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History of Engineering Thermoplastics

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ABSTRACT

When engineers design high-performance precision products made from plastics, they demand that the plastic materials should approach or even surpass conventional structural materials, particularly in areas such as modulus, strength, creep resistance, lubricity, thermal expansion, high-temperature properties, heat aging, and high-frequency dielectric loss. In response to these demands, polymer chemists have developed a series of high-performance "engineering" thermoplastics offering a wide variety of choice in balance of important engineering properties. These include the fluoroplastics, aliphatic and aromatic polyethers, polyacetals, polysulfones, aromatic polyesters, and aliphatic and aromatic polyamides.

Synthetic organic polymers have played a growing role in our civilization in the past century as they have joined and complemented conventional structural materials such as metals, ceramics, wood, leather, textiles, and paper. Their rapid growth has been due to advantages over conventional materials in terms of processability, wide range of rigidity/flexibility, toughness, wide range of lubricity/adhesion, thermal and electrical insulation, wide range of clarity/opacity and color, and resistance to corrosive chemicals, as well as overall advantages in economics.

In precise engineering design for high performance, plastics have often suffered from certain limitations: low modulus, strength, and creep resistance; less than perfect lubricity, high coefficients of thermal expansion, poor hot strength and heat resistance, and high-frequency dielectric loss. Reinforced thermosets have developed over the past 70 years to remedy many of these problems. They in turn have often suffered from difficulty of processing, resulting in limited design possibilities, and from sacrifices in lubricity, electrical properties, clarity, color, and overall cost.

The commodity thermoplastics—polyolefins, styrene polymers, and polyvinyl chloride—have developed during the past 35 years on the basis of easy processability, versatility in product design, broad range of modulus, toughening by polyblending, electrical and chemical resistance, broad clarity and color range, and overall low cost. Based on this combination of properties, they have grown to 75% of the total plastics market. As engineering materials, however, they still suffer major limitations in modulus, creep resistance, lubricity, coefficient of thermal expansion, hot strength, and heat aging, making engineers very wary of using them in demanding applications.

Even in the early days of the plastics industry, researchers were aware that it was possible to synthesize thermoplastic polymers which could solve one or more of these problems. During the 1950s they began hesitantly to offer these improved materials for engineering use, and to refer to them as "engineering thermoplastics." As the development, production, and application of these materials proved feasible, beneficial, and economical as well, this led to growing interest and activity in the field of such engineering thermoplastics.

The present review will cover nine chemical families which have contributed most to this development. The families will be arranged in order of their commercial appearance in the marketplace, and the development of each family will be traced in turn. Since most of these are the result of group efforts, it is difficult to give adequate recognition to individual inventors. From semicommercial development and field testing up to significant commercial use, it is also difficult to identify exact dates of commercialization. All apologies, therefore, to the insiders who know the true details.

FLUOROPLASTICS

With the commercialization of polytetrafluoroethylene (PTFE) by DuPont in 1948, the plastics industry gained a material outstanding for its lubricity, heat stability, flame resistance, electrical insulation, moisture impermeability, and chemical resistance. It has found many applications in self-lubricating bearings and seals, heat- and chemically-resistant gasketing, cookware, and high-temperature high-performance electrical insulation. Since it resists melt processing even above its melting point of 327°C, and must be processed by metallurgical sintering and machining techniques, or by specialized dispersion technology, most new developments in this family have been aimed at improving processability.

Polychlorotrifluoroethylene (CTFE) was actually developed earlier than PTFE, when M. W. Kellogg used it for processing uranium hexafluoride during World War II, but has grown more slowly into commercial practice. The chlorine atom breaks up the regularity and crystallinity, permitting easier thermoplastic processing and forming harder stronger products, but giving somewhat lower thermal, electrical, and chemical resistance, and less lubricity. It is used in gaskets and electrical insulation.

Tetrafluoroethylene/hexafluoropropylene copolymer (FEP) was developed by DuPont in 1960 to break up the regularity and crystallinity of PTFE homopolymer. This lowers processing temperature and facilitates processability, and also improves transparency, but gives somewhat lower heat resistance and lubricity. Important applications are in chemically-resistant coatings for process equipment, and in high-temperature wire and cable insulation.

Polyvinylidene fluoride (PVDF) was developed by Pennwalt in 1961 as an easier-processing fluoroplastic. It is used for extrusion of wire and cable insulation and chemically-resistant piping, molded as chemically-resistant valves and pumps, and dispersion-coated onto steel as corrosion-resistant building siding.

Polyvinyl fluoride (PVF) film was commercialized by DuPont in the early 1960s as a very weather-resistant material for outdoor applications, both as transparent film products and as pigmented protective coating over more sensitive plastics and other materials.

Ethylene/tetrafluoroethylene (ETFE) and ethylene/chlorotrifluoroethylene (ECTFE) copolymers are approximately alternating copolymers which have been offered by DuPont and Allied Chemical, respectively, since 1970. Compared with the perfluoro-homopolymers, these copolymers are much easier to process and give stiffer stronger properties, but at a certain sacrifice in heat resistance and lubricity. They are used in wire and cable coating, and in injection-molded electrical fittings and chemically-resistant valve and pump parts.

Perfluoroalkoxyethylene (PFA) has been copolymerized with TFE by DuPont since 1972, reducing crystallinity and melting point slightly, permitting thermoplastic processing without significant loss in maximum use temperature or other properties, except for a rise in the coefficient of friction. Main use is in chemically-resistant coatings for process equipment.

Hexafluoroisobutylene/vinylidenefluoride (CM-1) was developed by Allied Chemical in 1973 as an alternating copolymer offering thermoplastic processability and higher rigidity with no sacrifice in maximum use temperature but some loss of impact and electrical properties. Easy powder coatings suggests use in nonstick and nonwetting coatings.

NYLONS

Polyhexamethylene adipamide (nylon 66) was commercialized by DuPont in 1939 for fibers and in 1950 for molded plastics. The flexible aliphatic chain provided easy melt processing and impact resistance, while the crystallinity and hydrogen-bonding provided rigidity, strength, lubricity, abrasion resistance, hot strength, and chemical resistance. This has led to continuing steady growth in applications such as gears, bearings, cams, and wire and cable sheathing. High performance of nylon in such applications was the origin of the concept of "engineering thermoplastics," and helped pave the way for the many others which followed.

Polycaprolactam (nylon 6) was commercialized by Allied Chemical in 1956, with fairly similar properties for similar applications. Different crystalline structure, and a certain amount of residual oligomer at equilibrium, produced somewhat "softer" properties. On the other hand, "monomer casting" techniques permitted conversion of molten monomer directly into large moldings of high molecular weight, low residual oligomer, and much higher properties.

Higher aliphatic nylons were developed over the years by use of sebacic acid (nylon 610) and dodecanedioic acid (nylon 612), as well as aminoundecanoic acid (nylon 11) and dodecanolactam (nylon 12). In all of these the longer aliphatic segments reduced modulus and melting point but improved moisture resistance. Major uses have been in fish-line and brush bristles, with smaller markets in films and powder coatings.

Aromatic nylon was commercialized by Dynamit Nobel in 1969 based on 2,2,4-trimethylhexamethylene diamine and terephthalic acid. The irregular structure produced an amorphous transparent polymer, whereas the conventional nylons were all crystalline and opaque. The aromatic rings and hydrogen bonding produced high modulus, hot strength, and chemical resistance. These materials have been finding specialized uses such as flow meters, sight glasses, and transparent electrical equipment.

POLYESTERS

Polyethylene terephthalate (PET) was developed originally by ICI as a fiber with moisture- and crease-resistance superior to cotton. By 1954 ICI and DuPont were also offering it as biaxially oriented film, with strength, heat, electrical, chemical, and impermeability qualities superior to cellulosics. Despite its higher cost, it has grown steadily to major volume and lower price, particularly for use in photographic film, capacitor insulation, recording tape, and boil-in-bag food-packaging.

Despite its high qualities in stretched film, it has long resisted efforts to turn these qualities to advantage in molded plastics, due to slow crystallization and brittleness. In 1978 DuPont launched a major effort to overcome these problems by fast nucleation and short-fiber reinforcement. In this form it may finally be headed for growth into major markets such as under-the-hood molded parts in autos.

Polybutylene terephthalate is a more flexible molecule which crystallizes much more readily, giving fast molding cycles and tougher finished products. Introduced commercially in 1970, primarily with short glass reinforcement, it offers high rigidity, strength, dimensional stability, and resistance to heat, water, and chemicals. This has led to fast-growing use in auto parts, pumps, appliances, and electrical motors.

Polyoxybenzoate was developed by Carborundum in 1970 to bridge the gap between metals and plastics. High molecular rigidity and crystallinity produce extremely high modulus, dimensional stability, melting point and use temperature, thermal conductivity, and resistance to water and solvents. Typical applications suggested include high-temperature coatings, bearings, seals, pump seals, high-temperature electrical insulation, frying pans, and piston rings. Unfortunately, melt processing is extremely difficult. In 1976 they modified it by copolymerization with bisphenol A, terephthalic and isophthalic acid, producing lower melting point, injection moldability, and somewhat lower properties, and recommending it for similar applications.

Poly(bisphenol A terephthalate) was developed by Untila in Japan and introduced in the United States in 1978 by Union Carbide. It combines thermoplastic processability, ductility, impact and creep resistance, high use temperature, flame retardance, transparency, ultraviolet resistance, and reasonable cost. While it is too early to judge its ultimate place in the spectrum of engineering thermoplastics, it has been recommended for uses such as glazing, transportation, mine safety, and solar energy utilization.

REINFORCED THERMOPLASTICS

Starting during World War II, the combination of glass fabric with thermoset polyesters produced tremendous gains in rigidity, strength, toughness, creep resistance, and dimensional stability, permitting plastics for the first time to rival and even surpass steel, and leading to the typical layman's judgment, "That's not plastic, that's fiberglass." The use of glass fabric and thermosetting plastics, however, introduced many problems in processing and cost. Starting in 1954, Fiberfil introduced the concept of dispersing short glass fibers into thermoplastic molding materials to combine all of the above benefits with easy processing and low cost.

Naturally the marriage was not perfect and required some compromises. Glass fiber contents generally range from 10 to 40% by weight. Chopped fiber lengths range from 3/8 in. down to 1/8 in. or less, and milled fibers may run considerably less; due to flow and orientation problems in melt processing, the trend has generally been downward. Abrasion of process equipment and degradation of fiber length in recycling have also been problems. Properties have never equaled those of glass-fabric-reinforced thermoset polyesters. Nevertheless, short-fiber-reinforcement of thermoplastics has consistently produced major improvements in rigidity, strength, creep resistance, dimensional stability, and occasional improvements in impact strength and heat deflection temperature and chemical resistance.

Starting with polystyrene, the technology rapidly spread to nylon and thereafter concentrated mainly on improving the new engineering thermoplastics. Thus, as each new engineering thermoplastic is introduced commercially, the pure form is soon followed by short-glass-fiber-reinforced forms with all of the above benefits to the extent that some engineering thermoplastics are used largely or entirely in reinforced versions.

In addition to short glass fibers, a number of other fillers have shown promise in commercial practice. The most important is "mineral reinforcement," using particulate fillers. These give easier processing and often lower cost than glass fibers. Proper surface treatment, and often high aspect ratios, permit them to offer some improvement in properties, though not as high as can be obtained with glass fibers; so some grades use combinations of mineral reinforcement along with short glass fibers. Other frequent additives include flame retardants and blowing agents for structural foams. More specialized additives include solid lubricants like PTFE, graphite, and MoS_2 and conductive fillers such as carbon and metal powders. On the whole, such reinforced thermoplastics represent an increasing share of the total field of engineering thermoplastics for all these reasons.

POLYCARBONATE

In 1957 Bayer and General Electric simultaneously and independently reported the condensation of bisphenol A with phosgene in alkaline medium to produce high-molecular-weight polycarbonates of exceptional properties, and commercialization proceeded in the following year. Two-step synthesis from low-cost raw materials, and a stiff amorphous molecular structure, offered an unusual combination of thermoplastic processability, rigidity, extremely high impact strength, creep and heat resistance, moderate flame retardance, and transparency at moderate price, a combination which had never been available in any material before and has not been equaled in any material since. While the extreme impact strength has not yet been adequately explained, and is sensitive to thickness and notches, the material has proved so unique that it has found growing use in a wide range of applications from glazing, electrical products, and appliances to transportation, sports equipment, lighting, and signs. In addition, its success has stimulated intensified research and development on other newer engineering thermoplastics.

POLYACETAL

Polymerization of formaldehyde has been known for over a century, but the unstable polymer depolymerized so rapidly that few people took it seriously. Research at DuPont showed that end-capping with acetic anhydride, plus addition of antioxidants and acid acceptors, could produce good stability, leading to commercialization in 1959. The resulting "acetal resins" offered a combination of processability, rigidity, ductility, lubricity, creep and fatigue resistance, and solvent and stress-crack resistance at reasonable price. Soon afterward Celanese added the concept of copolymerizing small amounts of ethylene oxide units into the polyformaldehyde chain to stop unzipping depolymerization reactions which might occur; the only sacrifice was a slight softening of modulus and melting point. Later modifications were primarily the addition of short glass fibers for higher modulus, creep resistance, and dimensional stability, and the use of MoS_2 or PTFE powders for even higher lubricity. Market growth has been very successful, particularly for use in gears and bearings for autos, appliances, and machinery, and in plumbing fixtures, largely as replacement for metals to produce better and longer-lasting performance.

POLYPHENYLENE OXIDE

The well-known thermal stability of diphenyl ether tantalized polymer chemists for many years with the thoughts of polyphenylene oxide as a high-temperature plastic, but synthetic efforts always went awry. In 1965 General Electric finally solved the problem by commercializing the oxidative polymerization of 2,6-xylenol to form poly(2,6-dimethyl phenylene oxide). The stiff aromatic chain produced an excellent combination of rigidity, creep resistance, dimensional stability, high melting point, electrical resistance, water resistance, and moderate flame retardance. Unfortunately, it also produced extremely viscous melt properties which made melt processing impractical. By a lucky chance which is not yet entirely understood, the polymer proved to be remarkably compatible with polystyrene and impact styrene. Polyblends of the two provided easy processability and lower cost, with only partial sacrifice of the extreme properties of the pure polymer. This resulted in successful commercial growth. Most grades are also further compounded with short glass fiber reinforcement, flame retardants, and/or blowing agents for structural foam.

Major applications appear to be in television electrical parts, office equipment, water handling equipment, and similar products. Beyond the present polymer, oxidative polymerization appeared to open a great new frontier for polymer synthesis, but so far this has not resulted in any other new types of commercial polymers. This possibility still remains in the future.

POLYSULFONES

Aryl sulfone polymers first appeared commercially in 1966 when Union Carbide condensed the sodium salt of bisphenol A with bis(p-chlorophenyl)sulfone. This produced a stiff resonating chain with thermoplastic processability, rigidity, creep resistance, dimensional stability, hot strength, hot aging resistance, moderate flame retardance, very good electrical performance, amorphous transparency, and aqueous resistance, all at moderate price. Along with short glass fiber reinforcement, structural foam, and similar additives, this has led to a variety of heat- and water-resistant applications under the hood in autos, and in food handling, medical equipment, instrumentation, and appliances.

Union Carbide originally studied a wide range of polysulfone structures and chose the most economical one as a starting point. Meanwhile, 3M Corporation took the opposite approach, choosing the most heat-resistant one for their entry in 1967. They condensed diphenyl with oxy-bis(benzene sulfonyl chloride) by a Friedel-Crafts reaction, producing a polymer of much higher heat resistance, but also much higher price which severely impeded commercial growth.

ICI took an intermediate path in 1972, condensing bis(chlorophenyl)-sulfone with alkali to produce a polymer of intermediate heat resistance and price. They also took the initiative in developing and publishing a considerable amount of performance data for aid in engineering design. Since their marketing efforts have been largely in England, it is difficult to compare commercial success with the United States polymers.

Most recently, in 1977 Union Carbide offered a second polysulfone, this one made from the sodium salt of diphenol plus bis(p-chlorophenyl)sulfone. This one too has intermediate heat resistance. It is unique in its very high impact strength, which they believe is due to ease of rotation at the phenyl-oxygen and phenyl-phenyl bonds. Current high price would appear to aim it primarily at selected applications requiring this special balance of thermoplastic processing, impact strength, heat resistance, and clarity.

POLYPHENYLENE SULFIDE

Polymers containing the repeating phenylene sulfide group had been reported in the research literature for more than 50 years until

Phillips Petroleum finally commercialized this material in 1968. Condensation of p-dichlorobenzene with sodium sulfide, under controlled conditions, produced a polymer of high molecular rigidity and crystallinity with high resonance stabilization. This resulted in very high modulus, creep resistance, dimensional stability, high temperature resistance, flame retardance, and chemical resistance. For the most part it is used with particulate or short-fiber fillers which further enhance most of these properties. Initial applications were primarily heat- and chemically-resistant coatings, but continued development has optimized some grades for molding into products such as light bases, auto pumps, and carburetors.

This quick survey indicates that polymer chemists are showing increasing ability to develop new polymer structures to meet the needs of design engineers by providing them with a growing spectrum of engineering thermopolastics tailored to these needs. The increasing needs of modern technology, and the gradual depletion and energy limitations of metals, will undoubtedly accelerate this trend in the decades to come.

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