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# Engineering and Specialty Thermoplastics: Nylons

## State of Art, New Challenges and Opportunities

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***Abstract***
This chapter discuses a brief account on various types of nitrogen containing engineering polymers. Synthesis, morphology, structure, properties and applications of all different types of nitrogen containing engineering polymers are summarized in a concise manner. The new challenges and opportunities are also discussed.

## 1.1 Polyamide-imides

Polyamide-imides are thermoplastic amorphous polymers that have exceptional mechanical, thermal and chemical resistant properties. These properties put polyamide-imides at the top of the price and performance pyramid. Polyamide-imides are produced by Solvay Advanced Polymers under the trademark Torlon. Other high-performance polymers in this same realm are polyetheretherketones and polyimides. Polyamide-imides hold, as the name suggests, a positive synergy of properties from both polyamides and polyimides, such as high strength, melt processibility, exceptional high heat capability, and broad chemical resistance.

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Polyamide-imide polymers can be processed into a wide variety of forms – from injection or compression molded parts and ingots – to coatings, films, fibers and adhesives. Generally these articles reach their maximum properties with a subsequent thermal cure process.

## 1.2 Polyetherimide (PEI)

Polyetherimide (PEI) is an amorphous, amber-to-transparent thermoplastic with characteristics similar to the related plastic PEEK. Relative to PEEK, PEI is cheaper, but less temperature-resistant and lower in impact strength. Polyetherimide combines high temperature resistance, rigidity, impact strength, and creep resistance. Glass-fiber-reinforced PEI plastic grades are available for general-purpose molding and extrusion; carbon-fiber-reinforced and other specialty grades also are produced for high-strength applications and PEI itself can be made into a high-performance thermoplastic fiber. PEI has found use in medical applications because of its heat and radiation resistance, hydrolytic stability, and transparency; in the electronics field, it is used to make burn-in sockets, bobbins, and printed circuit substrates; automotive uses include lamp sockets and under-hood temperature sensors; and PEI plastic sheeting is used in aircraft interiors. The PEI's history started in 1970, when USSR researchers (1) introduced the concept that the insertion of a flexible linkage into the polyimide chains considerably decreased glass transition temperatures without significantly lowering of thermal stability. Due to the wide range of PEI's applications, scientists continuously report studies concerning PEI synthesis from new monomers (2–4).

## 1.3 Poly(ether-block-amide)

Polyether block amide or PEBA is a thermoplastic elastomer (TPE). It is also known under the tradename of PEBAX® (Arkema). It is a block copolymer obtained by polycondensation of a carboxylic acid polyamide (PA6, PA11, PA12) with an alcohol termination polyether (PTMG, PEG). PEBA is a high performance thermoplastic elastomer. It is used to replace common elastomers – thermoplastic polyurethanes, polyester elastomers, and silicones - for these characteristics: lower density among TPE, superior mechanical

and dynamic properties (flexibility, impact resistance, energy return, fatigue resistance) and keeping these properties at low temperature (lower than –40 °C), and good resistance against a wide range of chemicals. It is sensitive to UV degradation. Challenging high-performance polymeric materials are in high demand and poly(ether-block-amide) copolymers meet the requirements of advanced applications in various marketplaces. Thermoplastic elastomers with desired final properties can be tailored through addressed interplay of polymer segments having different chemical nature, length, and weight. Insightful investigations have suggested that the micro-phase separated morphology as the major factor for the outstanding properties of these copolymers that are not usually observed for each individual component. Excellent mechanical resistance enhanced chemical inertia and powerful perm-selective transport properties can be regarded as the result of the intricate interplay of the various constituents of these segmented copolymers. Excellent chemical, mechanical and transport properties of these polymers render them challenging systems for a broad range of applications, including high-performance waterproof breathable clothing, barrier films, engineered packaging, membrane separation processes. It is important to add that these materials are being used for many advanced industrial applications, including textile, packaging and medical devices. The latter appears to be a key issue to meet the requirements of advanced applications in textile, construction, food and waste processing, packaging and medical fields.

## 1.4 Aromatic Polyamides

Poly(amide)s, most commonly called polyamides, are polymers incorporating the amide group in their repeating unit (-CO-NH-) (5). Aromatic polyamides, wholly aromatic polyamides, or aramids, are considered to be high-performance materials owing to their outstanding thermal and mechanical resistance. The high performance properties of these materials can be attributed to their fully aromatic structure and amide linkages, which give rise to stiff rod-like macromolecular chains that interact with each other via strong and highly directional hydrogen bonds. These physical links deeply favor the development of effective crystalline micro-regions or domains, resulting in a compact intermolecular packing and cohesive energy. The better-known

commercial aramids, poly(p-phenylene terephthalamide) and poly (m-phenylene isophthalamide) are used in advanced technologies in every industrial field, and have been transformed into high-strength and flame resistant fibers and coatings with broad applications in advanced industrial products, such as heat and cut protective clothing, ballistic-protection products, sport fabrics, specialty paper products, transmission belts, friction products, industrial filters and membranes, and special pipes, among others. Owing to the above mentioned chemical and physical characteristics, they exhibit extremely high transition temperatures, which lie above their decomposition temperatures. They are sparingly soluble in common organic solvents and, accordingly, can only be transformed upon solution from polar aprotic solvents or strong inorganic acids. Hence, the expansion of the applications of aramids involves, from one side, increasing their solubility, thereby improving their transformability, and, from other side, incorporating new chemical functionalities in the polyamide backbone or lateral structure in order to provide key characteristics for their application in cutting edge technological fields. These fields are related with new electrochromic, luminescent or optically active materials, gas separation and ion exchange membranes, macromolecules with sensing and supramolecular capabilities, biomaterials for medical applications, materials with even higher mechanical and thermal resistance, etc. The first all-para oriented aramid, poly(p-benzamide) (PPBA), was marketed by Du Pont under the 'Fiber B' trade name. Production only lasted a few years, probably due to economic reasons. (6,7)

Poly(p-phenylene terephthalamide) (PPTA)-based fabrics offer four times the protection of cotton fabrics and eight times the protection of leather based clothes, offering heat protection as well. The PPTA fibers are extremely cut-resistant, which makes them ideal for use in: cut-resistant gloves, leg protection (e.g., for forestry workers), anti-vandalism fabrics (e.g., for bus and train seats), etc. The excellent energy absorption properties, tenacity and impact resistance makes PPTA valid for helmets and soft (bullet-resistant vests) and hard (armored police and civilian vehicles) ballistics. The superior performance-to-weight ratio of aramids makes them useful for reinforcing high-performance tires, conferring the stability to the tires, durability and reduced fuel consumption. The aramids are used in passenger car tires, motorcycle tires, bicycle tires, truck and bus tires, agricultural tires, off-road tires, airplane tires and solid tires.

Aramids encounter applications in the manufacture of hoses when hose specifications for bursting pressure, longevity, temperature and chemical resistance are extremely high. Transmission belts reinforced with aramids are used for applications demanding low creep, high dimensional stability, fatigue resistance, temperature resistance, precise synchronization and low operating noise belts, i.e., in the automotive industry.

The thixotropic aramide-reinforced resins provide viscosity control for applications in a full range of temperatures, from cryogenic to 350 °C, and media, providing inertness in most common chemicals, including organic solvents. Moreover, the high strength, light weight and thermal stability of paper made with these polymers allows manufacturers of aerospace and marine equipment to produce safe components that perform better and last longer than their alloy equivalents. Aramids are used to reinforce ropes and cables wherever safety and protection are essential, showing significant advantages over other synthetic yarns and steels in ropes and cables. Aramids are used in a wide range of composite applications in the industrial, leisure, civil engineering, ground transportation and aerospace markets, with new applications added daily, i.e., sails and reinforced hulls of sailing boats in the marine industry, rotor blades and structural parts in aerospace industry, wind turbines in new energy fields, high-pressure vessels and circuit breakers in industrial components, lightweight parts for heavy-duty purposes in ground transportation, etc.

## 1.5 Polyaniline

Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family. Although the compound itself was discovered over 150 years ago, only since the early 1980s has polyaniline captured the intense attention of the scientific community. This is due to the rediscovery of its high electrical conductivity. Amongst the family of conducting polymers and organic semiconductors, polyaniline is unique due to its ease of synthesis, environmental stability, and simple doping/dedoping chemistry. Although the synthetic methods to produce polyaniline are quite simple, its mechanism of polymerization and the exact nature of its oxidation chemistry are quite complex. Because of its rich chemistry, polyaniline is one of the most studied conducting polymers of the past

50 years. Polyaniline (PANI) is a unique polymer among a family of conducting polymers and has semiconductor properties. It was first called as "aniline black" in organic form as part of melanin, like organic polymer in 1934. Melanin is a natural material protecting the skin by regulating UV exposure through a polyaniline interaction. In the end of 1990, PANI became evident that it was highly useful polymer and could be used in applications varying from smart windows to electronic chips. PANI can be configured to conduct across a wide range, from insulation to conductive purposes. It is flexible appealing for manufacturing use and has granular form which can be mixed with an organic chemical and painted or sprayed onto a substance to form a smooth surface of polyaniline. From economic point of view, the PANI is significantly superior to other conducting polymers because the aniline monomer is less expensive than other monomers. The synthesis of PANI is simple and has many application fields. PANI has many potential applications in multidisciplinary fields because of its unique properties. PANI can be applied in different areas such as electronics, thermoelectric, electrochemical, electro-luminescence, chemical, membrane, coatings, sensors, and so on.

## 1.6 Polyimides

Polyimide (sometimes abbreviated PI) is a polymer of imide monomers. Polyimides have been in mass production since 1955. Typical monomers include pyromellitic dianhydride and 4,4′-oxydianiline. Polyimides (PI) are a class of thermally stable polymers that are often based on stiff aromatic backbones. Polyimides were first prepared by Bogert and Renshaw in 1908, and they were then widely used and rapidly developed in the early 1960s (8). Polyimides have received great attention as they are very useful for many high-tech applications (9). The use of polyimides as high-performance and high-temperature thermoplastic materials in various applications stems from the attractive combination of chemical, mechanical and physical properties. Polyimides have found wide usage as films, coatings, adhesives, and matrix resins due to their excellent electrical and mechanical properties, high thermal and chemical stability, good solvent resistance, and dimensional stability. They are generally used as flexible circuitry substrates, interlayer dielectrics and passivation and protective coatings in high density electronic

packaging devices. The chemistry of polyimides is in itself a vast area with a large variety of monomers available and several methodologies available for synthesis. The most widely practiced procedure in polyimide synthesis is the two-step poly(amic acid) (PAA) process. It involves reacting a dianhydride and a diamine at ambient conditions in a dipolar aprotic solvent to yield the corresponding poly(amic acid), which is then cyclodehydrated to the polyimide either thermally or chemically. The thermal imidization of the poly(amic acids) is especially useful when the final product is desired in a film or a coating form and chemical imidization is a useful technique for manufacturing molding powders.

Most polyimides are infusible and insoluble due to their planar aromatic and hetero-aromatic structures and thus usually need to be processed from the solvent route. One step method- high temperature solution polymerization is employed for polyimides that are soluble in organic solvents at polymerization temperatures. The process involves heating a stoichiometric mixture of monomers in a high boiling solvent or a mixture of solvents at high temperature. The imidization proceeds rapidly at these temperatures and water generated due to the reaction is distilled off continuously as an azeotrope along with the solvent. The properties of polyimides can be dramatically altered by minor variations in the structure. The subtle variations in the structures of the monomer components have a tremendous effect on the properties of the final polyimide. The infusibility and limited solubility of unsubstituted polyimides are characteristic properties which restrict synthesis, characterization, processing, and applications, particularly for a high molecular weight material. Thus, a variety of concepts for structural modifications such as bulky pendant groups, flexible alkyl side chains, alicyclic monomers, incorporation of pendent trifluoromethyl or trifluoromethoxy groups, noncoplanar biphenylene moieties, as well as flexible alkyl or aryl ether spacers have been used for the reduction of several types of polymer chain-chain interactions, chain packing and charge transfer electronic polarization interactions and thus to enhance the solubility and lower the phase transition temperatures. Another method is via copolymerization to synthesize copolymers to improve the processability. These copolymers can be synthesized from various aromatic monomers containing anhydride, carboxylic acid, and aromatic diamine by condensation. Polyimides may also be conveniently prepared by the reaction of a diisocyanate and a dianhydride. Other methods for synthesis of

polyimides are imide exchange, mitsunobu reaction, coupling by using organometals and etc.

Because of the outstanding excellent electrical and mechanical properties, high thermal and chemical stability, good solvent resistance, low dielectric constants and dimensional stability, polyimides are already used for many important industrial applications under extreme temperature conditions such as films, fibers, foams, membranes, binders, varnishes, plastics, matrix resins in high-temperature composites, glues, adhesives and injection molding products. Also aromatic polyimides have long been recognized as attractive for applications in the electronic industries, wire and cable insulation, electrical component seal assemblies and components for nuclear power plants, military aircraft and the space shuttle, flexible circuits, semiconductor pads, microprocessor chip carriers, coil insulation, magnetic wire insulation and solar arrays. Shundrina *et al* (11) prepared new highly fluorinated aromatic polyimides based on hexafluoro-2,4-toluenediamine and commercially available dianhydrides (6FDA and ODPA) were synthesized by one-pot high temperature polycondensation in benzoic acid melt.

## 1.7 New Challenges and Opportunities

The main difficulty in the preparation of polyetherimide is due to control of the stoichiometric ratio of the reactants during the melt polymerization technique process. The relatively high temperatures used in the melt polymerization reaction joint to the different volatilities of monomers (anhydrides, amines and chain termination agent) make the control of mixture stoichiometry very complicated. The ability of these polymers to embed different type and amount of organic and inorganic modifying agent opens new horizons towards the design of developed block copolymers with challenging desired features that can satisfy the increasingly needs of the market. Challenging performance in poly ether-block-amides polymers is achievable through molecular design of new monomers or blending of different polymers and/or creation of copolymers. There is lot of interest to make high performance nanocomposites using these polymers by mixing with nanofillers. Research is also progressing to prepare these polymers form bio based materials.

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