Engineering Thermoplastics from a Commercial Development Viewpoint

RUDOLPH D. DEANIN

Lowell Technological Institute, Lowell, Mass. 01854

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002

*Typical engineering thermoplastics include ultra-high-molecular-weight polyethylene, poly(4-methylpentene-1), poly-*p*-xylylene, chlorinated polyvinyl chloride, fluoroplastics, acetal resins, chlorinated polyether, polyphenylene oxide, polysulfone, polycarbonate, nylons, polyimides, and glass-fiber-reinforced thermoplastics. These most frequently offer advantages in processability, ultra-thin-film formation, rigidity, strength, impact-resistance, lubricity, abrasion-resistance, high-temperature strength and stability, dimensional stability, dielectric properties, clarity, chemical resistance, water resistance, and especially in an improved balance between combinations of these properties. Major applications are largely as mechanical parts in machinery and applicances; electrical insulation in electrical and electronic instruments; and tanks, pipes, fittings, and gasketing in process industry equipment. They are processed primarily by injection molding, occasionally by extrusion, and often even by machining. New materials will continue to join the list at a fairly steady rate, and a few may eventually grow to commodity status.*

Since their commercial appearance a century ago, plastics have grown at an accelerating rate, and will probably exceed metals in volume by 1985 (Figure 1). Their growth rate greatly exceeds conventional materials such as metals, ceramics, wood, rubber, textiles, and paper, largely because plastics frequently offer superiorities in processability, flexibility, strength/weight ratio, impact strength (greater than ceramics, textiles, and paper), range from lubricity to adhesion, abrasion-resistance, energy absorption of

In Engineering Plastics and Their Commercial Development; Foy, George F.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1969.

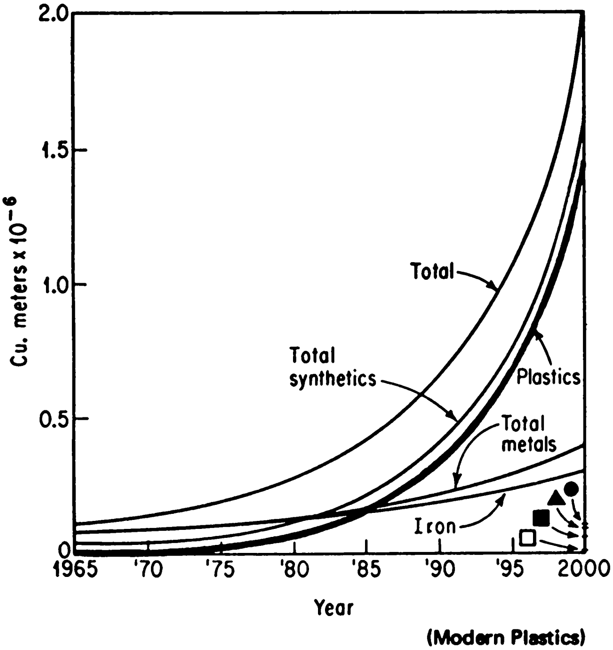

Figure 1. Annual consumption of metals, synthetics, natural fibers, and rubber, by volume (2) "Reproduced by permission, Modern Plastics Magazine, Mc Graw Hill, Inc."

● *Aluminum* ■ *Copper and zinc*
▲ *Synthetic rubbers and man-made fibers*
□ *Natural rubber and fibers*

foams, thermal and electrical insulation, range of color and clarity, and resistance to inorganic chemical corrosion(1).

At the same time, plastics suffer from a number of deficiencies which limit their acceptance and growth. Processability is still not easy or versatile enough for all applications. Rigidity is generally lower than metals, ceramics, and wood. Strength is generally lower than metals and ceramics. Brittleness is greater than metals and wood. Low hardness permits scratching and marring by abrasion of inorganic materials. Coefficient of thermal expansion is much higher than metals and ceramics, causing difficulty in matching components over a wide temperature range. Plastics become much more brittle at low temperatures, and soften sooner than metals, ceramics, and wood at high temperatures. They also suffer thermal decomposition and oxidation at high temperatures, and are more flammable than metals and ceramics. Outdoor weathering causes gradual and often fairly rapid deterioration. Resistance to organic chemicals is often poor. In some plastics absorption of moisture causes severe instabi-

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002

lity of dimensions and properties. Permeability is much higher than metals and glass, causing problems in packaging. And price is often higher than competitive materials.

For all these reasons, organic chemists and chemical engineers expend considerable ingenuity developing new plastic materials to remedy these deficiencies, and such new materials have been appearing commercially at a fairly steady rate for the past half century. Thermoplastics have enjoyed the greatest growth, because of their economical synthesis from low-cost raw materials and their adaptability to mass production by continuous processing techniques.

Engineering Thermoplastics

In the most general sense, all plastics are engineering materials, in that they offer specific properties which we judge quantitatively in the design of end-use applications. Among the large-volume established thermoplastics, we should certainly pay tribute to the engineering performance of the polyolefins, polystyrene, impact styrene, ABS, vinyls, acrylic, and cellulosic plastics.

Generally, however, when plastics marketers speak of engineering plastics, they use the term to distinguish the newer materials which are still used in smaller volume and at higher price, and often are still seeking their optimum markets and applications on the basis of specific superior properties which will justify their higher cost. Properties most often improved include processability, rigidity, strength, impact-resistance, lubricity, abrasion resistance, high-temperature strength and stability, dimensional stability, dielectric properties, clarity, chemical resistance, water resistance, and especially an improved balance between combinations of these properties. These improvements most often lead to applications as mechanical parts in machinery and appliances; electrical insulation in electrical and electronic instrumentation; and tanks, pipes, fittings, and gasketing in process industry equipment.

In such a flexible definition of engineering thermoplastics, the exact list and number of materials and/or families of materials will vary with the viewpoint of the specialist who prepares the list. For purposes of illustration, let us consider 13 thermoplastics, developed during the past decade or two, which are produced in small to moderate volume at medium to high prices, and are finding growing application in products where their superior properties justify their higher costs. Most of these descriptions of engineering thermoplastics are taken from the manufacturers' bulletins and unpublished discussions with manufacturers and users of these materials.

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002

Polyolefins. ULTRA-HIGH-MOLECULAR-WEIGHT POLYETHYLENE. This is easily made by conventional low-pressure coordination polymerization. Hercules Hi-fax 1900 has a molecular weight of 2.5-5.0 million. Its outstanding properties are low coefficient of friction (0.11); abrasion-resistance superior to nylon, polyurethane, and steel; unbreakable in the Izod notched impact test; and high resistance to most inorganic and many organic chemicals.

Its greatest deficiency is processability—it is hardly thermoplastic at all; Hercules sells mill shapes which must be machined into end products, while Formica has developed a continuous compaction-sintering machine for producing it in sheet and laminate form (3). In addition, its modulus, strength, and heat distortion temperature are no better than conventional medium-density polyethylene. Bar, plate, and rod stock sell for $2 up, before machining.

It is finding industrial machinery applications, based mainly on its high lubricity and abrasion resistance, such as timing screws on bottling lines, suction box covers for fourdrinier screens in papermaking, textile loom pickers, coal mining chutes, wear strips on brewery bottling and canning lines, and sporting goods such as runners for snow skis. Large-scale growth will probably depend upon development of new low-cost processing methods.

POLY(4-METHYLPENTENE-1). It was first discovered by Natta, later researched by many companies for synthetic fiber, and finally commercialized by ICI as a specialty molding resin. It is mainly isotactic, 40-65% microcrystalline, and has the lowest density of any plastic, 0.83, which may be approaching the theoretical minimum.

It also has a high melting point, 240°C.; excellent electrical properties; and higher clarity than any other polyolefin. Its weaknesses are low rigidity and solvent resistance; sensitivity to oxidation; and high permeability, which can sometimes be converted into a virtue.

At $1.25/pound it is finding applications in hospital and laboratory ware in this country; earlier marketing in Great Britain has developed additional applications in lighting fixtures, milking machine and liquor dispenser sight glasses, sink traps, slot enclosures for electrical motors, and packages for reheatable foods. Further specialty applications are developing gradually, but large-scale growth would depend upon the much lower potential price inherent in the propylene-based starting material.

POLY (P-XYLYLENE). It was discovered by Szwarc, researched by several companies, and finally commercialized experimentally by Union Carbide. It is prepared by pyrolyzing *p*-xylene at high temperature and vacuum, then condensing on a cool surface, and is

In Engineering Plastics and Their Commercial Development; Foy, George F.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1969.

thus primarily adapted to the production of uniform thin films and coatings.

It has excellent dielectric properties, between Mylar and Teflon; extreme solvent and water resistance; and very low permeability. While it has a crystalline melting point of 400°C., it degrades at 200-300°C. in inert atmosphere and oxidizes at 60-100°C. in air, so it is not a high-temperature material. Vacuum deposition is a difficult custom operation, which costs about $250/pound; the high melting point and insolubility prevent any conventional thermoplastic processing techniques.

It is of interest primarily for very uniform ultra-thin films and coatings (0.002-5 mils) in applications such as electrical resistors, thermistors, thermocouples, stator cores, connectors, fast-sensing probes, photo cells, memory units, dropwise steam condensers for recovery of sea water, pellicles for beam splitters in optical instruments, windows for nuclear radiation counters, panels for micrometeorite detection, dielectric supports for planar capacitors, encapsulation of reactive powders, and supports in x-ray and optical work. Any significant growth would depend upon a major breakthrough in process techniques and a consequent lowering in price.

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002

Polyvinyl Halides. CHLORINATED POLYVINYL CHLORIDE. It was produced in Germany up to three decades ago, but this was primarily a 1,1-disubstituted product of increased solubility for dry-spinning of fibers. Goodrich has developed a light-activated suspension chlorination process which produces 1,2-dichlorinated structures of increased hot strength, thermal stability, and flame resistance.

This Hi-temp Geon is superior to conventional rigid PVC primarily in its higher heat distortion temperature (208-234°F. at 264 p.s.i.). On the other hand, processing is somewhat more difficult, and cost of chlorination brings the price to $0.50. Primary applications are in residential hot and cold water tubing, hot water piping, and hot chemical process equipment such as pipe, plating baths, hot acid fume exhaust from steel pickling, spray etching, and metal finishing.

FLUOROPOLYMERS. These form one of our oldest and most spectacular families of engineering plastics. Polytetrafluoroethylene was developed by DuPont over two decades ago, and more recently by Allied Chemical, Hoechst, ICI, Pennwalt, and other manufacturers as well. It combines unusually low adhesion and friction, high temperature and flame resistance, excellent electrical properties, and extreme chemical inertness. Its high melting point and melt viscosity make thermoplastic processing extremely difficult, so that many

In Engineering Plastics and Their Commercial Development; Foy, George F.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1969.

products are more readily made by machining from stock shapes. It also suffers from low modulus and strength.

Its balance of properties is so unusual that even at $3.25/pound and specific gravity 2.2 it finds growing use in a wide variety of specialized applications ranging from electrical wire insulation in motors, locomotives, aircraft, missiles, spacecraft, lighting fixtures, stoves, ovens, switches, controls, and computers; electrical insulators for radar and television; and chemical pipes, fittings, valves, and pumps, hydraulic and fuel hose in aircraft, trucks, buses, and trains; to gaskets, packings, bearings, and cooking utensils.

More recently, modified fluoroplastics such as fluorinated ethylene/propylene copolymer, polychlorotrifluoroethylene, and polyvinylidene fluoride have been offered by DuPont, Allied Chemical, 3M, and Pennwalt respectively, to provide improved processability and mechanical strength at some sacrifice in heat-resistance, electrical properties, and chemical resistance; and at prices of $3.70-7.15 these have also been finding appropriate if smaller markets.

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002

Polyethers. ACETAL RESINS. These stabilized polyoxymethylenes were introduced dramatically by DuPont and Celanese as engineering plastics to replace non-ferrous metals. Good mechanical strength, resilience, fatigue-resistance, lubricity, abrasion-resistance, heat distortion temperature, water and solvent-resistance can approach the behavior of metals on a volume basis, while processability, color possibilities, and corrosion-resistance are superior. Major weakness is sensitivity to thermal, oxidative, and ionic degradation.

At $0.65 they are developing growing markets in autos, appliances, plumbing, and hardware, such as gears, bearings, switch housings, valves, fan blades, razors, office equipment, pumps, conveyor chain links, and handles. While growth has not been as phenomenal as originally hoped, last year's tonnage of 45.5 million pounds was certainly handsome for a 9-year-old specialty plastic.

POLY (3,3-BIS(CHLOROMETHYL)OXETANE) This is marketed by Hercules as Penton chlorinated polyether. Its thermal, flame, and chemical resistance are used primarily for corrosion-resistant equipment in the process industries, such as valves, fittings, pumps, meters, and linings for steel pipe and tanks, for service in many corrosive atmospheres up to 250°F. or higher. At $4.50/pound, growth possibilities appear limited by increasing competition from lower-cost materials.

POLYPHENYLENE OXIDE. This is actually poly (2,6-dimethylphenylene oxide) and was introduced by General Electric as the first

In Engineering Plastics and Their Commercial Development; Foy, George F.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1969.

commercial representative of the new technique of oxidative polymerization. It offered a combination of mechanical strength, creep resistance, dimensional stability, good constant electrical properties, moisture resistance, and exceptionally high heat distortion temperature (345°F.); its major limitations were difficult thermoplastic processing, low solvent resistance, and sensitivity to thermal oxidation.

It was then modified by polyblending with impact styrene to produce Noryl, with good thermoplastic processability and somewhat lower heat distortion temperature (265°F.). In this form at $0.59/pound, it has been finding growing acceptance in business machines, appliances, electrical equipment, and water distribution equipment.

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002

POLYSULFONE PLASTICS. These plastics which were commercialized by Union Carbide are actually aromatic polyethers containing periodic sulfone groups which provide additional resonance stabilization. They have good mechanical properties, creep resistance, and dimensional stability; but their outstanding quality is their high heat distortion temperature (345°F.) and resistance to thermal oxidative degradation. Limitations are difficult thermoplastic processability, amber color, and sensitivity to organic solvents.

At $1/pound they are finding applications in electrical and electronic equipment, hot household appliances, automotive under-the-hood parts, and aircraft ducts and panelling, as well as hot water service and metal/metal adhesives.

Polyester. BISPHENOL A POLYCARBONATE. This was developed simultaneously by Bayer and General Electric and represented a twin breakthrough: it was the first commercial application of interfacial polycondensation, and it demonstrated that the organic carbonate linkage was surprisingly stable in an aromatic high polymer. The resulting polymer has an unusual combination of high impact strength (12-17.5 f.p.i. for a 1/8 inch bar), heat distortion temperature (270°F.), and clarity but has poor resistance to alkali and many organic solvents.

Originally in a class by itself as a clear, impact and heat resistant thermoplastic, its growth has been slowed considerably by the onrush of more recent engineering thermoplastics. Nevertheless, at $0.80/pound, it reached 27 million pounds last year, going largely into lighting, appliances, electrical and electronic equipment; and continued growth prospects appear quite bright.

Polyamides and Imides. NYLONS. These probably were the first of the engineering thermoplastics, featuring a new combination of easy processability, mechanical strength, lubricity, abrasion resistance, hot strength, electrical resistance, and chemical resistance. A by-product of the synthetic fiber industry, they began replacing metals in applications such as mechanical components in automobiles and machinery, electrical equipment, and molded appliance parts. Competition from the newer engineering thermoplastics, and regeneration of waste fiber, has brought the price of standard nylon molding resins down to $0.75/pound, but they have retained their markets and continued to grow, reaching 73 million pounds last year.

The most serious technical limitation of nylons 6 and 66, their absorption of atmospheric moisture with consequent instability of dimensions and properties, has been overcome somewhat by the successive development of nylons 610, 11, and 12, offering lower moisture absorption and softer but stabler mechanical properties at prices of $1.20-1.60, and going into applications such as battery cases, pumps, timer gears, power tools, hydraulic and gasoline hose, gasoline containers, food packaging film, and hot melt adhesives for laminated textiles. Even considering the growing competition, the future of nylons as engineering plastics appears assured.

POLYIMIDES. They were developed first by DuPont and Monsanto for ultra-high-temperature applications such as electrical insulation, machine bearings, and structural components in instrumentation and aerospace development. These are theoretically linear but not at all processable by thermoplastics techniques.

American Cyanamid has been developing a thermoplastic polyimide XPI with somewhat lower temperature possibilities (heat distortion temperature 440°F.), which may open a new range of potential applications for such materials. Certainly the recent appearance of pots and pans with an external coating of polyimide, for decorative appearance and easy cleaning, represents a dramatic new breakthrough in the prejudice against using plastics in high-temperature applications.

Reinforced Thermoplastics

Short-Fiber-Reinforced Thermoplastics. They began with the use of short glass fibers to increase the modulus of polystyrene 14 years ago, and have grown to the use of 10-40% by weight of short glass fibers in nearly all the commercial thermoplastics. Such reinforcement combines some of the conventional benefits of glass fiber reinforcement in general, with most of the advantages of thermoplastic processability.

Properties most often improved are modulus, strength, and dimensional stability, approaching the properties of die-cast metals.

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002

Other properties which are improved in some systems include low-temperature impact strength and heat distortion temperature. Led by Fiberfil and Liquid Nitrogen Processing, many of the original resin manufacturers have now also begun to offer similar materials, and applications are growing lustily into a wide variety of engineering and high-performance products.

Future Growth

These are typical of the present engineering thermoplastics. Others which could have been discussed include poly-1-butene among the polyolefins; polyvinylidene chloride and polyvinyl butyral among the vinyls; the newer ABS, vinyl, and acrylic polyblends; linear phenoxy resins; and saturated linear polyesters. Most of the engineering thermoplastics will continue to grow into larger volume and broader applications, with corresponding decrease in cost. A few will drop by the wayside. And new ones will continue to appear at a fairly steady rate, offering continued improvements in specific properties, and especially in balance of critical properties for specific applications. Most probable areas for major growth are in block copolymers, in sophisticated composites—both semi-compatible polyblends and reinforced plastics—and in newer and easier processing techniques for high-temperature polymers.

Selection of Optimum Materials and Application

With this continued growth in variety of plastics materials, selection and matching of optimum combinations between materials and applications becomes a major problem. With at least 50 types of commercial plastics already available, each in a variety of copolymers, molecular weights, and different manufacturers, there are already too many for rational manual choice of the optimum material for any specific application; and the situation is growing worse at an alarming rate.

To avoid complete chaos, we badly need to convert to computerized searching in the very near future. Such a search system would start first with the absolute property requirements, P_i, and select only those materials which passed this first screening test. Second, it would balance the relative importance f_i of other properties p_i, preferably on the basis of cost per unit property. And third it would present the design engineer with the one or several materials whose balance of properties ΣP would be best suited to his needs.

$$\Sigma P = P_1 P_2 P_3 \ldots P_i \ldots P_n \, [f_1 p_1 + f_2 p_2 + f_3 p_3 + \ldots f_1 p_i + \ldots f_n p_n]$$

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002

In Engineering Plastics and Their Commercial Development; Foy, George F.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1969.

Materials manufacturers should issue computer cards instead of brochures. Large users of materials could run their own computers, while small ones might best unite to support one master computer run by SPE or SPI for their benefit.

Product Design Theory

In the ultimate pairing of materials and applications, small short-run decisions are generally based on the particular manufacturer's immediate position: a materials manufacturer will seek any conceivable use for his products, a processor will try to process any possible material into any possible end-product, and a manufacturer of consumer products will use any material and process which opens the market fastest.

But for large-scale markets with a long life projection, the selection must be much more objective and impartial. To make a new end product, the designer should first draw up preliminary designs which indicate the general properties that will be required, then use computer searching to identify the one or several materials most likely to meet his needs, then return to his product and examine optimum designs using each of these materials, then consider the process techniques required for each material⇌design combination, and finally refine this 3-way choice to make his final decision.

$$\begin{tikzcd}
\text{Specific Properties} \arrow[r, shift right, "2"'] & \text{Product Design} \arrow[l, shift right, "1"'] \\
\text{Process Technique} \arrow[u, phantom, ""] &
\end{tikzcd}$$

$$\begin{array}{c}\text{Specific Properties} \underset{2}{\overset{1}{\rightleftarrows}} \text{Product Design}\\ \updownarrow 3 \\ \text{Process Technique}\end{array}$$

Beyond this initial theoretical drawing-board-and-slide-rule approach, of course, lies the critical need for experimental proof in actual process machinery and prototype field trials, which should be included as a 4th dimension in such a schematic diagram, and is the final pragmatic judgment to determine technical success of any plastic product. This is the direction in which applications research and product design must grow in the future, in order to convert plastics art into plastic science.

Literature Cited

(1) Jacolow, Melvin F., managing ed., "Modern Plastics Encyclopedia," McGraw-Hill, New York, 1968-69.

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002

In Engineering Plastics and Their Commercial Development; Foy, George F.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1969.

(2) "Modern Plastics Guide to Marketing," p. 1, McGraw-Hill, New York, 1966-67.
(3) Power, G. E., Meyers, K.D., Fremont, R. E., *U. S. Patent* 3,286,008, (1966).

RECEIVED June 6, 1969.

Downloaded by MICHIGAN STATE UNIV on January 19, 2016 | http://pubs.acs.org
Publication Date: June 1, 1969 | doi: 10.1021/ba-1969-0096.ch002