/fillers lower in price than the resin matrix, the incentive is to load as high as product, process, and properties permit. Micropacking is a developing science that guides the selection and proportioning of filler shapes and sizes.

Using spheres of one size as a convenient example, a boxful of spheres will occupy about 52% of the volume of the box, leaving 48% voids to be filled by resin. This is true whatever the diameter of the spheres. But smaller spheres can be used to fill part of the voids between the larger spheres and substantially reduce the resin demand.

The effects of less-regular particles are harder to calculate but the behavior is much the same. More important, it is not necessary to restrict the filler blend to one shape. In fact, there are important benefits in using various combinations of spheres, flake, fiber, and irregulars, not only in the packing that can be achieved but in the physical properties obtained. Ideally the compounder seeks to build microscopic mazes that interlace mechanically when the fillers are mixed with liquid resin. Particles of different densities may be blended so some will sink and some will rise. Then the resin adheres, bonds it all together, and also shrink-locks the structure as it cures.

Flakes

Flakes have aspect ratios that make them useful in reinforcing plastics. Mica can be delaminated by wet or dry grinding to provide flake as thin as 1 micron with high aspect ratios, although commercial-grade mica flake is considerably thicker. The user must specify and pay for the high aspect ratio (HAR) flake. It is possible to separate flake with ratio of 10,000 to 1 but commercial-grade HAR is more likely to be in the 50 to 100 range, or less. In effect, the aspect ratio is bidirectional -- length-to-thickness and width-to-thickness. Glass flake is much thicker with substantially lower aspect ratio. Flakes tend to orient in parallel as the resin mix flows and form a layered fish-scale structure. This serves well as an impervious coating protecting against infiltration and corrosion.

Parallel flakes pack solidly, giving a relatively high filler content in minimal thickness. This flake orientation adapts well to molding processes such as vacuum forming and rotational molding, also processes with directed flow like extrusion, injection molding, and sprayup.

Disadvantages of flake are the sharp ends which bring high stress concentration and the need to guard against breaking thin flake in mixing and molding.

The reinforcement effect of flake relates to the aspect ratio the molder gets into the final product, not the ratio of the flake in the bag. The thinner the flake and the higher the ratio, the greater the problem of breakage. HAR mica can be dispersed in polyester with a slow-speed paddle mixer with relatively little loss. Flake can be mixed with thermoplastic powders, but a compounding extruder breaks some flake.

In another approach, a high-speed, high-shear turbine mixer is used to delaminate mica flake and compound it with PP. The end result is a smooth mix with flake ground to 10 micron diameter and aspect ratio about 16, substantially lower than the aspect ratio of HAR flake.

Process equipment must be suitable to retain the highest reinforcement properties in molding flake-filled resins. Spray gun size and nozzle must be adequate. For injection molding, molds with ample gates and sprues are helpful. Flake can be used to replace or augment fiber in sheet molding compound (SMC) and compression molding presents no problem.

HAR mica flake is much lower in cost than glass fiber and loading in both thermosets and thermoplastics can be higher without viscosity problems. It contributes to tensile and flexural strength and modulus but reduces impact strength.

Loss of impact strength can be mitigated or eliminated in many mica-reinforced thermoplastics by adding 10% by weight of polyester fiber. Chlorinated paraffin added to mica-reinforced PP is an economical surface treatment and improves tensile and flexural strength and modulus.

A number of wet-ground micas are available as filler/reinforcements for plastics. Producers assert that their process delaminates the muscovite flake to produce large, thin, high-aspect-ratio material. The muscovite is light in color.

Table I gives some published physicals on thermoplastics reinforced with HAR mica flake (Suzorite phlogopite). Tests with 70% loading of this mica in thermo-

Table I: Typical mechanical properties of mica-reinforced thermoplastics

	Resin and % mica by weight			
Properties	Polyester, 35% mica	Nylon 6/6, 50% mica	ABS, 50% mica	SAN, 50% mica
Tensile strength, 10^3 p.s.i.	6.96	13.76	9.47	9.9
Tensile modulus, 10^6 p.s.i.	—	2.57	2.12	2.55
Flexural strength, 10^3 p.s.i.	13.2	18.0	14.0	14.5
Flexural modulus, 10^6 p.s.i.	1.41	1.93	2.13	2.68
Izod impact notched, ft.-lb./in.	—	0.9	0.6	0.5
Compressive strength, 10^3 p.s.i.	—	16.0	16.4	15.56

setting polyester showed a flexural strength of 45,000 p.s.i. and flexural modulus of 14 million p.s.i.

Glass flake, thicker and with lower aspect ratio, has been used for impermeable and corrosion-resistant coatings. It provides a hard, scratch-resistant surface. Glass flake has also become an important reinforcement for RIM urethane-based auto parts.

Talc, a hydrated magnesium silicate found mostly as platelets, has a good enough aspect ratio to classify as a reinforcement/filler. The finely ground soft mineral doubles or triples flexural modulus in PP, PE, rigid PVC, and high-impact PS. A 40% loading increases tensile strength of the PE and PS, and slightly improves notched Izod impact strength of PE. The filler does not conduct electricity, and has low thermal conductivity and high resistance to heat shock.

Fiber-grade wollastonite is a mineral with about 15:1 aspect ratio. Coated with silane and used to replace half the glass in a polyester BMC formulation, the material improved all mechanical properties except notched Izod impact.

Spheres

Spheres clearly have no aspect ratio to provide reinforcement properties but their geometry affords important advantages in processing and end-product physicals.

Unlike the fiber with its directional strength, the sphere's effects are isotropic. Photoelastic stress is concentrated at the ends of a fiber, the edges of a flake or irregular particle, but stresses around a sphere are even and predictable. Spheres distribute stress evenly throughout the molded structure.

The sphere has the smallest surface area [illegible] shape are correspondingly less than [illegible] resin. This and a kind of ball-bearing action permit very high loading with relatively little rise in viscosity.

Table II: Average physical properties of solid glass spheres/nylon 6/6[a]

Properties	100% nylon	60% nylon, 40% glass spheres
Tensile break strength, 10^3 p.s.i.	11.5	14.2
Ult. elongation, %	60	2.5
Flexural modulus, 10^5 p.s.i.	4.3	7.31
Izod impact, ft.-lb./in.	1.0	0.6
Compressive strength, 10^3 p.s.i.	4.2	36.5
Deformation under load at 122°F.		
At 2000 p.s.i.	1.2	
At 4000 p.s.i.		0.8
Deflection temp., °F.		
At 66 p.s.i.	425	400
At 264 p.s.i.	160	165
Taber abrasion, mg./1000 cycles		37
Specific gravity	1.15	1.43
Melt index, g./10 min.		4.3

a—Potters 3000 spheres; Wellamid 6600 resin.

Sphere-filled products have reduced and predictable shrinkage and less distortion. With solid spheres, compressive strength is particularly high, and hard, smooth surfaces can be achieved.

With a selected silane surface coating, microscopic solid glass spheres (average diameter 25 microns) in nylon bring significant improvement in tensile strength, compressive strength, and flexural modulus. Table II gives properties of a 40% loading in nylon 6/6.

Using the same spheres at 60 parts per hundred of a polyester casting resin, the resultant casting showed higher tensile, flexural, and compressive strengths than the unfilled resin.

Fly ash from coal-burning power plants yields both solid and hollow glass-like ceramic spheres known as cenospheres. The solid spheres are considerably smaller than those manufactured for the plastics market.

Hollow spheres

Hollow spheres have the same geometric advantages as the solids with different results. Contribution to compressive strength is limited by the crush resistance of the sphere and this varies with the thickness and composition of the wall. Glass microspheres can be had in a number of sizes but average about 75 microns with wall thicknesses of 1 to 2 microns. Fly ash hollow spheres average a third smaller with double the wall thickness. Crush resistance of the fly ash runs three times higher to as much as 5000 p.s.i.

A major advantage of hollow spheres is their low density which may be used for buoyancy in boat hulls or for weight saving in parts for aircraft and automobiles. The spheres may be incorporated in the resin throughout the molded part or serve as a syntactic foam core, increasing stiffness with minimum addition of weight.

They improve impact strength, acting as miniature shock absorbers in the resin matrix. They tend to arrest cracks, hold fasteners, and help machining. They improve thermal and acoustical insulation.

The hollow sphere clusters mentioned earlier are irregular and have some aspect ratio so they can be expected to give some improvement in tensile strength. Flow characteristics are good even at high loadings if the proper resin is used. Also, they serve well in filler compounds.

Hollow spheres are used in such thermosets as epoxies and polyesters, and are processed by compression molding, hand layup, sprayup, and casting.

With weight a critical factor, automotive manufacturers are working with hollow glass spheres incorporated in SMC for body parts. Complete car bodies have been built for testing. One problem is that sanding of bonded joints can break spheres and create a porous surface.

The spheres also work well in such thermoplastic systems as vinyl plastisols.

There are a considerable number of hollow spheres on the market with a wide range in material, size, and price. Particularly with hollow spheres, low in density, it is important to calculate cost in terms of volume rather than weight. Spheres available include sodium silicate, carbon, aluminum oxide, epoxy, phenolic, vinylidene chloride, and polystyrene.

Irregular particles

While most often used as fillers for cost reduction, irregular particles like calcium carbonate and silica flour when properly utilized can offer increased modulus, abrasion resistance, and hardness to a product.

Coupling agents

Obviously resin and property enhancers must be chemically compatible. Coupling agents—silane or titanate—may be used to improve viscosity and interfacial bond. Suitability for the end-use environment is equally essential.

Processing

Process conditions and equipment can influence choice of property enhancers. In sprayup, particle size must not be too big for the gun and nozzle, and loading of fillers must be within the capacity of the spray system.

In injection molding, small gates and runners dictate small particle size and low viscosity. With a big part and small gate, heavy loading of fiber or flake is impossible. In extrusion, buildup of pressure at the orifice can limit use of the materials.

Fillers/extenders

By F.J. Washabaugh

Filler is a general term used to describe nonmetallic minerals, metallic powders, and organic materials added in fairly high percentages (over 5% on a volume basis) to plastics, and used as a reinforcement or as an extender.

A *reinforcing filler* provides a mechanical or thermal property improvement to the polymer matrix. The second category, *extenders*, consists of generally inexpensive fillers added either to reduce cost or to improve processing of the plastic.

Classification of fillers

Nonmetallic minerals comprise many natural and refined minerals. Mineral rocks such as kaolin, talc, calcium carbonate, and barytes are fairly inexpensive and are readily available.

Metallic powders are a generally more expensive class of ingredients used to

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F.J. Washabaugh is Senior Technical Service Engineer, Engelhard Corp., Menlo Park, Edison, NJ 08818.

produce thermally and electrically conductive moldings. Aluminum, bronze, zinc, and nickel are commonly used metallic fillers for conductive plastics.

Organic fillers include wood- and shell flours, starches, and carbohydrate by-products. Synthetic organics include PVDC spheres.

Filler selection

Probably the most widely used measure for selecting fillers is the *Mean Particle Size* (MPS), normally expressed as an equivalent spherical diameter in microns.

Often the *particle size distribution* must be studied as well. The percentages of coarse and fine fractions many times influence particle packing efficiency and optical effects in plastics. The shape of the particle size distribution can be described in terms of the Coarseness Parameter and the Dispersion Parameter both defined in ASTM D1366.

Abrasivity of a filler depends on both its Mohs' hardness and its percentage of coarse residue. In general, low Mohs' hardness fillers such as talc, kaolin, and calcium carbonate are less likely to damage process equipment than are harder materials such as wollastonite, silicas, and feldspar. For a given type of filler, abrasivity can be minimized by selecting products with low 325 mesh screen residue.

Chemical reactivity can be a negative factor for certain fillers. For instance, calcium carbonate particles have alkaline surfaces with little resistance to even weak organic acids. Some lightweight glass spheres have residual salts that give viscosity instability in liquid polyester formulations. Calcined kaolins, on the other hand, are supplied at very low moisture levels with surfaces that are nonreactive to acids, alkalies, and organics.

The *specific gravity* of a filler provides a good indication of the density of a plastic filled with that material (assuming dispersion is complete and filler crushing has not occurred).

Major filler types

Calcium carbonates are popular fillers for plastics because of their combination of low cost, high brightness, and ability to be used at high filler loadings. They generally are categorized as extenders since they are used for cost reduction and provide little reinforcement. Carbonates are supplied in five forms: water-ground, dry-ground, ultrafine-ground, precipitated, and surface-treated carbonates.

Carbonates grades have a broad range of MPS; some precipitated carbonates have an MPS of less than 0.1 micron, while some dry-ground types have an MPS of over 20 microns.

PVC compounds are the major use area for calcium carbonate. Flexible vinyl compounds often contain 5 to 50 p.h.r. of calcium carbonate (usually in the 1 to 6 micron MPS category). Finer precipitated grades are used to improve mar resistance, increase surface gloss, and reduce flex whitening. Rigid PVC can contain small amounts of precipitated calcium carbonate for improved impact and extrusion properties.

New developments in calcium carbonate include a low-cost, dry-ground grade for BMC, SMC, and other polyester applications. This product is reportedly agglomerate-free and does not affect paste thickening.

Kaolin is the most important mineral in the china clay family. The crystals are thin, hexagonal platelets with width 8 to 12 times the thickness.

Kaolin is produced in three forms: waterwashed, calcined, and airfloated. In waterwashing, separation of controlled particle size fractions is followed by bleaching, filtration, and drying. Calcined grades are uniform, high-brightness fillers with fairly low abrasivity. Air-floated grades are made simply by pulverizing dried crude kaolin and separating the coarse impurities by air classification.

Waterwashed and airfloated kaolins are generally considered to be extenders, while calcined kaolins are classified as reinforcing fillers because of the strength improvements they impart to nylons and other engineering plastics. The kaolins as a group are generally fine in particle size with an MPS range of 0.3 to 5.0 microns.

In BMC, SMC, and matched metal die molding, waterwashed kaolin helps control consistency and moldability and provides chemical resistance, improved electrical properties, and low water absorption. Waterwashed grades also extend polyolefins, vinyls, and phenolic molding compounds.

Calcined kaolin is widely used in vinyl wire covering compounds to improve insulation properties. When treated with silane coupling agents, calcined kaolin improves mechanical, electrical, and thermal properties in elastomers, crosslinked PE, and a number of other engineering thermoplastics. In nylon, calcined clays offer a low cost route to flexural moduli over 1 million p.s.i. Calcined kaolin has little tendency to orient and makes it easier to control warpage in large moldings.

Although inexpensive, airfloated kaolins find limited usage because of their variable particle size distributions. Furthermore, some airfloats tend to be fairly abrasive to process equipment since they contain hard mineral contaminants.

Talc, unlike fine kaolin, generally is considered a coarse filler. The MPS range for most industrial talcs is in the 2 to 20 micron range.

Talc is a hydrated magnesium silicate usually in platy form with an aspect ratio between 15 and 30. It is soft, having a Mohs' hardness of 1.0, and is quite oleophilic.

A primary application for platy talcs is in PP which may be filled with between 10 and 40% talc. In PP, talc imparts high rigidity and higher heat deflection temperature while maintaining good tensile, compressive, and impact properties. The market for talc-filled PP includes automotive, appliances, and food packaging. Talc is also widely used in polyester auto body compounds although in recent years hollow glass bubbles have replaced a portion of the talc in lightweight types.

A recent development is a surface-modified Western talc for nylon and other engineering thermoplastics.

Alumina trihydrate (ATH) is produced from bauxite. It is a low-aspect ratio mineral that falls into the extender category. The unique feature of ATH is an endothermic decomposition above about 220° C.; the resultant heat sink is the main reason for its utility as a flame-retardant filler.

ATH grades for plastics have a broad MPS range of less than 1 micron to over 50 microns. ATH extenders are particularly important in polyester sprayup, BMC, and SMC where flame/smoke suppression, high filler loadings, and chemical resistance are needed.

Organic fillers include wood- and shell flours, starches, ground corn cobs, and other vegetable by-products. They are low-cost extenders and are very much coarser than most of the nonmetallic fillers (MPS is 70 to 500 microns). A widely used filler for phenolics and other thermosets is woodflour, a powder ground from one or more of the hardwoods, sometimes blended with nut shells. Woodflours are readily available, lightweight (specific gravity of about 1.50), and easily wet by thermosetting resins. They are, however, likely to contribute low thermal resistance, low dimensional stability, and poor electrical properties. In thermoplastics, woodflours and other organic fillers have not met with success. The main problems have been severe degradation and decomposition at the processing temperatures of PP, PE, etc.

Hollow lightweight PVDC spheres are a synthetic organic filler used in syntactic foams and casting applications. These spheres are generally in the 30 to 50 micron MPS range and newer grades can withstand pressures of up to 1500 p.s.i.

Silica extenders represent a diverse group of minerals with a selling price range of several cents to over $1/lb. Silicas for plastics fall into three general categories: crystalline silica, diatomaceous earth, and precipitated silica. Particle sizes range from an MPS of less than 0.1 micron for precipitated silica to over 50 for certain ground silicas. The finer types are reinforcing fillers but most silicas are used as extenders.

Crystalline silicas are low-absorption products of high Mohs' hardness occurring naturally as sand, quartz, tripoli, and novaculite. The low oil absorption results in easy dispersion of the filler and low viscosity of the resin-filler mix. Sharp silica sands are used at high loadings in epoxy resin in both shell molding and resin cements. Shrinkage reduction is the key benefit of this use. Dielectric, physical, and processing properties of acrylics are improved by the addition of 30 to 40% quartz. In PE, quartz helps minimize crack formation and improves shrinkage, electrical properties, and water resistance.

Diatomaceous earth is a low density (2.3), low hardness mineral with properties unlike those of other silicas. It has been used at low loadings in polyolefin films to reduce blocking or film adhesion. Because of its very high oil absorption, it has been used to improve the surface of reinforced polyester moldings.

Precipitated silica is a specialty filler in the premium price range. Applications for precipitated silica include elastomer reinforcement, liquid system thixotrope, and as a nucleating agent for urethane and styrene foams.

Glass spheres, both solid and hollow, are extenders. Solid glass spheres, ranging from 10 to 50 microns in MPS, are used in polyesters and engineering nylons to im-

Table I: Economics of fillers

Materials	Specific gravity	Volume cost, ¢/cu. in.
Plastics		
Polypropylene homopolymer	0.91	1.47
Low density polyethylene	0.92	1.49
Polystyrene homopolymer	1.05	1.81
Nylon 6/6	1.13	7.50
Polycarbonate	1.20	8.00
Fillers		
Woodflour	1.5	0.35
Crystalline silica	2.7	0.55
Kaolin, waterwashed	2.6	0.65
Calcium carbonate	2.7	0.58
Alumina trihydrate	2.4	0.75
Talc	2.7	0.82
Kaolin, calcined	2.6	1.17
Mica, high aspect ratio, treated	2.8	2.70
Hollow glass spheres	0.4	2.88
Solid glass spheres	2.5	2.97
Wollastonite, treated	2.9	3.34

Note: Filler costs calculated on T.L. bag estimated prices, FOB mines.

prove flowability, to raise modulus, and to impart an isotropic nature to composites. Hollow microballoons are available in a similar size range. Lower specific gravity (<0.40) bubbles are successfully used in liquid casting and thermosetting resin applications. Also they have been used in syntactic foams to produce composites as low as 30 lb./cu. ft. in density that can withstand uniaxial compressive loads as high as 18,000 p.s.i.

Wollastonite is a naturally occurring calcium metasilicate. It is a high-melting, high-pH, acicular mineral sold in grades ranging from very fibrous to finely divided and available with a variety of surface treatments. It is a reinforcing filler used in polyesters, phenolic brake linings, epoxy molding compounds, urethanes, vinyls, and nylons. Its low moisture absorption is a particular advantage for both nylon 6 and nylon 6/6 compounding. On the negative side, impact strengths of plastics filled with wollastonite are generally low. Also, it must be carefully used to avoid abrasive wear to compounding equipment.

Micas, both muscovite and phlogopite varieties, are high aspect ratio plates that are true reinforcing fillers. They are generally coarser than talcs and range from −325 mesh to +40 mesh. Mica flakes reinforce in two directions. They have traditionally been used in thermosets like phenolics and epoxies for mechanical improvements as well as for electrical and heat insulation benefits. A number of new areas have emerged including polyolefins, reaction injection molding polyurethanes, and engineering plastics. Surface treatments have been employed to improve the generally poor impact strength of mica-filled plastics.

Other fillers find specialty uses and several are rapidly growing in importance. Feldspar, barytes, calcium silicates, and metallic powders fall into this category. Fine-mesh size attapulgites are now used in phenolic friction compounds and specialty engineering thermoplastics.

Filler economics

In any filler evaluation for a plastics application, the cost of the filler per unit volume should be directly compared to the cost of the resin matrix on the same basis.

Table 1, p. 148, summarizes such figures for some of the major types of fillers. With engineering plastics in the 7 to 8¢/cu. in. category, nearly all extenders and reinforcing fillers can result in substantial cost savings. The commodity plastics at 1 to 2¢/cu. in., however, present a far different picture. Here, the economic incentive is greater for the lower-cost fillers such as calcium carbonate, kaolin, silica, and ATH.

Flame retardants

By R.L. Markezich and J.J. Duffy

Polymers can be modified by a number of flame retardants to hinder ignition or flame spread. These flame retardants typically act by one of three ways—solid phase inhibition, vapor phase inhibition, or heat absorption.

1) Solid phase inhibition. These additives promote extensive polymer crosslinking at the surface to form a carbonaceous char upon heating. Char insulates the underlying polymer from the heat of the flame, preventing production of new fuel and further burning.

2) Vapor phase inhibition. These act by changing the flame chemistry and quenching radical chain reactions.

3) Heat absorption. This system evolves water during heating, cooling the surface and increasing the amount of energy needed to maintain the flame.

Additive flame retardants

Among the most widely used additive-type flame retardants are alumina trihydrate, phosphorous compounds, and halogenated compounds used in combination with a synergist such as antimony oxide, and in certain cases, zinc oxide or borate.

Alumina trihydrate (ATH) requires high loadings to achieve modest flame retardance, but because the material is inexpensive, it is the largest single flame retardant used in the U.S. The flame retardant mechanism of alumina trihydrate is an endothermic (heat-absorption) cooling of the flame upon release of water of hydration. ATH produces little smoke and is nontoxic. Its main use is in unsaturated polyester, epoxy, urethane, and some wire and cable applications.

Halogenated aliphatics. Bromo- and chloro-paraffins are generally liquids or low-melting solids. While they have their limitations: low-heat stability, and are plasticizing, they are still very economical and can be used successfully to flame-retard many systems, including PE, PVC, polyurethane foam, and PP. Generally they are used in conjunction with a synergist such as antimony oxide. One chlorinated flame retardant that is more stable and is nonplasticizing is the hexachlorocyclopentadiene adduct of cyclooctadiene. Besides antimony oxide, other synergists,

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R.L. Markezich and J.J. Duffy are Scientists, Occidental Chemical Corp., 2901 Long Rd., Grand Island, NY 14072

control.

Metering system. The metering system takes the conditioned intermediates from the supply tanks and delivers them to the mixing head at the desired rate and pressure. There are two basic types of metering systems: high pressure axial or radial piston pumps, and lance displacement cylinders. The piston pumps are hydraulic pumps that have been modified to handle chemicals. They are capable of continuously metering at pressures up to 3500 p.s.i. Lance pistons, which are driven by a separate hydraulic pump, displace the reactants from a high pressure metering cylinder. In addition to more precise metering, they have the capability of processing filled systems.

Mixing head. The mixing head contains a cylindrical mixing chamber where the intermediates are mixed by direct impingement at pressures ranging from 1500 to 3500 p.s.i. It also contains a cylindrical cleaning piston which, after the shot is complete, moves forward to wipe the remaining materials out of the mixing chamber. In addition, there is a valving mechanism to shift the material flow between recirculation back to the tank and flow into the mixing chamber. This allows the circulating materials to reach an equilibrium at the proper temperature, pressure, and flow rate before shifting into the mixing position.

Mold carrier. The mold carrier holds the tool in the proper orientation for molding, provides enough clamping force to overcome the in-mold pressure, opens and closes the mold, and positions the open mold in an accessible position for demolding, cleaning, and preparing the mold for the next shot. There is a wide variety of designs and sizes available.

Tooling

Since the in-mold pressures in RIM are generally relatively low (25 to 100 p.s.i.) a variety of tooling constructions have been used. These include machined steel or aluminum, cast aluminum or kirksite, sprayed metal or electroplated shells, and filled epoxy. Although some of these constructions are relatively inexpensive when compared with other large-volume production tooling, it should be remembered that the low viscosity liquid that fills the mold will duplicate exactly the surface of the tool. Consequently, when good surface characteristics and high tolerances are required, machined tooling has generally been the chosen route, particularly for higher volume production runs. The ability to use less costly tooling methods for prototype and for short runs, however, remains a significant advantage of the RIM process.

Materials

RIM was developed as a processing technique for polyurethane and to date the bulk of the usage has been with that material. Fortunately, polyurethanes and related polymers are a tremendously diverse group of materials with a range of properties to fill the needs of quite different applications.

Polyurethane rigid structural foam. One of the earliest applications for RIM, this material is characterized by light weight and rigidity. It consists of a solid skin and a lower density cellular core. It is used in equipment housings, furniture, building components, and a variety of industrial and consumer applications.

Low modulus elastomers are materials that have found wide use in the automobile industry for fascia, bumper covers, and trim parts. Newer applications include integral window seals and a wide variety of applications where it is replacing molded rubber. Most of these materials are not pure polyurethane, but polyurethane/polyurea hybrids with improved processing and properties when compared with the earlier all-urethane systems.

High modulus elastomers. Modifications to the chemistry of producing the low modulus elastomers allow for the processing of tough polymers with flexural modulus as high as 250,000 p.s.i. These are used in a variety of large industrial and consumer parts.

Reinforced RIM elastomers. By the addition of fillers such as milled glass fiber, glass flake, or mineral fillers, the properties of the material can be altered to meet the requirements of the part. This technology is used to increase flexural modulus, improve thermal properties, and improve dimensional stability.

Integral skin foams are flexible urethane foams with a high density skin. They are used in applications such as steering wheels, arm rests, and protective covers that must combine a tough surface and a soft feel.

Polyurea RIM. One of the leading candidates for automotive body panels, all-polyurea systems have improved high temperature stability. These systems are also characterized by very fast reactivity and rapid cycle times.

Polyacrylamate is a proprietary system (Ashland Chemical's Airmax) that is designed for use with preforms or glass mats. Composites possess high flexural modulus, good impact resistance, and high temperature stability. Systems with similar performance from isocyanate-based polymers are also being introduced by urethane suppliers.

While currently RIM systems based on chemistry unrelated to polyurethanes are not in significant commercial production, a good deal of development work has taken place and future prospects are promising for several polymer systems.

Nylon RIM. Commercialization of polymers based on caprolactam is now being carried out by DSM, a Netherlands-based producer that purchased Monsanto's Nyrim technology. Nylon RIM polymers offer high toughness and abrasion resistance and are under evaluation for a variety of industrial and automotive applications.

Polydicyclopentadiene is a proprietary thermosetting polymer developed by Hercules. PCPD offers high-impact resistance and stiffness and is currently being used for production of snowmobile components.

Other polymers that have been evaluated for RIM processing include epoxies, polyesters, phenolics, acrylics, and styrenics. Although none of these is currently commercial, work is continuing and the polymer base of the RIM process is likely to continue to expand, yielding new property balances and cost-property options.

Reinforced plastics/composites processing

Automated tape placement

By G.W. Ewald

Tape placement, or tape laying, of reinforced plastics/composites materials with automated equipment has emerged as an important fabrication technique to position fibers during the manufacture of advanced composites structural products.

Fibers preimpregnated with thermoset resins and carefully collimated side-by-side on a paper backing create a thin tape with the paper backing acting as a carrier for ease of handling.

For machine dispensing, the tapes are supplied typically in spooled 3-in. widths of any desired length.

Equipment types

Although the earliest machines were designed to lay tape only on flat surfaces, their design in principle was quite similar to modern machines. Being designed to lay narrow (3-in.) tape, but required to lay up wide parts, the function of the machine was to place successive courses of tape side-by-side until the proper product width was achieved. Modern tape placement machines perform the same basic function.

Several machine motions (axes) are required and are generally described in the nomenclature of machine tools, e.g., a spar mill, which many tape placement machines resemble. On a typical machine, the tape dispensing head is mounted on a post

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G.W. Ewald is Vice-President-Marketing, Goldsworthy Engineering Inc., 23930 Madison St., Torrance, CA 90505

which in turn is mounted on a gantry carried on ways straddling the machine bed or area in which tooling is placed. Five axes of coordinated motion are required for layup of contoured parts:

1) X—the longitudinal movement of the gantry along the ways over the machine bed.

2) Y—the transverse movement of the tape dispensing head across the bed.

3) Z—the vertical movement of the tape head.

4) C—tape head rotation about its vertical centerline.

5) A—a "swarfing" motion of the tape head used only for contour tape laying to maintain perpendicularity of the tape laydown shoe to the tool surface.

In a typical layup sequence, the tape head dispenses tape for a specified distance along the X-axis, stops and lifts using the Z-axis, turns 180 deg. using the C-axis, indexes over one tape width with the Y-axis, lowers and repeats the sequence moving in the reverse direction.

Single- vs. two-stage machines

Two types of machines are currently marketed: 1) single-stage machines in which all of the tape cutting and tape laying are sequentially performed in one machine, and 2) a two-stage machine consisting of two separate machines—a tape preparation machine, which cuts all the tape courses for a complete part and stores those prepared courses in a tape reel cassette, and a tape layer machine, which receives the prepared cassette then performs only the function of tape laying. Both types of machines use gantry systems for achieving the necessary laydown motions.

The single-stage machine tape head, in operation, is threaded with a spool of prepreg material and thereafter must perform all the functions of tape laying: shear the starting angle, lay a specified length of tape, stop or slow to shear the ending angle of that course, resume to the end of the course, stop, raise its head, rotate, index one tape width, lower and repeat the cycle in the reverse direction.

Single-stage machine tape heads, because their function depends on retaining the integrity of the tape backing paper to guide the tape through the head, must cut the tape without cutting the backing paper. Also because the end of one course cannot be separated from the start of the next, elaborate mechanisms are employed to prevent trapping of the ends of courses. For these reasons single-stage tape machines are quite complex and generally less versatile than two-stage machines.

The first stage of a two-stage machine receives the prepreg material, removes the original tape backing paper, cuts the starting angle of each course, measures the course length, cuts the ending angle, reinstalls the cut course onto a new backing paper with a space between it and the next course to prevent course trapping, and stores the cut courses on a spool to be later transferred to the second machine.

The tape preparation function, being separate from the laydown function, permits 100% shear dependability, inspection of the tape before reaching the laydown machine, removal of all cutting scrap resulting from differing starting and ending angles of sequential courses, and greater versatility in cutting, including the capability of edge slitting and contouring, important in laying compound curvatures.

Contour tape laying

All tape laying systems have the ability to layup compound curvatures. The single-stage systems use a machine software program that predicts the gaps and overlaps allowing the operator to examine, then redesign, the ply orientation if gaps and overlaps are excessive or shows that the part cannot be made with constant-width tape. The two-stage system, having the slitting ability to edge-contour each course, provides software that causes the tape preparation machine to shape each course to fit the tool contour.

Applications

Virtually all products employing automated tape placement techniques in their manufacture are aircraft parts: horizontal and vertical stabilizers, wing skins, flaps, ailerons, or any other highly stressed aircraft control surface where great strength, stiffness, and light weight are required, and especially where carbon composites are used in the design. Because 40 to 60% of the weight of aircraft of the near future is expected to be advanced composites, automated tape placement techniques, as the only alternative to hand layup, will become increasingly important.

Closed mold processing

By Dave Clavadetscher

Closed die molding in the reinforced plastics industry involves the use of two matched dies: a male die (the core), and a female die (the cavity). When closed and filled with a reinforced plastic composite, the matched die mold is subjected to heat and pressure to cure the plastic.

Matched dies can be simple or complex in shape. They can be made of aluminum, plastic, rubber, steel, etc. Although the lightweight material dies are less expensive to make, they are not durable enough to withstand high-volume production; therefore, hardened steel or other hard metal dies prove more economical in the long run and are used for most matched die molding applications. These dies, when designed for compression molding, should incorporate machined surfaces for telescoping pinchoffs as opposed to metal-to-metal mashoff as is the custom in the design of conventional injection molds.

Advantages of matched metal die molding include part-to-part uniformity and the capability to produce detailed configurations and finished surfaces on both sides of a part.

There are four commonly used variations of the closed mold process: compression, injection, and transfer molding; and stamping. Each is capable of handling a variety of resin-reinforcement-filler formulations, depending on the molding compound and the size of the part being molded.

Compression molding

Since compression molding is suited to relatively high volume, and design of complex shapes, low tooling costs are an advantage. Minimal fiber degradation occurs in the molding process, so mechanical properties remain high.

Although thermoplastics can be compression molded, the process generally is used with thermosetting resins in the form of wet molding of precombined composites, such as bulk molding compound (BMC), sheet molding compound (SMC), thick molding compound (TMC), and pelletized molding compound (PMC). Heat and pressure are applied after the mold has been closed on the cold material. Temperatures of applied heat range from 225 to 330° F., and pressures vary from 100 to 2000 p.s.i.

Typical applications are grille opening panels for passenger cars, truck hoods, appliance components, business machine housings and components, and electrical apparatus.

Injection molding

For injection molding, a plastic material is forced from a low-temperature barrel into the cavity of a matched die mold, held closed by a clamping mechanism. Pressure is used to force the heated material from the first barrel through a sprue, or runner, to the mold.

Both reinforced thermoplastic and thermoset resins are injection molded. With thermoplastics there is no material waste because material left in the sprue, etc., can be reused, whereas thermosets cannot. With either type of compound, some fiber degradation occurs in the injection process, resulting in the loss of physical properties. However, because of its capacity for high-volume production, good surfaces, and detailed shapes, injection is the fastest growing of all closed mold processing systems. Applications are growing rapidly in the automotive, appliance, electrical, and cookware industries.

Transfer molding

Transfer molding is similar to both compression and injection molding. Measured charges of a thermoset molding compound are placed in a heated pot and then forced by plunger into a heated, closed mold where the compound cures. As the material is transferred into the mold, displaced air is expelled through specially designed vents as in injection molding. The matched dies are not designed with telescoping pinchoffs.

Transfer is faster than compression

Dave Clavadetscher is Vice President-Molding Compound Div. Mgr., Premix Inc., P.O. Box 281, North Kingsville, OH 44068

molding, because the material to be molded is preheated. Also, the transfer process does not produce vertical flash lines.

Transfer molding lends itself to small, intricate parts such as electrical brackets, pot handles, and hand-held tool housings. Multiple cavities usually are involved.

Stamping

Molding cycles of only 10 to 20 sec. make stamping the fastest of closed mold processing systems. Reinforced thermoplastics are first heated to just above their softening point, and then put into an open matched mold. This mold quickly closes or strikes the material, stops for about 6 to 15 sec. for cooling, then opens for part removal and reloading.

Only one strike and one die set are necessary for stamping of reinforced thermoplastics, as compared to steel stamping which requires several strikes in a number of dies and presses.

Parts formed by stamping have high impact resistance and strength. Typical applications are reinforcing components or management systems for flexible thermoplastic passenger car fascia, and fender liners.

Resins and reinforcements

An almost unlimited number of resins can be used in closed mold processing systems.

Thermoplastics, reinforced and nonreinforced, which can be melted down after molding and reused, and thermosets, reinforced and nonreinforced, which undergo a chemical change when heated and cannot be remolded, are suitable for the various molding systems.

Thermoplastics most commonly used include polypropylene, nylon, and thermoplastic polyesters. Polypropylene affords good mechanical, chemical, electrical, and thermal properties. Nylon offers high fatigue resistance and heat deflection, and thermoplastic polyesters are noted for their strength, good molded surfaces, as well as electrical, mechanical, dimensional, and thermal properties.

Unsaturated polyesters are the most frequently used thermosets. They have good mechanical, electrical, and chemical resistant properties, and superior dimensional stability. In addition, these resins crosslink completely, creating no volatiles. Other volume thermosets used in reinforced composites include epoxy resins, which exhibit high chemical resistance; phenolics, which demonstrate good electrical properties; and silicones, which have the highest resistance to heat. Silicones also exhibit low water absorption, as well as good weatherability, and dielectric properties.

The most common reinforcement is glass, which is available as fibers, spheres, or flakes. Other common reinforcements used separately or combined include carbon, graphite, and synthetic fiber. Applications include door hinges, wheels, leaf springs, etc.

Composites

Traditionally, only reinforced plastics composites have been used in closed mold processing. These composites are formulations of resins, fillers, reinforcements, etc., and serve to make charging the mold easier. In addition, composites make possible the tailoring of mechanical properties to meet special requirements. Materials can be combined or compounded in many ways to form a composite. The two basic methods are wet molding and precombined composite systems.

Wet molding composites

Wet molding composites are so-called because the resins and reinforcements are combined at the press. If possible, the resin is poured over the reinforcement before being put into the mold. If this is impractical, the reinforcement must be placed directly into the mold and the resin distributed over it. The reinforcement remains in one position during the molding process while the resin flows to encapsulate it. Machined and polished dies with telescoping pinchoffs are necessary for this process since they must contain the resin as well as hold the reinforcement.

Wet molding composites generally are used for medium to large parts of constant thickness. Depending on the shape of the intended part, however, either glass mat or glass fiber preform reinforcements can be used. Mat generally is used for simple, shallow parts, or for deep ones with little or no compound curvatures. Preform reinforcement is necessary when part design includes deep draws or considerable contouring.

A preform is simply the building of reinforcement into the exact shape of the part to be molded. This can be accomplished by direct fiber, plenum chamber, or water slurry methods.

In all preform methods, a perforated, sheet metal screen is made to duplicate the end product. Reinforcement fibers are distributed over this screen and compacted by means of air suction behind the screen. When fibers reach the desired thickness, they are sprayed with a binder resin and heated for a short period. This process keeps the fibers in place during the molding operation, when resin is squeezed into the preform.

Mat reinforcement involves cutting of patterns from rolls of compacted strand fibers. Layers are added according to the requirements of the finished product. As in preform, the resin is then poured over the reinforcement prior to molding.

Precombined composites. In comparison to wet molding, precombined composite systems offer greater efficiency in producing reinforced plastic composites. The ready-for-molding systems include Premi-Glas[1] BMC, SMC, TMC, and PMC.

BMC is the oldest of the precombined molding systems. A high concentration of fillers along with resin and short reinforcement fibers are combined in a blade-type mixer. This batch process produces a bulk form composite which is weighed and hand loaded into molding dies.

Advantages of BMC include its low

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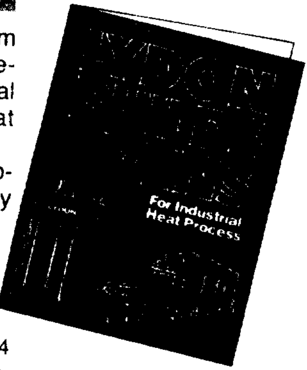
[1] 1—Registered trademark of Premix Inc.



material cost and its ability to be molded into detailed configurations such as bosses, inserts, or ribs. A drawback, however, is the high fiber degradation which occurs during the mixing process, resulting in lower mechanical properties.

SMC incorporates resins, fillers, catalysts, and release and thickening agents to produce a composite considerably stronger and easier to handle than BMC.

SMC is produced on a continuous process machine by dropping chopped strand fibers onto a layer of resin and filler supported by a moving plastic film. A second layer of resin and filler-coated plastic is then placed on top of the reinforcement and the entire formulation passed through a series of rollers. The rollers impregnate the reinforcement fibers throughout with the resin paste. The composite, in sheet form, is rolled up and allowed to mature and thicken for a few days. When it is ready for molding, the plastic film coatings are stripped off and the dry compound stacked or rolled to form a mold charge.

SMC is produced in thicknesses of up to [illegible] in. and is ideal for compression molding. Because its fibers flow with the resin, it is suited for parts that require variations in wall thickness as well as molded-in ribs or bosses. Parts produced from SMC also have high mechanical properties, since fiber length can be varied from 1 in. to continuous strand and/or combinations. Another advantage is the minimal fiber degradation during the continuous mixing process.

TMC composite offers an improved method of wetting-out polyester resins, fillers, and glass to form a three-dimensional glass fiber distribution. Horizontal, vertical, and parallel glass patterns give TMC significantly improved properties over SMC, which has a two-dimensional fiber structure, and over BMC, which suffers glass degradation. Complete wetting during this process also results in low porosity of the composite, which means less rework on the end product.

TMC is produced in thicknesses up to 2 in., then guillotine-cut and packaged into boxes. The composite is a good choice for compression, injection, and transfer molding, especially for applications in the automotive, appliance, and electrical fields.

Pelletized molding compounds

PMC employs similar raw materials to the other precombined systems in a free-flowing ⅛-in. pellet. These compounds can be formulated to meet general-purpose and Underwriters Laboratories requirements and exhibit exceptional pigmentation. The pelletized compounds are designed for automatic molding and are designed for low amperage electrical enclosures, appliance housings, and under-the-hood auto electrical applications.

Surface finishes

Good surface appearances are important to the matched die molding process, especially as reinforced plastics become more common in external product parts. For this reason, methods are being developed to counteract the effect of unsaturated polyester shrinkage during the curing process. This shrinkage, of approximately 8%, occurs perpendicular to the reinforcing fibers, creating a fiber pattern on the surface of the part. One way to mute the pattern is to add inert fillers, reducing shrinkage to about 5%.

Addition of thermoplastic additives to resin composites also will reduce surface patterns. The process, however, results in some loss of physical properties as compared to wet mat molding.

Molded-in coatings

Molded-in surface coatings are another way to improve the surface finish. The compression press is opened about 0.040 in. near the end of the molding cycle to allow for the injection of a surface coating. The mold is quickly closed, causing the coating to flow over the part surface and cure. If the mold is not in perfect condition, however, any scratches or nicks will show up on the part surface.

Another molded-in coating method involves an all-solid powder which is sprayed on the mold before it is charged. The powder melts on the hot mold and fuses into a film which is allowed to cure partially so that it will not tear under the pressure of the molding process.

Molded-in shielding

Because of the increase in electromagnetic pollution, another growing concern for molders is the ability of composites to incorporate shielding properties against electromagnetic interference (EMI). This interference is in the form of stray radio air waves and can interrupt the operation of a business machine if its housing is molded of an unshielded compound.

To effectively shield a product from EMI, a metallic barrier must be inserted between the transmitter of the stray EMI and the receiver. This type of barrier has been added to glass fiber-reinforced plastics by conductive coating, flame spray, spray plating, and vacuum metallizing methods. All of these approaches have proved 99% effective.

Continuous RP laminating

By A.B. Menzer

The continuous laminating of reinforced plastics materials consists of impregnating various reinforcements with resins on an in-line conveyor. The resulting laminate is cured and trimmed as it passes through the various zones of the conveyor.

Materials. The most common resins used in the process are polyesters made up of various glycols and acids. Many additives are used to improve performance of the resin, such as UV stabilizer for better weather resistance, fire-retardant halogenated compounds, and fillers such as aluminum trihydrate, calcium carbonate, and glass spheres. The typical reinforcing material is glass fibers, with most machines chopping continuous rovings into nominal 2-in. lengths. Future developments may include combinations of other high-strength reinforcing materials such as carbon fibers. Some product still is produced with glass mat or woven roving. Surfacing veils also are used.

Process and equipment. Basic components of a continuous RP laminating line are shown in Fig. 1, p. 312. The resin usually is mixed in batches of from 5 to over 500 gal. The resin mix is metered onto a carrier film or, in some cases, it is metered onto a stainless steel belt.

The metering is usually controlled by a doctor blade. Some processes can apply a continuous gel coat. The first carrier film, which creates the panel's surface, generally is polyester, cellophane, or nylon, and can be smooth, embossed, or matte finish.

The glass free-falls into the resin mix and is allowed to wet out. Mechanical compactors can be used to accelerate the wetout process. A second carrier film is used to encapsulate the resin and glass mix. The resulting envelope is pulled through a set of squeeze rollers to eliminate any entrapped air and to set the sheet thickness.

Next, the laminate enters a heated cure area. Inside this cure area, the sheet is formed either by wood or metal shoes into a desired configuration. If the sheet is to be made flat, most machines use some sort of tenter device to maintain even tension on the film across the sheet.

When the laminate is fully cured and leaves the area, the release film is stripped from the sheet, and the sheet is trimmed to its final width by saws, slitters, or high-pressure water jets. Then, the sheet is cut to its finished length.

Operating parameters. The majority of machines produce material approximately 4 ft. wide, but some can produce material as wide as 9 ft. Although some configurations (or shapes) are over 5 in. deep, the majority are less than 2 in. deep. Corrugated, ribbed, and v-beam panels are the most common shapes. Generally, sheets are produced in thicknesses ranging from 0.04 to 0.18 in. Machine speeds vary widely but can be over 60 lineal ft./min. The high-volume machines can consume a full tank wagon of resin in a single 8-hr. shift. Some of the larger producers have machinery which uses over 20 million lb. of resin and over 5 million lb. of glass per year. The capital requirements vary from $250,000 to some machines on the drawing boards at over $1 million. With the modest cost of equipment and with labor cost typically at one-tenth of the raw materials cost, this process is dependent on the efficient use of materials.

Product and performance. An outstanding characteristic of continuously laminated products is light transmittance. This can vary from over 95% transmission to fully opaque. Products also are available in a wide range of colors and decorative ef-

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A.B. Menzer is President (retired), Dyrotech Industries Inc., subs. Crane Corp., 104 N. Chicago St., Joliet, IL 60434.

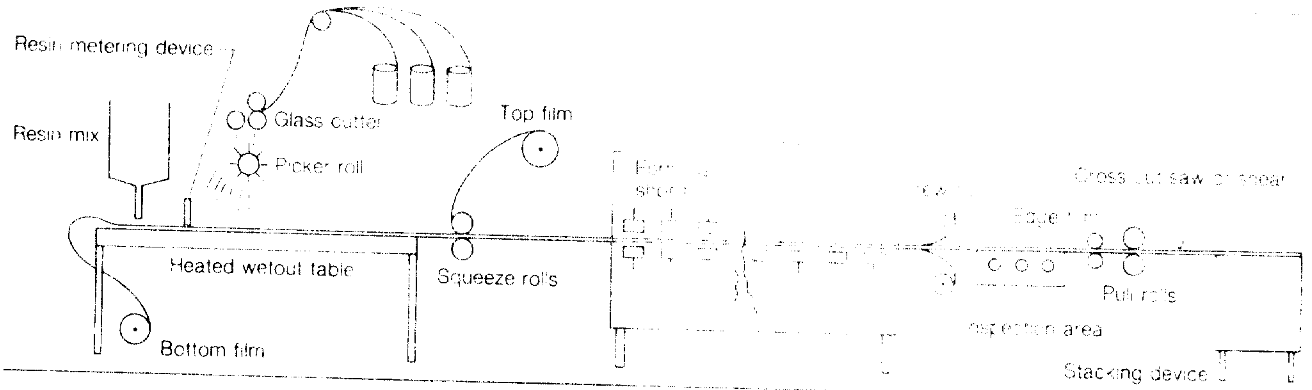

Fig. 1 Continuous RP laminating line.

fects. These products typically are impact- and chemical-resistant. Most meet the requirements of the USDA for use as wall and ceiling liners in meat and food processing areas. Due to shipping and handling limitations, configurated sheets usually are available up to 40 ft. in length. Flat sheets, because they can be coiled for shipping, can be purchased over 1000 ft. in length. Reinforced plastics products are available with widely varying degrees of weather resistance but most producers are able to make a product with an outdoor service life in excess of 10 yr.

Among formulations available are products with low flame spread, low toxicity, and low smoke development (ASTM E-84).

Applications. The original backbone of this industry, industrial skylights, still is a major factor, particularly when panels are produced to match configurations of metal building roofs and/or sidewall panels. Another large use of RP panels is the greenhouse market. The transportation market uses the panels for truck-trailer and container liners, and similarly, the opaque panels are used as sanitary USDA-accepted wall liners in food processing plants, animal confinement buildings, and fast food kitchen areas. The panels also are used widely as garage doors.

Future. Revolutionary cure systems such as electron beam and RF initiation will greatly increase productivity. A new generation of fire-retardant panels is already available which have passed the FM Corner Test (one of the most stringent fire tests recognized by building code officials).

Filament winding

By C. D. Hermansen

Filament winding is the process of laying a band of resin-impregnated fibers onto a mandrel surface in a precise geometric pattern. The process provides an efficient method of producing cylindrically shaped parts and has the potential for producing the highest strength-to-weight ratio of any of the composite manufacturing processes because of the ability to place continuous fibers in the direction of the loads with some tension. This allows the fibers to share the loads evenly and thus permits the material properties to be tailored to the specific design.

Part configurations that are surfaces of revolution are all good candidates for filament winding, but irregular or non-axisymmetric parts do not lend themselves to this process as readily.

Wet filament vs. prepreg materials

The wet filament winding process can be extremely cost-effective since materials are used in their least expensive forms. Other advantages include the long shelf life of the materials, no need for refrigeration, less likelihood of voids, and minimization of material waste.

The prepreg materials offer the advantages of faster winding speeds, less mess, easier to work with and to clean up, less resin content variation, less likelihood of toxicity and lower resin content.

Filament winding has the following advantages over other methods of fabrication: high fiber-strength retention, high degree of automation, high production rate, high reproducibility, simple design and analysis, shorter lead times, and lower tooling costs. The problems that have deterred the use of filament winding for fabrication of structural parts have been selection of the proper high-performance resin matrix, control of resin content, void content, limitations in structural design analysis, in-process inspection methods, and external surface finish. All of the deterring factors can be minimized or eliminated by proper application of currently available technology. Void content is not generally a problem in lower performance applications like pipe and tubing nor in rocket motor cases where burst strength is the primary design criterion. In these applications the fiber strength is the dominant factor in ultimate part strength. The critical defects for structural components include void content, delaminations, debonds, and wrinkles. All of these become very important when the resin properties govern the ultimate strength of the part.

Materials selection

Glass fiber is the most widely used reinforcing fiber, but aramid and graphite rovings are becoming less costly and their unique properties make them the best choice in many applications. Boron and various metal wires also are used in some cases.

Resins include various thermoplastics, epoxies, phenolics, polyurethanes, and polyimides. The thermoplastics still need some of the process procedures and tooling to be more fully developed in order to make them available for widespread use.

The fiber/resin selection process requires studying the data on the material properties as published by the suppliers (and, possibly, from in-house testing) for meeting all the design requirements. Suppliers are constantly introducing new materials and these should be reviewed for their application to the particular composite product.

The primary functions of the resin are to bind the fibers together and distribute the load between fibers as well as protect them against damage and from environmental degradation. While the fibers are the principal load carriers, the resin is the key factor in determining the shear, transverse tension, compression, and flexural properties of the composite.

Mandrels and tooling

A wide range of materials have been used for mandrels with steel being the most common. In many applications the mandrel can become an integral part of the product, typical examples being stainless steel or aluminum-lined compressed gas containers and thermoplastic-lined liquid containers.

Extractable mandrels include: steel both solid and segemented, aluminum, plaster, salts, PVA-bonded sand, air-filled bladders, and various composites. Plaster is probably the most difficult to use of the molded type of mandrel. Proper selection of the man-

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C. D. Hermansen is Sales Manager, En-Tec Engineering Technology Inc., 145 W. 2950 St., Salt Lake City, UT 84115

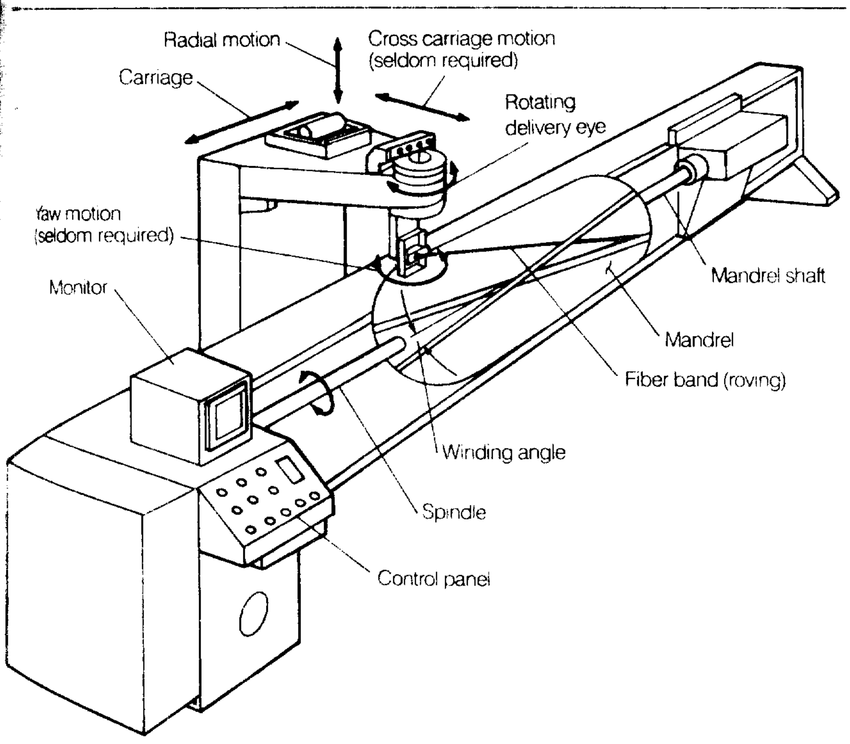

Fig. 1 Typical winding machine.

drel material and its surface preparation will eliminate crooked parts and prevent seizing of the part to the mandrel or damage to the fiber as the mandrel is removed. Composite mandrels are becoming more popular because they are less expensive, lighter, and have superior thermal and fatigue properties.

Inflatable mandrels are used to produce smooth outer surfaces especially for aircraft and airfoil shapes. Molding and hand laying operations are being used more frequently with filament winding to further expand the potential of this process. A combination of processes often will be the best approach to fabricating a particular product, especially as the size of the part increases.

Machinery

Fig. 1 shows a typical winding machine with the four most commonly used axes of motion: spindle, carriage, radial motion, and rotating eye. If there is a need, other axes can be added such as the yaw axis or cross carriage. Other possible uses of currently available extra axis capability are a secondary carriage with or without radial motion, or a robot arm.

Almost all cylindrical parts ranging from ¼ in. to 30 ft. in diameter can be produced. Part configurations that are close to surfaces of revolution can sometimes be wound when some slippage can be tolerated. Complex shapes require more sophisticated machinery.

Applications

A wide variety of parts representing the aerospace, military, commercial, and automotive markets are produced by filament winding. These include storage tanks, fuel drop tanks, leaf springs, fuselages, wind turbine blades, helicopter blades, tubing and pipe, and tool handles for mining and power industries.

Open mold processing

E.L. Shreve

Open mold processing employs a single-cavity mold and produces only one finished surface which is determined by the surface of the mold in contact with the matrix.

Mold design (usually female) places limitations on radii and corner areas that require extensive rolling out for elimination of trapped air pockets. Part design may have to be altered in the tooling stage to insure quality, ease of production, and demolding.

General categories of open mold processing are: 1) hand layup, 2) sprayup, and 3) reinforced plastics-backed (rigidized) vacuum forming, including encapsulation and potting.

Open mold tooling costs are relatively low. Plant facilities can be spartan, or complex involving computers for temperature control and application/production rates. Production can be the classic flow pattern or a one-mold station where all of the procedures are accomplished.

Demolding the part involves a mold release that is most easily spray-applied, although most wax releases are hand-applied and rubbed out. Sometimes a combination is used. Techniques must be practiced to prevent sticking in the mold and even damage to the mold or part.

For polyester, clear or pigmented surfacing resin (gel coat) is applied, usually by spraying, to the mold surface prior to layup/sprayup. Gel coat in contact with the mold hardens, while the side away from the mold stays tacky to bond with the layup/sprayup. The gel coat (some items may not be gel-coated but painted later) reproduces the mold surface, adding sheen and/or color while later becoming an integral part of the built-up matrix.

Wax releases can permeate surfaces and affect paint adhesion. A barrier coat such as polyvinyl alcohol isolates the matrix from the waxed mold surface yet affords release and is easily removed (water soluble) after demolding, leaving a wax-free paintable surface.

Most open mold processing is polyester-based, but activity is increasing in high-density foamed urethane. Higher exotherm may require dedicated molds, but tooling cost can be offset by faster cycle rates. Processing (less gel-coat) is similar, although chop length may be much shorter.

Faster cycle rates and other economies allow direct competition with polyesters and certain physical properties may suggest urethane as first choice.

Hand layup

This oldest and simplest method is best-suited to low-to-medium volume and for medium-to-large parts requiring high strength.

Advantages include design and mold flexibility, unlimited physical size, economical design changes, and opportunity for last-minute use of reinforcement bars, blocks, and ribs. Rework of damaged pieces or rejects is possible.

Disadvantages are the need for labor with above-average RP knowledge, high labor costs per unit, and the lowest production rate.

In hand layup, the reinforcement is manually fitted after the mold is wetted with catalyzed resin, and it is then saturated with resin. This can be spray-applied (wet out), as can the wet coat in the mold. Layers of reinforcement and resin are added to build the desired laminate thickness. Inserts, balsa wood blocks, metal inserts, fasteners, and supports can be welded in place (generally covered completely with laminate). Squeegees, stipple brushes, and finned rollers are used to thoroughly wet the reinforcement, lay down fiber ends, and remove trapped air bubbles. It is then cured at room temperature (can be heat accelerated), then demolded, trimmed, and drilled for sub-

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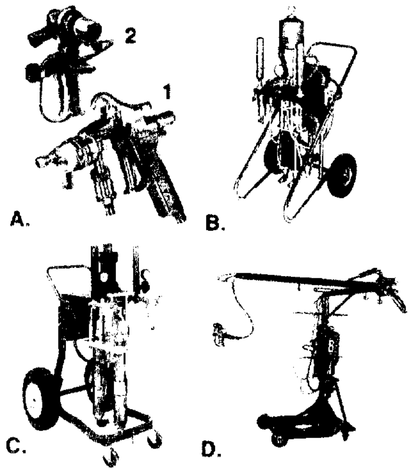
E.L. Shreve is Manager, Plastic & Resin Equipment Div., Binks Manufacturing Co. 9201 W. Belmont Ave., Franklin Park, IL 60131



sequent assembly operations.

Examples are boat hulls, automotive components, pools, bath/shower items, panels, housings, prototype parts, and tooling for other RP items.

Recently developed machines can impregnate rolls of mat, fabric, or roving with resin and catalyst. Saturation of the roll product is in a predetermined glass-to-reinforcement ratio, and the machine positions the correct length over the mold, applies pressure, and institutes rolling techniques producing a part almost automatically. Production rates up to 20 to 30 ft/min. are possible.

Sprayup

Sprayup is best suited to low-to-medium production, but has a greater production rate (faster mold turnover), more uniform parts with skilled operators, and uses more complex molds. Installations can be highly mechanized, while portable equipment allows in-field repair, on-site fabrication, or product maintenance.

In this process, reinforcement fibers (usually glass) are deposited simultaneously in a mold by specialized spraying equipment. Hand or automatic spray guns/dispensing devices, airless (hydraulic) or air atomization, are in common use. A recent development, a marriage of both called air-assisted, augments airless with external air to shape and improve the pattern. This utilizes the best features of both types, and is rapidly becoming a standard. Each has its particular advantages and choosing one over the others can be a tradeoff. Glass roving passes through a chopper, is chopped to predetermined length, and is projected to merge with an atomized resin-catalyst stream. The stream precoats the chop and both are deposited simultaneously on the mold surface. Special equipment controls fluid volumes and pressures, catalyst-to-resin ratio, glass volume, and chop length. The deposited matrix is rolled to remove air and lay down fiber ends.

Matrix deposition is dependent upon operator skill. Multiple passes can build up nearly any required thickness. Typical glass fiber-reinforced (RP) uses are electrical consoles, boat, aircraft, and automotive components, helmets, and tanks.

The bulk of open mold products are RP, but another grouping known as cultured marble and cultured onyx are products that are man-made simulations of natural marble. Examples are bathroom vanity tops, lavatories, bathtubs, tub-shower surrounds, toilet bidets, and a host of matching bathroom accessories.

These open mold products consist of a polyester system, highly filled with inorganic particulates and pigments, formed in a mold previously coated with a clear gel coat. The gel coat enhances the surface, while accenting the random striations and veining, to reproduce the beauty of natural polished marble.

Resin supply is by pressure tank, piston pump, siphon, or piped from a bulk tank circulating system. Commonly the catalyst supply system is a pressure vessel with an in-line flow meter.

A new device referred to as a slave pump is mechanically coupled with a resin pump and supplies catalyst. Percentage of catalyst is altered by selection of the appropriate pivot hole patterns. Theoretically percentage is preselected. In practice, however, a visual flow meter is common.

An advance in resin control is an electronic ratio control system. A computer constantly monitors flow/ratio and displays data in digital form. Stoichiometric control is automatic once programmed. The unit is self-diagnostic and visual-audible signals are energized if malfunctions allow rates in excess of tolerance. Faults and locations are pinpointed and displayed. Recorded values are useful in inventory/cost controls.

Special automatic units (vertical-rotary-horizontal or universal articulating robots) greatly enhance quality and production rates. Panels in various widths (made in endless lengths) or seamless necked tanks, can all be made completely by machine. Waist and shoulder pivot, elbow extension, and wrist pitch-yaw-rotate movements can be combined with a traverse axis to provide a total of seven axes. Products produced by robots include snowmobile hoods and car fenders.

Custom automatic mechanical (non-robot) package installations can include conveyers, exhaust and resin supply systems, pumping stations, and a traversing carriage with spray gun and chopper. Controls allow automatic gel coat and sprayup with automatic rollout. One such unit has dial-in adjustment of glass-to-resin ratio.

Vacuum bag

In this process, the layup/sprayup is covered with a film of polyvinyl acetate, polyethylene, or nylon. The film is sealed to the matrix at the edges and a vacuum is drawn on the bag formed by the film. Atmospheric pressure forces out entrapped air, improves resin distribution, lays down fiber ends, and glazes the surface. Physicals are enhanced and surfaces away-from-mold are improved.

Pressure bag

A variation of the vacuum bag process using positive pressure, can only be used with a female mold. Tailored sheet (usually elastomer) is placed over the matrix, and a pressure of about 500 p.s.i. is applied above the membrane and maintained until the matrix is cured. Void-free, uniform physical characteristics, denser laminates, and molding-in of cores and inserts are advantages.

Autoclave

In the autoclave process (an extension of vacuum/pressure bag process), the laminate is prepared by the vacuum pressure bag process and the entire bagged assembly is placed in an autoclave. Pressures run from 50 to 100 p.s.i. at temperatures up to 500° F. The pressure permits greater reinforcement loading and densities than are possible under ambient conditions.

Rigidized vacuum forming

This process bridges the gap between layup/sprayup and closed mold methods. Limiting factors are size and type of product. Volumes range from low-medium ([illegible] units) to high (10,000 units).

Reinforced plastics-backed thermoforming needs a single-cavity mold and room temperature curing of the matrix.

An advantage over gel-coated items is that the surface quality is assured before application of the backup matrix.

In this process, a preformed sheet (acrylic, ABS, or PVC) is placed in a mold and the layup/sprayup process bonds a backup matrix intimately to the sheet, which takes the place of the surfacing agent or gel coat. A preselected pattern or sheen gives the part its eye appeal. Physical characteristics are tailored beforehand, and thickness is controlled by sheet thickness selection. Secondary or subsequent operations, except trimming, are eliminated.

Principal disadvantages are an additional investment in vacuum forming equipment and handling and storage of bulky formed sheets. Preformed parts with defects cannot be repaired as can gel-coated items.

Molds form only the plastic sheet. The sheet-forming mold can be recycled immediately. A large production rate can result from a single mold, because a formed sheet is produced faster than the matrix will cure. Uses include bath/shower enclosures, vanities, contoured sink tops, and snowmobile, dune buggy, and boat components.

Cold mold thermoforming

This process produces finished surfaces on two sides but still is an open-mold process. The thermoformed sheet is placed in one side of a cold matched mold. A preform positioned in the mold forms one surface, and layup/sprayup/impregnated mat is applied to the inside of the preformed sheet. The sheet/preform matrix cures in the closed mold at room temperature. Bonding of the matrix to sheet is a chemical process assisted by displacement pressure in the now closed mold.

Variations allow cold molding of matrix, thermoforming, and curing in the same press with sequencing.

Encapsulation

This process uses an open mold, sometimes with multiples of single cavities staged for production. It lends itself to low-cost, high-volume automation for the production or encapsulation of relatively small items. It is used for position retention, vibration dampening, security masking, and heat sinks for electrical components. Inserts of any compatible material, size, and shape can be encapsulated in almost any quantity.

Equipment can be hand-held or automatic equipment that senses the mold presence, and size-shape-volume characteristics, and then dispenses the exact mixed quantity required.

Materials may require specialized compounding to achieve desired flow patterns or self-leveling characteristics. Typical thixotropic agents which are added include milled glass fibers and glass, and various other short fibers. For reinforcement, the fiber or filler is combined with the catalyzed resin and dispensed (usually poured) into the open mold cavity. Fillers decrease shrinkage, cracking, and provide heat sink characteristics to increase useful temperature ranges. Cure usually is room temperature. This is an advantage, because mold distortion is minimized and the process is less expensive. Post-cure at above-ambient temperatures sometimes is practiced.

Centrifugal casting

This process produces cylindrical items that include tubes, pipe, containers, and tanks.

The centrifugal force results in self-leveling of the compound against the mold to produce uniform wall thicknesses and good surface quality. The outside surface duplicates the mold surface, while the inside surface is smoothed by the centrifugal force. The force also compresses the matrix, removes air voids, and improves laydown of fiber ends. External surfaces can be gel-coated for eye appeal or color coding. Threads can be molded in or by inserts bonded in place in post-molding operations. Bolt-flange adaptions are another possibility.

Originally the process was a hand operation, but spraying is now almost universal. In sprayup, the prepared mold is rapidly revolved. Chopped mat, directed onto the inside wall surface, is retained by centrifugal force. Conventional dispensing equipment applies resin inside the mold on top of the chopped strand. Centrifugal force insures that the resin will weep through to the mold surface. Compressive force applied is controlled by the speed of rotation. Cure is chemical although additional heat sometimes is applied to lower the viscosity of the applied resin and improve inside surface. Matrix cure can also be hastened by heat to the exterior of the mold from lamps, radiant heaters, or directed hot-air sources.

A variation of sprayup dispenses premixed resin onto the chop through a low-pressure nozzle on the end of a lance. The lance is inserted into the mold and the dispensing is done as the lance is withdrawn at a controlled speed. Mold rotation and the lance travel are such as to describe an overlapping helix inside the mold. Multiple passes will achieve desired thickness of matrix.

The process can be reduced to a one-step operation by preparing the mold and dispensing a premix compound onto the rotating mold. A typical compound is reinforcement that has been wetted/saturated with catalyzed resin, although a short fiber and catalyzed resin in a slurry form also is used.

Finished parts with surface defects usually can be repaired by filling and sanding. Exterior color coating can be applied by spraying, although colored matrix can be used, or a coating can be applied to the mold surface.

Pultrusion and pulforming

By J.D. Martin

Pultrusion is a versatile composite process for producing continuous cross-sectional lineals. Reinforcing fibers are pulled through a liquid resin bath then into a long machined steel die where heat initiates an exothermic reaction polymerizing the thermosetting resin matrix. The composite profile emerges from the die as a hot, constant cross-sectional profile that cools sufficiently to be clamped and pulled by the action of a pulling mechanism. The process concludes when the product is automatically cut to specified lengths.

Some of the properties achieved are a high strength-to-weight ratio, electrical insulation, corrosion resistance, and thermal insulation. These properties make pultruded profiles ideal as ladders, cable trays, gratings, thermal breaks, and window lineals.

Processing

Conventional pultrusion has three basic elements: upstream material handling and forming, the heated die, and downstream product handling/tooling. The typical process line has six sections to it: the reinforcement dispensing creels, reinforcement forming and resin impregnation station, heated die station, process controls, clamping/pulling device, and automatic cutoff saw.

Over 90% of the products produced by pultrusion are glass fiber-reinforced polyester. As the market demands higher service temperatures and better corrosion resistance, pultruders use vinyl ester resins. For higher mechanical properties, especially flexural modulus at elevated temperatures, carbon fiber-reinforced epoxy resins are selected.

There are two types of pultruded products. The first is solid rod and bar where axial reinforcement fibers are utilized to provide high tensile strength and modulus. The second is structural profiles where a balance of axial and multidirectional reinforcing fibers are utilized to create a structural element.

In the first stage of pultrusion processing, axial reinforcing fibers are dispensed from the inside of a package on a bookshelf-style creel. These creels utilize ceramic guide eyes to reduce abrasion of the fibers. When no twist is desired, glass fiber rovings or carbon fiber tows are pulled from the outside of a package mounted on a rotating spindle or a simple mandrel. When a structural profile is to be produced, multidirectional reinforced fiber mats or biaxial fabric materials are mounted on a mat creel station and are dispensed tangentially. Fine fiber mats for improved surface, corrosion-resistant veils, and UV-resistant surfacing materials are also

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J.D. Martin is President, Pultrusion Technology Inc., 1670 Enterprise Pkwy., Twinsburg, OH 44087.

dispensed in this manner.

It is important in the material handling step that the fibers be organized and oriented from the creel sections through to the resin impregnation bath. For this reason, the axial fibers are generally pulled through the mat creel system where they are organized on specific planes and pulled along with the mat products to their initial layered construction.

Resin impregnation/material forming

The reinforcing fibers then move into a resin impregnation station. Here, resin formulated with pigments, mold releases, catalysts, and other additives is held in one of three types of resin pans. The most typical is a resin dip pan, a long metal trough. From the horizontal plane established in the creels, the reinforcing fibers dip down into the resin bath through a series of breaker bars that separate the mat and rovings, allowing each to be thoroughly impregnated. The wet fibers then move out of the resin pan up onto the horizontal plane and into a series of forming guides that perform two functions: preshaping the wet reinforcing fibers and stripping off excess resin before the materials enter the die.

A second system is called a straight-through resin bath. Here the reinforcing fibers enter the back of the resin bath through a carding plate, generally made of abrasion-resistant materials such as UHMWPE, where slots for the mat and holes for the axial fibers have been machined. The wetted materials exit through a similar carding plate at the front of the bath. The fibers then move through the forming guides to the die. The advantage of this bath is that the fibers are not stressed when taken off of the horizontal plane as with the dip technique. Material-induced stresses cause warping or bowing in the finished profile.

The third type is the resin injection system—no resin bath is used. The reinforcing fibers enter a forming collar at the front of the die. Resin, under pressure, is pumped into this collar and wets the fibers just before they enter the die. The advantage of this process is the elimination of a long resin bath and the occasional spills associated with it. The disadvantage is that the reinforcement does not get much exposure to the resin. Also, in the case of filled resins and thick parts the filler material can be filtered out as it is pressured through the compacted reinforcements. The shape of the part and the resin/reinforcement formulation dictate the type of impregnation system utilized.

Heated die station

Not all pultrusion machines come with a heated die station. Yet it is important that the heat going into the formulated resin be controlled. Either strip heaters or cartridge heaters are used to provide thermal heating of the die. Pultrusion dies are generally 36 to 60 in. in length. For epoxies, shorter lengths are typically used because of the adhesive-like characteristics of the resins. Both single- and multi-zone heating systems are used. It is important in processing to control the initiation temperature of the resin, the location and height of the peak exotherm, and the rate at which heat is taken away from the profile after exotherm.

Too low a temperature within the die can result in an incomplete cure and therefore less than the anticipated properties of the profile. Too high a temperature can result in a product exhibiting thermal cracking due to uncontrolled exotherm.

In the production of large-diameter glass fiber-reinforced solid rod and bar, radio frequency preheating is typically used to augment thermal heat in the die. The radio frequency (RF) preheater is placed before the steel die entrance and the resin-impregnated fibers pass through the dielectric heating electrodes. The advantage is that the mass is uniformly heated throughout its cross section. This reduces the amount of time that the material must stay in the die and results in an increase in line speed. Another major advantage of RF preheating is in allowing thick sections to be manufactured without large thermal stresses within the rod which result in micro-cracking and associated reductions in the electrical insulation, chemical resistance, and structural integrity of the product.

Clamping/pulling station

A clamping and pulling device is required to pull the material from the die. There are two types of pulling systems. One is the cleated tractor-like belted puller. Typically two of these belts are offset from one another and the cured profile is fed between the two belts. This puller system is inexpensive and a lot of pulling force can be developed when required for large parts. A disadvantage is that the cleats must be shaped to receive the top or the bottom section of the profile. This can create a great deal of expense since there must be up to 80 cleats each for each profile being pultruded. Also it reduces the possibility of pultruding two dissimilar parts at one time. Large, thin-wall shapes are also more difficult to produce since the clamping pressure cannot be isolated from the pulling pressure.

The second system is a more expensive but more versatile type known as the reciprocating clamp/puller system. Two clamping and pulling mechanisms are placed in tandem and alternatively clamp and pull the profile on a continuous basis. The clamping and pulling process is synchronized through the use of programmable controllers to the extent that the product never sees a pause in the pulling motion or force. In each one of the clamp units, a top and bottom pad, generally machined urethane, is positioned to cradle the top or the bottom of the profile being pulled. The changeover from one part to another is achieved simply by changing the two puller pads. Because they are made from rigid urethane, they have enough durability to pull on the hot profile without disintegrating but also to cushion the profile during clamping without crushing the product. The pulling motion is generally achieved by a ballscrew drive, hydraulic cylinder, or a chain drive. The clamping action is pneumatic or hydraulic.

Cutoff station

As the product emerges from the pullers, it moves into the final station, the automatic flying cutoff saw. Here the product trips a mechanical limit switch or a light beam to actuate pneumatic cylinders clamping the part to the saw table. The saw table moves throughout the duration of the cutting sequence and returns to its home position when the cut is completed.

Equipment

As the market has dictated tighter tolerances and higher properties, pultrusion operations have been forced to respond with machinery that provides tighter control over the clamping and pulling function and the heating functions.

Currently, machines are in use that can produce profiles up to 60 in. in width and up to 24 in. in height. There is no limitation, however, to the size of a pultrusion machine that can be built.

Materials

A wide variety of raw materials has been developed specifically for the pultrusion process. These include faster-processing methyl methacrylate-based resins and the introduction of single-stage epoxies that have processing characteristics like those of polyesters.

New direct-draw glass fiber rovings have better sizing chemistry to enable them to process and wet out with superior characteristics. These low-cost products can now provide properties that were previously available only in conventional roving products. Biaxial nonwoven fabrics are now available to provide increased transverse strength and higher impact properties than previously available from woven fabrics.

Surfacing materials are likewise being improved to make possible the processing of lower-cost materials for corrosion resistance and improved ultraviolet resistance.

Applications

The electrical market with glass fiber ladders, third rail coverboard, transformer spacer stick, hot-line maintenance tools, and standoff insulators is the largest single market for pultruded composites.

The chemical processing industry is the second largest user for glass fiber sucker rods, walkway gratings, stair and handrail supports, and structural supports for a wide variety of chemically resistant environments. Additionally, a great deal of pultruded material is used in the water and wastewater treatment area and in scrubbers for air pollution control equipment.

In the consumer recreation market, pultrusions are used for fishing rods, sailboat battens, snowmobile track rods, tent poles, CB radio antennas, and bows and arrows.

In the construction market, pultruded composites are beginning to make penetration against wood, vinyl, and aluminum as pultruded composites are now being utilized for window and door framing units.

In the aerospace and defense markets, aramid fibers, S-2 glass fibers, and carbon fibers are being used with high-performance resins like epoxies to provide exceptionally lightweight yet strong and impact-resistant profiles.

Pulforming

Pulforming is a process that was developed to produce profiles that do not have constant cross-sectional shape, but have a constant cross-sectional area at any point along the length of the profile.

The materials are pulled from reinforcement creels and impregnated with resin and in some cases combined with a bulk molding compound charge. The material can be preheated using RF energy as in the pultrusion process.

At this point, the process technology departs from the conventional pultrusion process. Beyond the fiber impregnation area is a horizontal table on which is mounted a continuous ring of open female molds. As it operates, the table rotates like a carousel pulling the wetted fibers through the process. The second mold half or in some cases a flexible steel belt is closed or held against the bottom mold. Since the mold and the belt are heated, the material within the closed mold is pulled and cured accepting the contoured mold profile.

When a two-part mold is used it opens at the completion of the cycle, moves to the side, and is redirected to the front of the machine to repeat the process. The finished, cured product continues its path and moves into a cutoff saw which is synchronized to cut at the end of each part. To produce curved pulformed parts, a heated steel belt is used to close the mold. The radius of the part determines the number of molds utilized in this process. A curved part made in this manner could be an automotive leaf spring. Other products are hammer handles and ax handles. The process can also produce other curved parts that do not incorporate undercuts in their design.

Rotational molding

By Spencer Kreiser

Rotational molding is a plastics process for producing hollow, seamless products of all sizes and shapes. This molding process is a supplement to the more conventional injection and blow molding processes. Normally, thermoplastic materials are rotationally molded but the crosslinkable polyethylenes and some thermoset materials have been growing rapidly in use in recent years.

Because the process does not involve high injection pressures, high shear rates, or precise metering of chemicals, the molds and machinery are relatively low-cost and long-lasting.

Advantages of the process include:

1) Unlimited product design freedom.
2) Machinery cost low relative to production capability.
3) Complex parts can be molded without the need for part assembly.
4) Multiple products and multiple colors can be molded at the same time.
5) The variety of molds that is available keeps tooling costs lower than for most processes.
6) Parts are manufactured with very little stress because pressure is not required.
7) Added strength in the corners and uniform walls are inherent to the process.
8) For impact and stiffness, parts can have a multilayer construction.
9) Can be geared up to high production runs on selected parts.
10) Ease of color and material change.
11) Scrap losses are minimal.
12) Double-walled items can be produced.

Process

The basic process is simple. A powder or liquid polymer is placed in a mold; the mold is first heated while being rotated about two perpendicular axes simultaneously, and then cooled. During the first portion of the heating stage, when molding powdered material, a porous skin is formed on the mold surface. This gradually melts as the cycle progresses to form a homogeneous layer of uniform thickness. When molding a liquid material, it flows and coats the mold surface until the gel temperature of the resin is reached, at which time all flow ceases. The mold is then indexed into a cooling station where forced air and/or water spray cool the mold. It is then positioned in a work zone where the mold is opened, the finished part removed, and the mold recharged for the following cycle.

The most popular rotomolding system uses a horizontal rotating unit commonly called the carousel. This normally has three arms on which molds are mounted; however, up to five arms have been used. The arms can be indexed automatically from station to station.

Various types of heating systems have been used; however, the cleaner, lower-cost, safer operation offered by hot air systems has caused them to be most widely adopted. The potential hazards and operational maintenance problems that generally are associated with spraying molten salt or oil onto a rotating mold have virtually eliminated such types of equipment from commercial use.

Cooling usually is the most ignored portion of the entire cycle. Development work has proved, however, that the utilization of proper cooling cycle control helps to insure more dimensionally stable parts and in some cases improved physical properties. Slow cooling of crystalline polymers is preferred when minimum part distortion and good low-temperature properties are needed. In amorphous polymers, on the other hand, the rate of cooling has little effect on physical properties since there is basically no crystal growth to be controlled.

Many attempts at automating the mold opening and loading sequence have been tried in past years; however, due to the diversity of parts that can be molded simultaneously on this equipment, such efforts have proved basically unsuccessful. Complete automation of mold filling and unloading is feasible only on very high production runs of the same part.

Machinery

Relatively simple one-arm rotocast machines with an oven and a cooling chamber are available for laboratory and exploratory development. Small prototype parts up to about 20 gal. in size can be produced with this type of machine.

Most production rotational molding operations use three-arm machines (see Fig. 1) where one arm is always in each of the three stations: load-unload, oven, or cooling. There are several different sizes of this type of machine and tanks up to 5000 gal. can be produced every time the carousel is rotated from one station to the next.

In recent years, several shuttle-type rotational molding machines have been designed and built to rotocast much larger products. One of these machines is currently producing 22,500-gal. tanks. With this type of machine, the mold and material are mounted on a large shuttle cart that is self-driven and moves on tracks from the oven to the cooling chamber. One, two, or three carts can be utilized independently of each other with one oven and cooling chamber.

Molds

In comparison with injection and blow molding equipment, rotational molds are inexpensive. While a number of different metals is used, cast aluminum molds are the most practical for small to medium-

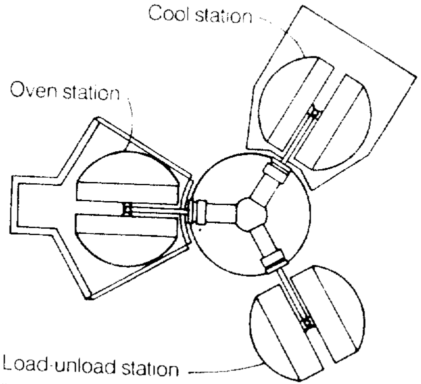
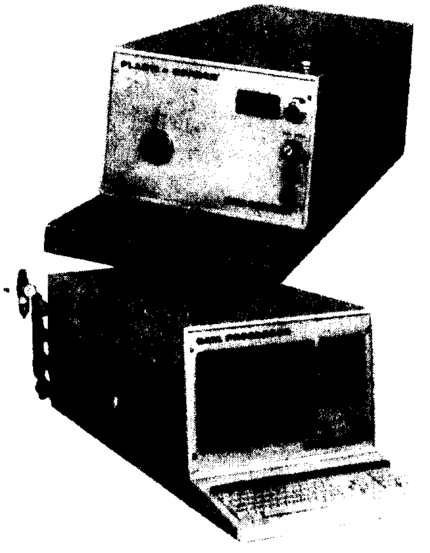


Fig. 1 Typical three-arm rotational molding unit shown in cross section.

Spencer Kreiser is Marketing Manager-Plastics Machinery Group, McNeil Akron Inc., 96 E. Crosier St., Akron, OH 443[illegible]



sized parts requiring multiple cavities.

Cost varies with the quality or detail required for the end product. A pattern must be made for the first cavity, which greatly increases the initial cost, but subsequent cavities are moderately priced, thus markedly lowering the total cost.

Electroformed nickel molds have the advantage of good surface reproduction without the problems of mold porosity often encountered in cast aluminum molds, but electroformed nickel molds cost more than aluminum molds. Sheet metal usually is used for prototype molds and for extremely large parts cast in single-cavity molds.

Experimental molds for prototype parts can be made from glass fiber-reinforced epoxies. Because rotational oven cure temperatures usually are quite high (500 to 800° F.), these molds will degrade in a short time. They can be used for liquid thermosetting polyester and epoxy materials that cure at room temperature.

Applications

There is an ever-increasing number of products being rotationally molded every year. Typical products are agricultural sprayers, storage and feed tanks; automotive dashboards; door liners and gear shift covers; industrial chemical storage tanks and shipping containers; business and residential furniture, planters, trash containers, whirlpool tubs, and light globes; recreational boats, canoes, camper tops, playground equipment, water and refuse tanks for recreational vehicles and boats, and fuel tanks for snowmobiles and motorcycles; toys, including hobby horses, dolls, sandboxes, small swimming pools and athletic balls; advertising display signs, racks, and mannequins. Other application areas for the method include construction barriers, septic tanks, portable toilets, and shelters.

New process controls

Many rotational molding machines are now in operation with microprocessor controls and programmable controllers. Various mold cycle data can now be stored, retrieved, and put into operation in seconds. Automatic trouble shooting is now a feature of microprocessor controls and programmable controllers with built-in failure alarms.

Testing

By H.J. Bultman Jr.

The trend in testing is towards use of the computer. More and more, where possible, signals from the test machine are transferred directly to a computer. These signals are processed automatically to give specific information. This information can be printed out or stored on a disk for future recall.

The computer is the data acquisition system. This method of data acquisition with the proper programs can speed up testing, reduce costs, and provide better data presentation.

Test methods still cover sampling procedures and the apparatus and procedures used to determine the properties, composition, or performance that may be specified. Standards referred to in the United States are those prepared by the American Society for Testing and Materials. The group responsible for the Plastics Test Methods is Committee D-20, which is composed of producers, users, and general-interest participants. Voluntary consensus standards with regard to test methods are arrived at in this forum.

The form and style for an ASTM Standard is the responsibility of the group's board of directors. All standards carry a statement addressing precision and bias; this gives the user of the method an idea of the nature of the sample to be prepared and analyzed and information regarding the nature of the data obtained by using the method. Each method is reviewed for reapproval every five years. All new and revised ASTM Standards include metric units.

The world organization on test methods is the International Organization for Standardization (ISO). Many ASTM Standards are accepted by ISO as prepared.

In all testing, conditioning of the test specimen is essential. The temperature and moisture content of plastics affects physical and electrical properties. ASTM standards have been established to get comparable test results at different times and in different laboratories. For conditioning, the standard that is most referenced is D-618.

Mechanical properties

Tensile properties are an indication of the strength of a material in tension. The force necessary to pull the specimen apart is determined, along with how much the material stretches before breaking. The test procedure (ASTM D-638) is to prepare a specimen, as specified in the standard, by injection molding or by machining from compression molded plaques. Both ends of the specimen are firmly clamped in jaws of a tensile machine. The jaws are moved apart at rates of 0.2, 0.5, or 20 in./min., pulling the sample from both ends. Stress is automatically plotted against strain (elongation) on graph paper.

Flexural properties tests are specified in ASTM D-790. The specimen is placed on two supports and a load is applied in the center (three-point) or by two load points (four-point). The three-point loading is designed for materials that break at comparatively small deflections. The four-point loading is for materials that undergo large deflections during testing. The load is applied at a specified rate and the loading at failure is the flexural strength. The

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H.J. Bultman Jr. is Vice President, Custom Scientific Instruments Inc., 13 Wing Drive, Whippany, NJ 07981.

Key to codes

1. Basic resins*
2. Casting resins or compounds
3. Laminating resins or compounds
4. Molding or extrusion compounds
5. Organosols and plastisols
6. Powders (finely divided)
7. Solutions, emulsions, or dispersions
8. Blends, alloys, etc.

P Primary material producer
C Proprietary compounder
D Distributor, jobber, sales agent, etc.

*Including basic components for multicomponent reactive resins systems such as polyurethanes, epoxies, and polyesters; excluding hardeners, catalysts, promoters.

Huels Corp., Piscataway, NJ (1) **D**
—see ad page 29
Montedison USA Inc., New York, NY (1, 4, 8) **P**
Nuodex Inc., a Hüls Co., Piscataway, NJ (1) **P**
—see ad page 29

Phenolic

American Hoechst Corp., Specialty Products Group, Waxes, Resins, Polymers, Somerville, NJ (1, 7) **PD**
Ametek Inc., Haveg Div., Wilmington, DE (1, 3, 4) **P**
Ashland Chemical Co., Div. Ashland Oil, Inc., Columbus, OH (1, 7) **P**
Atlas Minerals & Chemicals, Inc., Mertztown, PA (7) **C**
Ball Chemical Co., Glenshaw, PA (7) **C**
Borden Chemical, Div. Borden, Inc., Columbus, OH (1, 3, 7) **P**
CdF Chimie North America, Inc., Larchmont, NY (1) **P**
Ciba-Geigy Corp., Composite Materials, Fountain Valley, CA (3) **C**
Dolph, John C., Co., Monmouth Junction, NJ (7) **C**
Durez Resins & Molding Materials, Div. of Occidental Chemical Corp., No. Tonawanda, NY (1, 2, 3, 4, 6, 7) **P**
—see ad page 31
Fiberite Corp., Winona, MN (4) **C**
—see ad pages 16B-16C
Fiber-Resin Corp., Burbank, CA (3, 8) **C**
George, P. D., Co., St. Louis, MO (1, 7) **P**
Georgia-Pacific, Atlanta, GA (1, 2, 3, 4, 6, 7) **P**
Hexcel, Dublin, CA (3) **P**
Ironsides Resins, Div./Ironsides Co., Columbus, OH (1, 3, 7, 8) **P**
Lewcott Corp., Worcester, MA (1, 3, 7) **P**
Maruzen Petrochemical Co., Ltd., New York, NY (1, 7) **P**
Owens Corning Fiberglas Corp., Toledo, OH (1) **P**
PMC Specialties Group, Inc., Rocky River, OH (1. 2, 3, 4) **P**
Perma-Flex Mold Co., Columbus, OH (4) **C**
Plaskon Electronic Materials, Inc., Toledo, OH (4) **P**
Plaskon Electronic Materials Inc., Los Angeles, CA (4) **C**
Plaslok Corp., Buffalo, NY (4) **C**
Plastics Engineering Co., Sheboygan, WI (1, 3, 4, 6, 7) **P**
—see ad page 19
Reichhold Chemicals, Inc., White Plains, NY (1, 2, 3, 4, 6, 7) **P**
Resinoid Engineering Corp., Skokie, IL (4) **P**
Rogers Corp., Rogers, CT (4) **C**
Rogers Corp., Rogers, CT (1, 4)
Soc-co Plastic Coating Co., Cucamonga, CA (5, 7) **C**
Union Carbide Corp., Specialty Chemicals Div., Danbury, CT (1, 3, 7) **P**
U.S. Polymeric, Div. Hitco, Santa Ana, CA (4) **C**
Valite, Div. Valentine Sugars, Inc., Lockport, LA (1, 4) **P**
Werner Consultants Inc., Wallingford, CT (1, 4) **D**

Polyamide-imide

Advance Coatings Co., Westminster, MA (2, 7) **C**
Amoco Chemicals Co., Chicago, IL (1, 4, 7) **P**

Ciba-Geigy Corp., Composite Materials, Fountain Valley, CA (3) **C**
Fluorocarbon Co., Tribol Div., Anaheim, CA [illegible] **PC**
General Electric Co., Insulating Materials, Schenectady, NY (7) **P**
Hexcel, Dublin, CA (1) **P**
Hysol Div., The Dexter Corp., Seabrook, NH [illegible] **P**
Upjohn Co., CPR Div., Torrance, CA (4) **P**
Whitford Corp., West Chester, PA [illegible] **C**

Polyaryl ether

Union Carbide Corp., Specialty Polymers & Composites Div., Danbury, CT (1, 4) **P**

Polyarylate

Celanese Engineering Resins, Chatham, NJ (1, 4) **P**
General Polymers Div., Ashland Chemical Co., Columbus, OH (1) **D**
Union Carbide Corp., Specialty Polymers & Composites Div., Danbury, CT (1) **P**

Polyarylsulfone

RTP Co., Winona, MN (4) **C**
Union Carbide Corp., Specialty Polymers & Composites Div., Danbury, CT (1) **P**

Polybutadiene

Arco Chemical Co., Philadelphia, PA (7) **P**
Colorado Chemical Specialties, Inc., Golden, CO (1, 2, 3, 4, 7) **P**
Conap, Inc., Olean, NY (2) **C**
Dolph, John C., Co., Monmouth Junction, NJ (2) **C**
Enterplast Inc., Kingwood, TX (1) **D**
Firestone Synthetic Rubber & Latex Co., Akron, OH (1) **P**
Goodyear Tire & Rubber Co., Chemical Div., Akron, OH (1) **P**
Hauthaway, C. L., & Sons Corp., Lynn, MA (3, 7) **C**
Heller, H., & Co., Inc., White Plains, NY (1, 4, 8) **D**
Langtex Corp., Houston, TX (1) **D**
Muehlstein, H., & Co. Inc., Greenwich, CT (1, 6, 7) **D**
Prolastomer, Inc., Waterbury, CT (4, 8) **C**
Reichhold Chemicals, Inc., Emulsion Polymers Div., Dover, DE (1, 7, 8) **P**
Santech Inc., Toronto, Ont., Canada (4, 7, 8) **C**
Synthetic Products Co., Synpro-Ware Dispersions, Cleveland, OH (7) **C**
TSE Industries, Clearwater, FL (4) **P**
Ube Industries, Ltd., New York, NY (1) **P**

Polybutylene

Ampacet Corp., Mount Vernon, NY (7) **C**
Bostik Construction Products, Huntingdon Valley, PA (2) **C**
Enterplast Inc., Kingwood, TX (1) **D**
Heisler Compounding Div., Container Corp. of America, Wilmington, DE (8) **C**
Heller, H., & Co., Inc., White Plains, NY (1, 4, 8) **D**
Shell Chemical Co., Houston, TX (1, 4) **P**

Polycaprolactone

Conap, Inc., Olean, NY (2) **C**
Custom Chemicals Inc., Elmwood Park, NJ (2, 7) **C**
Polyurethane Specialties Co., Inc., Lyndhurst, NJ (2, 3, 4) **P**
Prolastomer, Inc., Waterbury, CT (4, 8) **C**

Polycarbonate

Advance Resins Corp., Chicopee, MA (4) **D**
Ashley Polymers, Brooklyn, NY (4) **D**
Avin Exports, Inc., Houston, TX (1) **D**
Bamberger, Claude, Molding Compounds Corp., Carlstadt, NJ (1, 4) **D**
Borg-Warner Chemicals, Inc., Parkersburg, WV (8) **D**
Bruck Plastics Co., Broadview, IL (1, 4) **CD**
Cadillac Plastic & Chemical Co., Birmingham, MI (1) **CD**
Coz Div. Allied Products Corp., Northbridge, MA (4, 8) **D**
Custom Compounding Inc., Aston, PA (6) **CD**
Deer Polymer Corp., Holden, MA (1, 4) **D**
Delta Polymers Co., Fraser, MI (4, 8) **D**
Dow Chemical Co., Midland, MI (1) **P**
—see ad pages 53-58
Enterplast Inc., Kingwood, TX (1) **D**
Fine, L., Company, Inc., Peabody, MA (1, 4) **D**
Fleet Plastics Corp., Haverhill, MA (4, 8) **D**
General Electric Co., Plastics Operations, Pittsfield, MA (1, 4, 6) **P**
—see ad **pages 39, 184, 447-510**

General Polymers **Div.**, **Ashland** Chemical Co., Columbus, OH (1) **D**
Heller, H., & Co., Inc., White Plains, NY (1, 4, 8)
—see ad page 59
Holland, M., Co., Northbrook, IL (1) **D**
Inter-America Marketing Systems, Inc., New York, NY (1) **D**
LNP Corp., Malvern, PA (4) **C**
Langtex Corp., Houston, TX (1) **D**
Lovco Plastics Inc., Deerfield, IL (1, 4) **D**
Mimco, Montgomery, AL (1) **C**
Mitech Corp., Willoughby, OH (4) **C**
Mobay Chemical Corp., Pittsburgh, PA (1, 4, 6, 8) **P**
Muehlstein, H., & Co. Inc., Greenwich, CT (4, 8) **D**
Multiplastics, Wallingford, CT (4) **C**
Nylon Polymers, Inc., Fort Myers, FL (1) **D**
Permuthane, Peabody, MA (1, 7) **PC**
Plastic Compounders of Mass., Inc., Haverhill, MA (1, 4, 8) **C**
Plastics Distributing Corp., Ayer, MA (1) **D**
Plastics Service Inc., Cos Cob, CT (4) **D**
Plexchem International Inc., Dix Hills, NY (1) **D**
Polyfil Inc., Irvine, CA (4, 8) **C**
Polymer Resources, Ltd., Stamford, CT (1, 4) **D**
—see ad page 72

RTP Co., Winona, MN (4) **C**
Rhe-Tech, Inc., Whitmore Lake, MI (1, 4, 8) **C**
Sanncor Industries, Inc., Leominster, MA (1, 3, 7) **P**
Shuman, Philip, & Sons, Inc., Depew, NY (1, 4) **CD**
Shuman Plastics, Inc., Depew, NY (1, 4) **C**
—see ad page 23

Standard Polymers Corp., Cresskill, NJ (1, 4) **CD**
Thermofil, Inc., Brighton, MI (4, 8) **C**
Thor Enterprises, Fair Lawn, NJ (4) **C**
Triad Plastics, Inc., Paramus, NJ (1) **D**
Washington Penn Plastic Co., Washington, PA (2, 3, 4, 6) **CD**
Wilson-Fiberfil International, Evansville, IN (4) **C**

Polyester, aromatic

Adhesive Products Corp., Bronx, NY (2) **P**
Dartco Manufacturing Inc., a Dart & Kraft Co., Augusta, GA (1, 4) **P**
Dartco Manufacturing Inc., a Dart & Kraft Co., Bloomfield, NJ (1, 4) **P**
Furane Products Co., Isochem Operations, Lincoln, RI (7) **C**
General Electric Co., Insulating Materials, Schenectady, NY (7) **P**
Heller, H., & Co., Inc., White Plains, NY (1, 4, 8) **D**
Morton Thiokol, Inc., Morton Chemical Div., Chicago, IL (7) **P**
—see ad page 123
Nylon Polymers, Inc., Fort Myers, FL (1) **D**
Osborn, C.J., Inc., Merchantville, NJ (7) **P**
Rohm and Haas Co., Philadelphia, PA (1, 8) **P**
Polyester, aromatic: Basic resins, alloys
Ruco Polymer Corp., Hicksville, NY (6) **P**
Sohio Chemicals & Industrial Products Co., Ekonol Resins, Sanborn, NY (1, 6, 8) **P**

Polyester, unsaturated

ATS Corp., Atlanta, GA (1) **P**
Abatron, Inc., Gilberts, IL (2, 3, 8) **PC**
Adhesive Products Corp., Bronx, NY (2) **P**
Ad-Tech Plastic Systems Corp, Charlotte, MI (2, 3, 7) **C**
Advance Coatings Co., Westminster, MA (2, 3, 4, 7, 8) **P**
Advance Resins Corp., Chicopee, MA (4) **D**
Akemi Plastics Inc., Eaton Rapids, MI (2, 3) **C**
Alpha Corp., Alpha Resins Div., Collierville, TN (1, 2, 3, 4, 5, 6, 7) **P**
Ashland Chemical Co., Div. Ashland Oil, Inc., Columbus, OH (1, 2, 3, 4) **P**
BASF Corp., Chem. Div., Parsippany, NJ (1) **P**
—see ad page 15
Ball Chemical Co., Glenshaw, PA (1) **P**
Bean Fiber Glass, Inc., Jaffrey, NH (3) **D**
Berton Plastics, Inc., Teterboro, NJ (2, 3, 8) **D**
Budd Co., Plastics Div., Madison Heights, MI (4) **C**
Burns & Russel Co., FSR Specialty Chemicals Div., Baltimore, MD (1, 2, 8) **PC**
Ciba-Geigy Corp., Plastics & Additives Div., Hawthorne, NY (1, 2, 6) **P**
Cook Paint & Varnish Co., Kansas City, MO (1, 3, 6, 7) **P**
Cosmic Plastics, Inc., San Fernando, CA (4, 6, 8) **C**
Dolph, John C., Co., Monmouth Junction, NJ (2) **C**
Durez Resins & Molding Materials, Div. of Occidental Chemical Corp., No. Tonawanda, NY (4) **C**
—see ad page 31
Dynaloy Inc., E. Hanover, NJ (7) **C**
Eastman Chemical Products, Inc., Sub. Eastman Kodak Co., Kingsport, TN (1) **P**
—see ad pages 33-36
Erskine-Johns Co., Los Angeles, CA (2, 3) **D**
Ferro Corp., Coatings Div., Cleveland, OH (6, 7) **P**
Fiberite Corp., Winona, MN (4) **C**
—see ad pages 16B-16C
Freeman Chemical Corp., Sub. of H. H. Robertson Co., Port Washington, WI (1, 2, 3, 4, 7, 8) **P**
GCA Chemical, Stamford, CT (1) **D**
General Electric Co., Insulating Materials, Schenectady, NY (1, 2, 4, 7) **P**
George, P. D., Co., St. Louis, MO (2, 3, 4, 5) **P**
Glastic Co., Cleveland, OH (3, 4) **C**
Haysite Reinforced Plastics, Erie, PA (4) **C**
Heller, H., & Co., Inc., White Plains, NY (1, 2, 6, 8) **D**
ICI **Americas Inc.,** Wilmington, DE (3, 6, 7) **P**
—see ad pages 91-100
Interplastic Corp., Commercial Resins Div., Minneapolis, MN (2, 3, 4, 6) **P**
Jet Moulding Compounds Ltd., Ajax, Ont., Canada (4) **C**
King Fiberglass, Arlington, WA (3) **D**
Koppers Co., Pittsburgh, PA (1, 2, 3, 7) **P**
LNP Corp., Malvern, PA (4) **C**
Lovco Plastics Inc., Deerfield, IL (1, 4) **D**
MKB Industries, Stratford, CT (4) **D**
Nylon Polymers, Inc., Fort Myers, FL (1) **D**
Owens Corning Fiberglas Corp., Toledo, OH (1, 3, 4, 5, 6, 7, 8) **P**
PPG Industries, Inc., Resin Products, C&R Div., Pittsburgh, PA (1, 2, 3, 4, 8) **P**
Perma-Flex Mold Co., Columbus, OH (4) **C**
Plastic Compounders of Mass., Inc., Haverhill, MA (1, 4, 8) **C**
Plastics Engineering Co., Sheboygan, WI (4) **P**
—see ad page 19
Plexchem International Inc., Dix Hills, NY (1) **D**
Polymer Engineering Inc., Wolcott, IN (4) **C**
Polyproducts Corp., Roseville, MI (2, 3) **CD**
Premix, Inc., N. Kingsville, OH (3, 4) **C**
Reichhold Chemicals, Inc., White Plains, NY (1, 2, 3, 4, 7) **P**
Silmar Div., Engineered Materials Co., Standard Oil, Hawthorne, CA (1, 2, 3) **P**
Sohio Chemical Co., Cleveland, OH (1, 2, 3, 4) **P**
Thalco, Uniglass Industries, Div. United Merchants & Mfrs., Inc., Los Angeles, CA (1, 2, 3, 7) **D**
Thermoset Plastics, Inc., Indianapolis, IN (1, 2) **C**
USS Chemicals, Polyesters, Linden, NJ (2, 3, 4) **P**
—see ad page 49
USS Chemicals, Div. of U.S. Steel Corp., Pittsburgh, PA (1, 2, 3) **P**
—see ad page 79

Polyester, thermoplastic, copolymer

Adhesive Products Corp., Bronx, NY (2) **P**
Advance Coatings Co., Westminster, MA (1, 2, 3, 4, 7, 8) **P**
Eastman Chemical Products, Inc., Sub. Eastman Kodak Co., Kingsport, TN (1, 4) **P**
—see ad pages 33-36
Emser Industries, Sumter, SC (1, 6) **P**
GCA Chemical, Stamford, CT (1) **D**
Goodyear Tire & Rubber Co., Chemical Div., Akron, OH (1, 3, 7, 8) **P**
Heller, H., & Co., Inc., White Plains, NY (1, 4, 6, 8) **D**
Huels Corp., Piscataway, NJ (1, 6) **D**
LNP Corp., Malvern, PA (4) **C**
Miles, A. L., Co., Houston, TX (2, 3) **D**
Nylon Polymers, Inc., Fort Myers, FL (1) **D**
Plexchem International Inc., Dix Hills, NY (1) **D**
Polyfil Inc., Irvine, CA (4, 8) **C**
Ruco Polymer Corp., Hicksville, NY (6) **P**
Triad Plastics, Inc., Paramus, NJ (1) **D**
Washington Penn Plastic Co., Washington, PA (2, 3, 4, 8) **CD**

Polyester, thermoplastic, PBT

Adell Plastics, Inc., Baltimore, MD (4) **C**
BASF Corp., Engineering Plastics, Bridgeport, NJ (1) **P**
—see ad page 15
Bruck Plastics Co., Broadview, IL (1, 4) **D**
Cadillac Plastic & Chemical Co., Birmingham, MI (1) **D**
Celanese Engineering Resins, Chatham, NJ (1, 4) **P**
Coz Div. Allied Products Corp., Northbridge, MA (4) **D**
Custom Compounding Inc., Aston, PA (6) **CD**
Deer Polymer Corp., Holden, MA (1, 4) **D**
Delta Polymers Co., Fraser, MI (4, 8) **D**
Fluorocarbon Co., Tribol Div., Anaheim, CA (8) **PC**
GAF Corp., Wayne, NJ (1, 4, 8) **P**
General Electric Co., Plastics Operations, Pittsfield, MA (1, 4, 6, 8) **P**
—see ad pages 44, 184, 447-510, 12, 28, 48

General Polymers Div., Ashland Chemical Co., Columbus, OH (1) **D**
Heller, H., & Co., Inc., White Plains, NY (1, 4, 6, 8) **D**
Huels Corp., Piscataway, NJ (1, 2, 4) **D**
Hysol Div., The Dexter Corp., Seabrook, NH (4) **P**
Jet Moulding Compounds Ltd., Ajax, Ont., Canada (4) **C**
LNP Corp., Malvern, PA (4) **C**
M. A. Industries Inc., Polymer Div., Peachtree City, GA (4, 8) **C**
—see ad page 43
Montedison USA Inc., New York, NY (1, 2, 3, 4, 8) **P**
Muehlstein, H., & Co. Inc., Greenwich, CT (1, 4) **D**
Nuodex Inc., a Hüls Co., Piscataway, NJ (1, 4, 8) **P**
Nylon Polymers, Inc., Fort Myers, FL (1) **D**
Plastic Compounders of Mass., Inc., Haverhill, MA (1, 4, 8) **C**
Polyfil Inc., Irvine, CA (4, 8) **C**
Polymer Resources, Ltd., Stamford, CT (1, 4) **D**
—see ad page 72

RTP Co., Winona, MN (4) **C**
Shuman, Philip, & Sons, Inc., Depew, NY (4) **D**
Shuman Plastics, Inc., Depew, NY (4) **D**
—see ad page 23
Thermofil, Inc., Brighton, MI (4, 8) **C**
Thor Enterprises, Fair Lawn, NJ (4) **C**
Wellman, Inc., Plastics Div., Johnsonville, SC (1, 4, 8) **P**
Wilson-Fiberfil International, Evansville, IN (4) **C**

Polyester, thermoplastic, PET

Allied Corp., Plastics & Performance Materials Div., Morristown, NJ (1, 4, 8) **P**
—see ad page 174
Deer Polymer Corp., Holden, MA (1, 4) **D**
Du Pont de Nemours, E. I., & Co., Wilmington, DE (1, 4) **P**
Eastman Chemical Products, Inc., Sub. Eastman Kodak Co., Kingsport, TN (1, 4) **P**
—see ad pages 33-36
General Polymers Div., Ashland Chemical Co., Columbus, OH (1) **D**
Goodyear Tire & Rubber Co., Chemical Div., Akron, OH (1, 2, 4) **P**
Hafner Industries Inc., New Haven CT (8) **C**
Heller, H., & Co., Inc., White Plains, NY (1, 4, 6, 8) **D**
—see ad page 59
Jet Moulding Compounds Ltd., Ajax, Ont., Canada (4) **C**
Lovco Plastics Inc., Deerfield, IL (1, 4) **D**
M. A. Industries Inc., Polymer Div., Peachtree City, GA (4, 8) **C**
—see ad page 43
Mobay Chemical Corp., Pittsburgh, PA (1, 4, 8) **P**
Morton Thiokol, Inc., Morton Chemical Div., Chicago, IL (7) **P**
—see ad page 123
Muehlstein, H., & Co. Inc., Greenwich, CT (1, 4) **D**
Nylon Polymers, Inc., Fort Myers, FL (1) **D**
Plastics Distributing Corp., Ayer, MA (1) **D**
Pro-Alloy, Inc., Los Angeles, CA (1) **D**
RTP Co., Winona, MN (4) **C**
Thermofil, Inc., Brighton, MI (4, 8) **C**
Thor Enterprises, Fair Lawn, NJ (4) **C**
Wellman, Inc., Plastics Div., Johnsonville, SC (1, 4, 8) **P**
Wilson-Fiberfil International, Evansville, IN (4) **C**

Polyester gel coat

Ad-Tech Plastic Systems Corp, Charlotte, MI **C**
Advance Coatings Co., Westminster, MA (3, 7) **P**
American Colors Inc., Sandusky, OH **P**
American Hoechst Corp., Specialty Products Group, Waxes, Resins, Polymers, Somerville, NJ
Cook Paint & Varnish Co., Kansas City, MO **P**
Ferro Corp., Coatings Div., Cleveland, OH (4) **P**
Freeman Chemical Corp., Sub. of H. H. Robertson Co., Port Washington, WI **P**
Glascoat Inc., Miami, FL **D**
Glidden Coatings & Resins, Cleveland, OH **P**
Idaho Chemical Industries, Boise, ID **D**
Interplastic Corp., Commercial Resins Div., Minneapolis, MN **P**
King Fiberglass, Arlington, WA **P**
Owens Corning Fiberglas Corp., Toledo, OH **P**
PPG Industries, Inc., Resin Products, C&R Div., Pittsburgh, PA **P**
Plasticolors, Inc., Ashtabula, OH **C**
Ram Chemicals, Gardena, CA **C**
Thalco, Uniglass Industries, Div. United Merchants & Mfrs., Inc., Los Angeles, CA **D**

Polyetheretherketone (PEEK)

International Polymer Corp., Houston, TX (4, 8) **C**
LNP Corp., Malvern, PA (4) **C**
Polyfil Inc., Irvine, CA (4, 8) **C**
RTP Co., Winona, MN (4) **C**
Shamban, W. S., & Co., Santa Monica, CA (8) **C**
Tetrafluor, Inc., El Segundo, CA (4) **C**
Union Carbide Corp., Specialty Polymers & Composites Div., Danbury, CT (1) **P**
Wilson-Fiberfil International, Evansville, IN (4) **C**

Polyetherimide

General Electric Co., Plastics Operations, Pittsfield, MA (1) **P**
—see ad pages 101, 184, 447-510, 102
LNP Corp., Malvern, PA (4) **C**
RTP Co., Winona, MN (4) **C**
Shamban, W. S., & Co., Santa Monica, CA (8) **C**
Thermofil, Inc., Brighton, MI (4) **C**
Wilson-Fiberfil International, Evansville, IN (4) **C**

Polyethersulfone

Fluorocarbon Co., Tribol Div., Anaheim, CA (4, 8) **PC**
ICI Americas Inc., Wilmington, DE (1, 4, 6) **P**
—see ad pages 91-100
LNP Corp., Malvern, PA (4) **C**
Polyfil Inc., Irvine, CA (4, 8) **C**
RTP Co., Winona, MN (4) **C**
Shamban, W. S., & Co., Santa Monica, CA (8) **C**
Thermofil, Inc., Brighton, MI (4) **C**
Washington Penn Plastic Co., Washington, PA (2, 3, 4, 8) **CD**
Whitford Corp., West Chester, PA (7) **C**
Wilson-Fiberfil International, Evansville, IN (4) **C**

Polyethylene, chlorinated

Advance Resins Corp., Chicopee, MA (4) **D**
Dow Chemical Co., Midland, MI (1, 4) **P**
Eastman Chemical Products, Inc., Sub. Eastman Kodak Co., Kingsport, TN (7) **P**
—see ad pages 33-36
Enterplast Inc., Kingwood, TX (1) **D**
Fleet Plastics Corp., Haverhill, MA (4, 8) **D**
Gelman, Herman A., Co., Brooklyn, NY (2, 3, 4, 5, 6, 7, 8) **D**
Harwick Chemical Corp., Akron, OH (1) **D**
Heller, H., & Co., Inc., White Plains, NY (1, 4, 8) **D**
Muehlstein, H., & Co. Inc., Greenwich, CT (4) **D**
Plastics Service Inc., Cos Cob, CT (1) **D**
Plexchem International Inc., Dix Hills, NY (1) **D**
Santech Inc., Toronto, Ont., Canada (4, 8) **C**
Teknor Apex Co., Pawtucket, RI (4, 8) **C**
Washington Penn Plastic Co., Washington, PA (1, 2, 3, 4, 7, 8) **PC**

Polyethylene, crosslinked
(see Crosslinked thermoplastics, p.777)