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# FOCUS ON POLYIMIDES

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# INTRODUCTION

Polyimides (PIs) occupy a particular place in commercial plastics because of their ability to tolerate and function in extremely high temperatures. They are also well-known for other beneficial properties including insulating capability, chemical resistance, and excellent mechanical attributes. Once the first aromatic polyimides were created, a multiplicity of variations arose with an equally diverse range of applications. This was partly driven by need but also by experimentation and chemical exploration. These high performing polymer resins now are in demand more than ever to meet the most difficult and technological application challenges. From jet engine parts to medical tubing to fire retardant materials, new polyimides continue to surpass earlier performance limits. With their combination of properties and their ability to be tailored toward application specifics, polyimides offer some of best options for performance in high heat and other difficult environments.

# SYNTHESIS AND STRUCTURE

### Synthesis

Polyimides were first described in the mid-1950s [1]. These were linear chain type in nature and did not contain ring moieties. Soon after, synthesis methods were developed to incorporate aromatic ring structures into the polyimide chain creating the family of polymers that is ubiquitous today **(Fig. 1)** [2]. Polyimides are a highly diverse class of polymers, but they all possess the repeated $NR(C{=}O)_2$ imide linkage throughout their chain structure. Nearly all polyimides of industry importance today, however, are of the aromatic heterocyclic type.

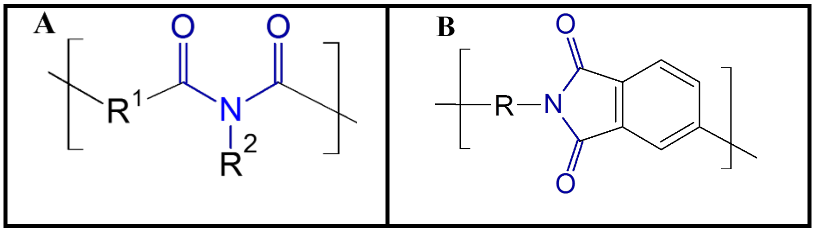


**Figure 1: General polyimide chain structures.** The imide linkage $NR(C{=}O)_2$ (shown in blue) for these representative examples of: **A)** a linear polyimide, and **B)** an aromatic heterocyclic polyimide. (R, $R^1$ = alkyl or aryl; $R^2$ = alkyl, aryl, or H).

There are several common methods used to synthesize polyimides for industry. One of the first and still a primary method uses dianhydrides and diamines. A specific example of this two-step method uses pyromellitic dianhydride (PMDA) and *p*-phenylenediamine (PPD) **(Fig. 2)** [3]. The first step produces a polyamic acid copolymer with the diamine. The copolymer is subsequently heated to ~250 °C (482 °F) dehydrating the acid to produce the PI**.** Dehydration can also be carried out using a solvent to create an azeotrope to remove the water or through a chemical dehydration. Removing water by heating, however, is the simplest technique and requires no other reagents to be added to the mixture.

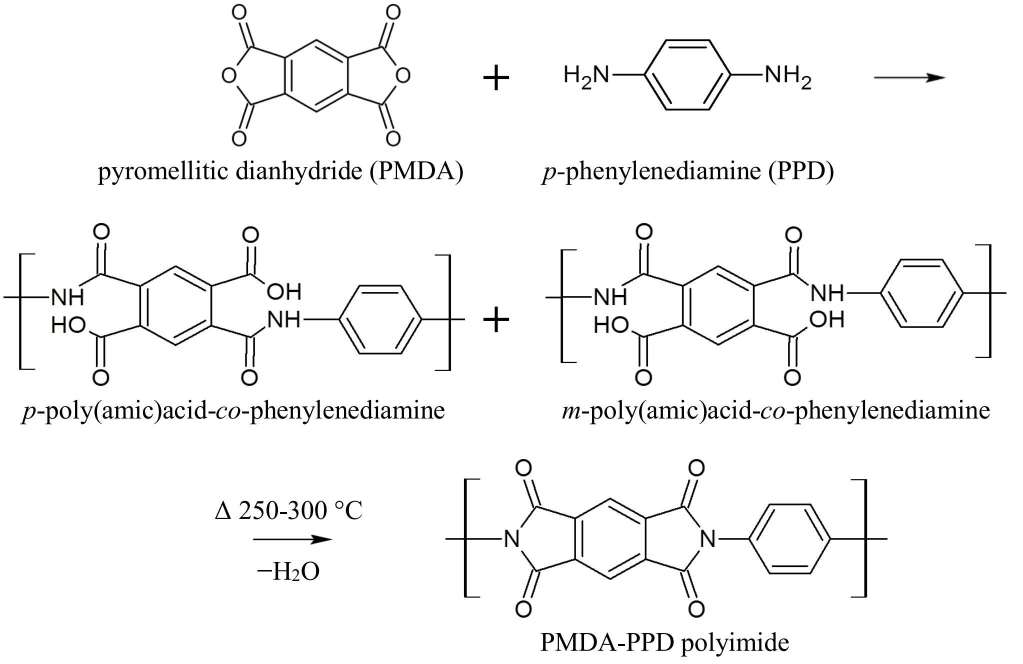


**Figure 2: Representative reaction scheme for synthesis of polyimides from dianhydrides and diamines.** A fundamental approach to polyimide synthesis uses pyromellitic dianhydride (PMDA) and *p*-phenylenediamine (PPD) for reactants. Step 1 forms a copolymer of polyamic acid and PPD. Step 2 dehydrates the copolymer by heating resulting in the polyimide.

Another means by which PIs are made uses diisocyanates and dianhydrides [4]. In this method, the diisocyanate replaces the diamine to provide the imide nitrogen. This method also requires heating to 250 °C (482 °F) because of the poor reactivity of the diisocyanates towards the dianhydrides. A common example of the diisocyanate route uses 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (4,4′-BTDA) and 4,4′-diphenyl methane diisocyanate (MDI) **(Fig. 3)**. Catalysts such as alkali metal fluorides or alkali metal methoxides can be used to speed this one-step reaction [5, 6]. Alternatively, certain solvents may be used (depending on the dianhydrides) such as dimethylformamide (DMF), and the reaction is then heated to ~210 °C (410 °F) under vacuum. The diisocyanate route has been used commercially in particular for the production of fibers and other non-woven materials [7].

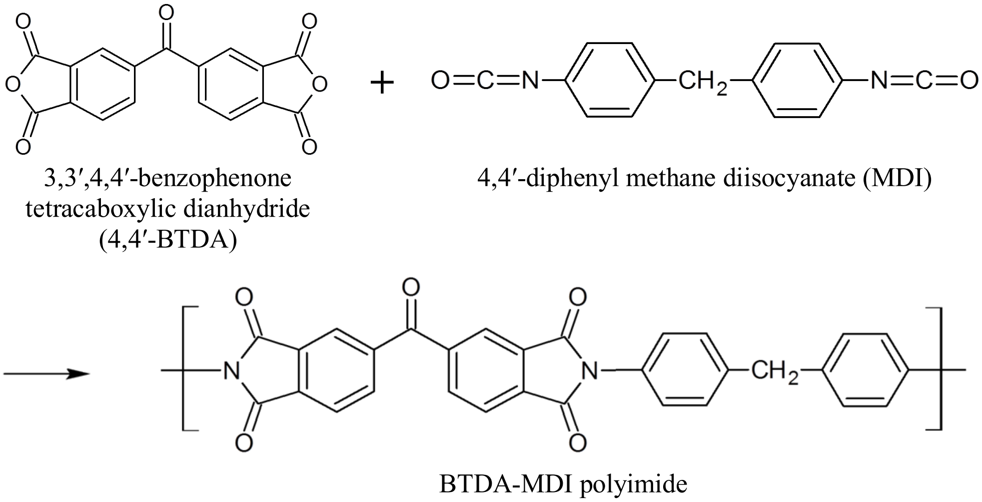


**Figure 3: Representative reaction scheme for synthesis of polyimides from dianhydrides and diisocyanates.** Polyimide synthesis may also proceed via a diisocyanate route. One common industry method uses the monomers 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (4,4′-BTDA) and 4,4′-diphenyl methane diisocyanate (MDI). The diisocyanate-dianhydride route is a one-step reaction, but solvents and catalysts (not shown) may also be used to speed the reaction.

A third primary polyimide synthesis uses an aqueous route [8]. This method uses dianhydrides and diamines with water as the solvent and proceeds via carboxylic salt and amine salt precursors. The first step hydrolyzes the dianhydride to a carboxylic acid under reflux with water. The acid is then neutralized with the diamine resulting in a precipitate. This initial product is then dried and heated to 180 – 220 °C (356 – 428 °F) to dehydrate it producing the polyimide in a manner similar as the first method described earlier. Example dianhydrides and diamine monomers for aqueous polyimide synthesis include 4,4′-bisphenol A dianhydride (BPADA) and *m*–toluenediamine (TDA) (**Fig. 4**). This method has been used to produce both thermoset and thermoplastic type commercial polyimides [9, 10].

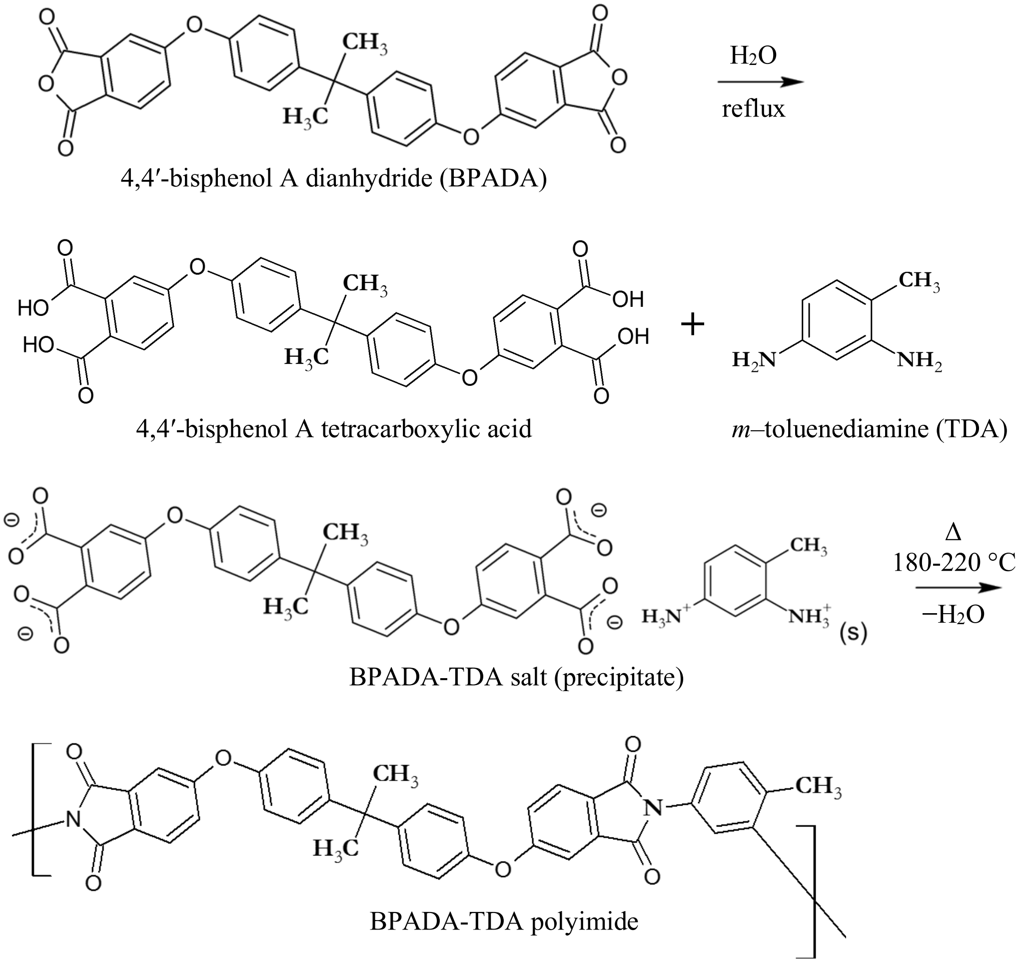


**Figure 4: Representative reaction scheme for synthesis of polyimides via an aqueous medium.** With water as the solvent, 4,4′-bisphenol A dianhydride (BPADA) is hydrolyzed under reflux to produce a carboxylic acid. The acid is then neutralized with a diamine such as *m*–toluenediamine (TDA) producing a precipitate which is dried and heated to create the polyimide.

## Structure

A key feature of polyimides is their unique chain interactions stemming from their repeated imide moieties. Polyimides, especially aromatic heterocyclic ones, benefit from special inter- and intra-chain interactions. The nitrogen atoms of the imide moieties possess greater electron density than the carbonyl (C=O) groups. The electron withdrawing power of the carbonyl oxygen draws the electron density away from the nitrogen. This shift in electron density also affects neighboring atoms beyond the nitrogen. These “donor” and “acceptor” arrangements are termed *charge transfer complexes* (CTCs) [11, 12]. Whenever there are alternating donor-acceptor segments within a polymer such as polyimides, CTCs can be formed. The CTCs that occur *within* the polymer chain are largely responsible for the stiffness of polyimides **(Fig. 5A)**. These donor and acceptor interactions also occur *between* adjacent polymer chains **(Fig. 5B)**. Adding to the CTCs, stacking interactions of $C_6$ aromatic (benzene-type) rings stemming from positive and negative faced quadrupole moments further attract neighboring chains. These forces hold the PI chains very tightly together allowing minimal chain movement or slippage. Collectively, these charge transfer and stacking interactions produce a potent cumulative effect on aromatic heterocyclic PIs. These forces result in a polymer that is extremely strong, stiff, and has a very high glass transition ($T_g$) and melting temperature ($T_m$) – the hallmark features of polyimides.

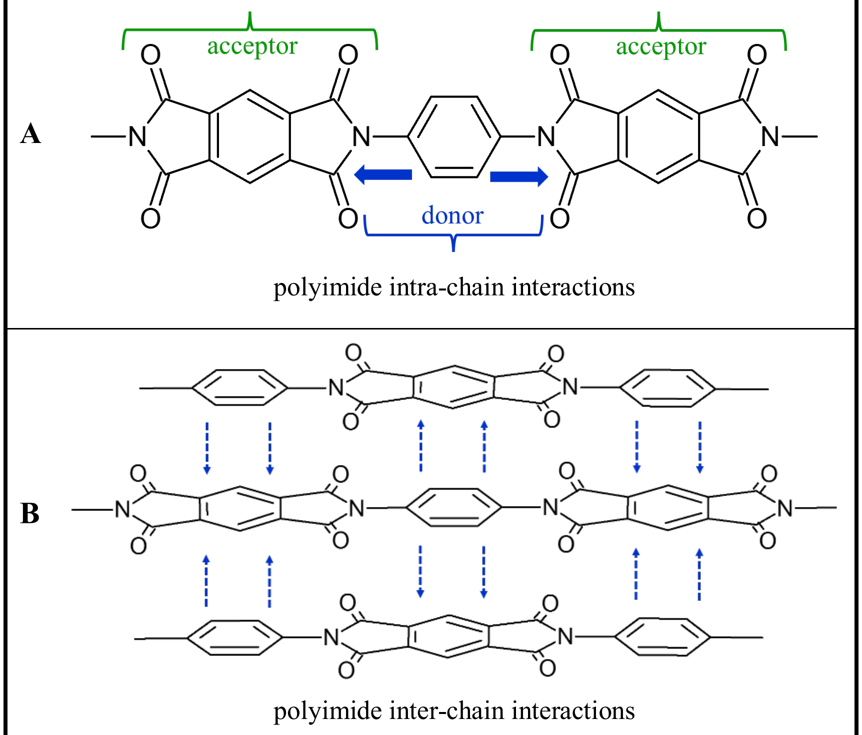
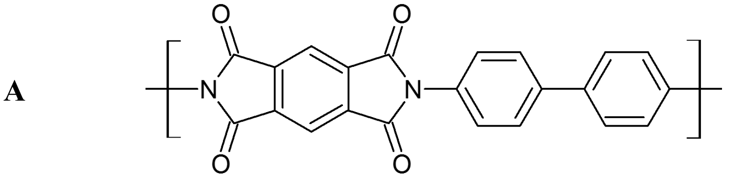


**Figure 5: Polyimide inter- and intra-chain interactions.** Donor-acceptor arrangements occur both **A)** within and **B)** between polyimide chains creating charge transfer complexes (CTCs). These attractive forces have a significant cumulative effect and are largely responsible for the characteristic high temperature performance of polyimides.

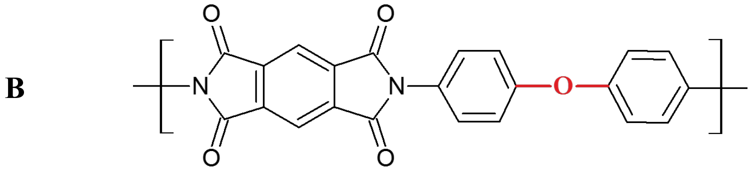
## PROCESSING

Polyimides can be grouped into two types: thermoset and thermoplastic. Thermoplastics can be re-melted after they have hardened; thermoset materials cannot. Within the polyimide family, simple aromatic polyimides are among the strongest of these polymers and typically fall into the thermoset group **(Fig. 6A)**. This is due to the strong CTC attractions and ring moiety stacking interactions which greatly constrain the polymer chains from movement. These strong interactions, consequently, frequently render simple aromatic PIs not processable.

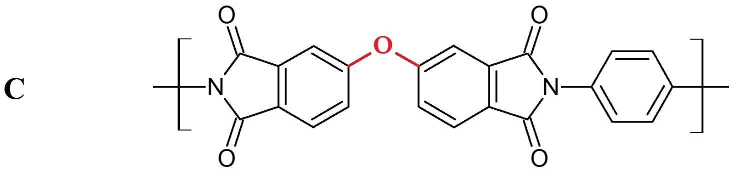
To address the limited processability of PIs, monomers with flexible moieties or linkers can be introduced into the polymer chain during synthesis. Using the isocyanate synthetic route, for example, 4,4′-diphenyl methane diisocyanate (MDI) can be used to introduce a flexible aliphatic methylene ($-CH_2-$) linker into the polymer chain **(Fig. 3)**. Similarly, an amine monomer such 4,4′-oxydianiline can be used to introduce a flexible ether (R–O–R) linkage into PI chain (R = alkyl) **(Fig. 6B)** [3]. A flexible ether linkage can also be introduced into the polymer via dianhydrides like 4,4′-oxydiphthalic anhydride (4,4′-ODPA) **(Fig. 6C)** [3]. Polyimides with an ether in the chain are thus termed polyetherimides (PEIs). Similarly, trimellitic anhydride (TMA) can be used to introduce an *amide* (N–C=O) linkage into the chain **(Fig. 6D)** [13]. Polyimides with amide and imide linkages are called polyamide-imides (PAIs; also known as nylons). Although not imparting as much chain flexibility as the ether and amide moieties, anhydride monomers like 3,3′4,4′-benzophenone tetracarboxylic dianhydride (4,4′-BTDA) can be used to introduce a ketone (RCOR′) linkage **(Fig. 3).** Flexible linkages increase the overall flexibility of the polymer chain and mitigate some of the effects of the inter-chain attractive forces. With the increased freedom of movement of the polymer chain, the $T_g$ and $T_m$ are reduced bringing the polymer into the melt processable realm. The inclusion of flexible monomers also increases solubility of the PIs further contributing to their processability and availability of processing methods **(Table 1)** [14]. Though it is common to refer to PAIs, PEIs, and PIs generically or collectively merely as PIs, most commercial thermoplastic polyimides are PEIs [13].



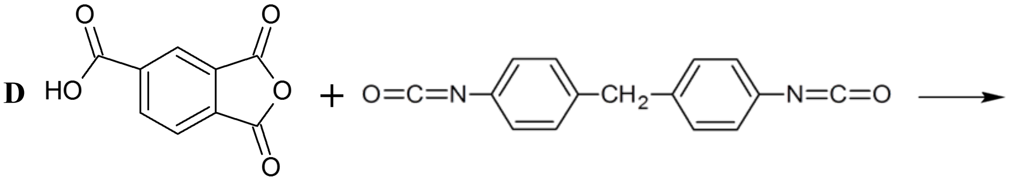
rigid-type polyimide



ether linkage from the diamine 4,4′-oxydianiline
(polyetherimide, PEI)

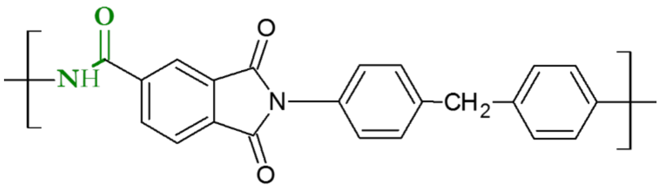


ether linkage from the dianhydride
4,4′-oxydiphthalic anhydride (polyetherimide, PEI)



trimellitic anhydride (TMA)

4,4′-diphenyl methane diisocyanate (MDI)



amide linkage from trimellitic acid (polyamide-imide, PAI)

**Figure 6: Polyimide chain modifications to affect flexibility and processability. A)** Rigid-type polyimides with no flexible linker are the most difficult to process and are more likely to be a thermoset rather than a thermoplastic. The diamine **(B)** and the dianhydride **(C)** can both be used to introduce flexible either linkages (red) into the polyimide creating a polyetherimide (PEI). **D)** An amide linkage (green) can be incorporated to improve chain flexibility via monomers such as trimellitic anhydride producing a polyamide-imide (PAI).

| Processing Method | Suitability |
|---|---|
| Injection molding | Yes |
| Extrusion | Yes |
| Blow molding | Yes |
| Compression molding | Yes |
| Impregnation and coating | Yes |

**Table 1: Polyimide polymer family processing suitability.** Polyimides as a group can be processed by several methodologies but require a variety of solvents. Note that simple aromatic heterocyclic polyimides are the most difficult to process, while PAIs and PEIs are amenable to more processing techniques.

## POLYIMIDE PROPERTIES

### PHYSICAL

While polyimides can be a diverse family of polymers, most of the industry-important ones display similar physical properties **(Table 2)**. Polyimides are characteristically very heat resistant and resistant to burning. These features make them especially preferred in applications where exposure to heat is a significant concern. For medical purposes, polyimides can be sterilized by multiple methods including ethylene oxide (ETO), gamma irradiation, and e-beam. Despite their comparatively higher water absorption, polyimides can even be sterilized by autoclave with minimal concern regarding deformation, loss of mechanical properties, or crazing [13]. Polyimides are also being explored for expansion into the opto-electrical sensor and optical components sectors [15-17]. By varying the monomers used to produce the PI, the fractional free volume of the polymer material can be altered causing changes in the material's refractive index. These manipulations can be used to tailor the polyimides for specific optical and opto-electrical applications. Thus, aside from their inherently beneficial physical properties, polyimides are also very adaptable to optimize physical properties for application effectiveness.

| Property | ASTM | Value (natural polymer) |
|---|---|---|
| Appearance | – | **amber / yellow / gold** |
| Density (g/cm$^3$) | D792 | **1.3 – 1.7** |
| Water Absorption (50% rh; %) | D570 /<br>ISO 62-1 | **0.4 – 4.1** |
| Refraction Index | D542 | **1.2 – 1.9** |
| Limiting Oxygen Index (LOI) 3.2 mm thickness | D2863 | **35-53** |
| Biocompatible | USP Class VI | **Yes** |
| Chemical Resistance | – | **very good to excellent** |
| Sterilization | – | **autoclave, ETO, gamma, e-beam** |

**Table 2: Polyimide family typical physical properties.** Polyimides show excellent heat resistance and will normally not burn in air. They also are biocompatible and tolerate multiple sterilization protocols. (Properties shown are ranges for the PI family; they are not all-inclusive and do not reference a single material).

## MECHANICAL

Polyimides offer some of the top performance characteristics of almost any thermoset or thermoplastic polymers. These high molecular weight polymers made from stiff, rigid molecules exhibit excellent mechanical properties **(Table 3)**. These properties are typically retained through a much wider range of temperatures than most polymer plastics due to their strong intra- and inter-chain interactions. For this reason, polyimides have a high presence in the aerospace industry where material strength and heat tolerance are frequently required concomitantly. PIs' temperature stability also supports their excellent long-term continuous use and creep resistance. PI products typically possess very good to excellent lubricity and wear characteristics allowing them to be used in applications where repeated rubbing or sliding contact is necessary such as bearings, bushings, and washers. Polyimide tubing provides high column strength, and its lubricious surface supports better pushability for medical device tubing that must be inserted within the body [13]. Polyimide mechanical benefits also extend to uses as stress buffers. The mechanical properties of polyimides also allow them to be used in place of some metals and glass giving them even greater versatility.

| Property | ASTM | Value (natural polymer) |
|---|---|---|
| Tensile Strength (MPa) | D638 | **38 – 120** |
| Elongation at Break (%) | D638 | **1.5 – 90** |
| Modulus of Elasticity (GPa) | D638 | **2.3 – 4.7** |
| Flexural Modulus (GPa) | D790 | **1.4 – 5.3** |
| Flexural Strength (MPa) | ISO 178 / D790 | **42 – 170** |
| Hardness (Rockwell) | D785 | **35 – 120** |
| Impact Strength (23 °C) | ISO 180 | |
| notched (J/cm) | | **0.4 – 1.4** |
| unnotched (J/cm$^2$) | | **1.8 to no break** |
| Coefficient of Friction | D1894 | **0.17 – 0.77** |

**Table 3: Typical polyimide family mechanical properties.** Polyimides possess excellent mechanical properties. These properties hold true over unusually wide temperature ranges making them preferred materials for dynamic environments. (Properties shown are ranges for the PI family; they are not all-inclusive and do not reference a single material).

## THERMAL

The thermal properties of polyimides are perhaps the best recognized for this class of polymers **(Table 4)**. The strong polymer chain interactions give polyimides very high glass transition temperatures, many extending beyond 300 °C (572 °F) and some as high as 400 °C (752 °F). Such high $T_g$s indicate that the polymer chains at the molecular level are highly constrained from movement giving polyimides their exceptional thermal stability at both low and high temperatures. This attribute means that polyimides are often the best choice for applications in automotive and aerospace industries and can routinely be used at temperatures from -270 °C (-454 °F) to upwards of 370 °C (698 °F). These high glass transition temperatures mean that most polyimides will decompose (breaking atom-atom bonds) before they will melt further emphasizing the difficulty in processing them. Almost all of the commercially important polyimides are UL 94 V-0 flammability rated meaning that should they burn, they quickly extinguish themselves – another reason for their widespread use in automotive and aerospace sectors. Thus the unique chemical nature, especially of aromatic heterocyclic polyimides, allows them to be used in applications where many other polymer materials cannot.

| Property | Method | Value (natural polymer) |
|---|---|---|
| Thermal Conductivity (W/m-K) | D433 / ISO 22007-4 / C-177 | **0.12 – 0.73** |
| Maximum Service Temperature (°C) | UL 746 | **500** |
| Minimum Service Temperature (°C) | UL 746 | **-270** |
| Melting Point (°C) | D4591 / D3418/ ISO 12086 / DOW Method | *decomposition* |
| Glass Transition Temperature (°C) | E1356 (DSC) or E1545 (mechanical) | **150 – 500** |
| Decomposition Temperature (°C) | E1131 | **200 – 550** |
| Coefficient of Thermal Expansion, Linear (µm/m-°C) | D696 | **40 – 58** |
| Flammability Rating (UL 94) | D2863 | **V-0** |

**Table 4: Polyimide family thermal properties.** Polyimides are capable of temperature endurance at some of the highest (and lowest) temperature extremes. This feature in particular is highly preferred for applications that require mechanical performance in these environments. Polyimides are also difficult to burn and self-extinguishing should they ignite. (Properties shown are ranges for the PI family; they are not all-inclusive and do not reference a single material).

## ELECTRICAL

The dielectric properties of polyimides are of great interest in industry because of their use as film coatings for electrical components **(Table 5)**. Things such as circuit boards, which require insulating coatings to maintain discrete signal paths, use polyimides not only for their low dielectric constant but also for their heat resistance where electrical parts could become hot during use. Polyimides are also frequently used to coat (insulate) electric lead wires. Conductivity of polyimides can be influenced by the type of monomers used to make them as well as incorporating certain side chain moieties. Similar to many of the other properties of polyimides, their dielectric attributes generally are very consistent over broad temperature spans up to those approaching their $T_g$. Multiple steam sterilization cycles and gamma radiation exposure have only minimal effects upon electrical properties of the top performing polyimides [13]. While polyimide dielectric aspects are somewhat inferior to perfluorinated fluoropolymers such as PTFE or FEP, their consistency through such large temperature ranges gives them a significant advantage over most competing materials.

| Property | ASTM | Value (natural polymer) |
|---|---|---|
| Dielectric Constant (1 MHz) | D150 | **3.1 – 6.0** |
| Dielectric Strength (kV/mm) | D149 /<br>IEC 60243-1 | **118 – 280** |
| Volume Resistivity (Ω–cm) | D257 /<br>IEC 60096 | **$10^{12-18}$** |

**Table 5: Typical electrical properties for the polyimide family.** Polyimides possess very good dielectric properties which are retained throughout wide temperature spans. This trait is particularly beneficial for electrical applications that may become hot during normal use. (Properties shown are ranges for the PI family; they are not all-inclusive and do not reference a single material).

## FINISHING

While polyimides are perhaps best known as surface coatings, films, or tape, finished goods can also be produced from polyimides. Larger shaped parts can be produced via compression molding while smaller ones can be made using presses. Plates, rods, and tubing can also be made from polyimides. These goods can be machined with the typical tools used to work metals such as brass. Fully hardened metal tools are also recommended. The thermal stability of polyimides allows them to be machined to very fine tolerances which would otherwise be affected as the part becomes hot from machining. A point of consideration, however, is the possibility of moisture absorption. While this is low for most polyimides, moisture absorption can affect final dimensions. Therefore, it is often recommended to keep machined polyimide parts dry until ready to install. Where feasible, this is often accomplished by sealing the part in a bag along with a desiccant. With the wide range of polyimides available, resin manufacturers usually offer guidance for finishing polyimide parts made from their resin.

## APPLICATIONS

Since the commercialization of polyimides in the 1950s, their applications have expanded into almost every industry. Still, the applications for polyimides are not exhausted. New innovative chemical modifications and syntheses such as microwave synthesis have opened new avenues for polyimide use. Flexible electronics and biosensors are just some of the more recent developments [18, 19]. Polyimides are also being highly utilized in other sensor technologies and for polyimide-modified electrodes [20]. By far, however, polyimides are most abundantly used as coatings for insulated wire and fiber optics. Many are easily applied as a varnish and then simply heated to form the final polyimide onto the wire. Polyimides are highly prevalent as coatings and films for a large segment of the electronics industry. From a medical perspective and aside from tubing, polyimides present attractive options for encapsulation of implantable devices such as pacemakers, muscular stimulators, and cochlear implants [21]. Polyimides are also amenable for use as a structural adhesive and in composite forming. In this application, a polyimide layer or coating can add mechanical strength and temperature tolerance. Polyimides are being explored for use as gas separation membranes [22]. These membranes present perm-selectivity for gases such as carbon dioxide, methane, oxygen, and nitrogen [23, 24]. Polyimide fibers have been commercialized for use in the textile industry for water-proofing, fire resistant clothing, and filtration. While it is not possible to give adequate discussion to all of the applications of polyimides, those presented here occupy some of the most important industry and innovation applications.

| Application or Industry | Key Benefits |
|---|---|
| Aerospace and automotive | UL 94 V-0 flammability rating, low smoke; excellent wear characteristics for polyimide parts; very high heat limit |
| Nuclear | Radiation resistance |
| Exterior (outdoors), outer space | UV resistance coating to protect or increase product longevity |
| Electrical, electronics | Dielectric properties, insulated wire; structural support for circuit boards |
| Medical | Biocompatibility; sterilizable by multiple methods |
| Fiber optics | Abrasion and heat resistant coating |

**Table 6: Survey of polyimide applications.** Polyimide mechanical, dielectric, and radiation performance means that a polyimide can likely be found to suit almost any application. Polyimides' biocompatibility is particularly beneficial in the medical industry for their ability to tolerate multiple sterilization cycles.

## SUMMARY

The polyimide family represents some of the highest temperature rated industrial polymers known **(Table 7)**. Polyimide chain interactions through CTCs result in a polymer that is both stiff and extremely strong. These chain interactions allow polyimides to maintain properties such as dielectric and mechanical performance through extremely broad temperature ranges. These same interactions contribute to the excellent wear characteristics of polyimide parts. The features that make polyimides so preferred in environmental extremes can also be a detriment as they can render the polymer no longer processable. To address processability and material properties directly, diverse monomers can be used to introduce flexible linkers such as ethers (R-O-R) and amides (N–C=O) into the polymer chain. Through clever synthesis techniques, polyimides can be processed more readily expanding their application possibilities. Polyimide products now include film, coatings, insulated wire, tubing, machined parts, flexible sensors, and much more as new inventions continue to come forth.

| Advantages / Benefits (+) | Limitations (–) |
|---|---|
| • Very high working temperatures<br>• Retention of properties throughout large temperature range<br>• Thermal stability<br>• Very good chemical resistance<br>• Light weight<br>• Excellent UV resistance | • Many not melt processable; requires high temperatures, solvents<br>• Cost<br>• Chemical sensitivity to some acids and bases and hydrolysis<br>• Cannot be used above $T_g$ without post-annealing |

**Table 7: Polyimide advantages and limitations.** Polyimides are unique for their ability to function in very high temperatures. This feature can be limiting to their processability which can add to manufacturing cost.

## ABOUT ZEUS

Zeus is the world’s leader in polymer extrusion technologies. For over 50 years, Zeus has been serving the medical, aerospace, energy exploration, automotive, and fiber optics industries. Headquartered in Orangeburg, South Carolina, Zeus employs approximately 1,700 people worldwide and operates multiple facilities in North America and internationally. You can find us at www.zeusinc.com.

## CONTACT US

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