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Subchapter 10.1

Research and development of high-performance polymeric materials including polyimides and fluoro-polyimides and their industrialized products

Summary

In Subchapter 10.1, some details of relevant historical background and research and technology development and industrialization (RTDI) time-line of several high-performance polymeric materials including polyimides and fluoro-polyimides and their industrialized products are provided and discussed. In addition, it contains many relevant and interesting sub-topics highlighting several technical areas including the selection of appropriate monomers and chemicals, molecular design of chemical structures to be synthesized, followed by synthesis, and characterization by means of modern analytical techniques and reliability-testing methodologies, which encompass thermal, electrical, corrosion, mechanical (inclusive of fracture mechanics, tribological properties, etc.), its ancillary manufacturing/fabrication processing methodologies, and its commercial/industrial applications, etc. which are included in this Subchapter 10.1.

Keywords

High-performance polymers, thermoset resins, polyimides, research, technology development and industrialization (RTDI), commercial products introduction, historical polyimide market, literature and patents survey on worldwide polyimide R&D activities, polyimides (PI), poly(amic acid) (PAA), thermoplastic polyimides, thermoset polyimides, polyamides (PA), aromatic polyamides, aromatic polyimides, poly (amide-imides) (PAI), fluorinated polyimides (6F-PI), fluorinated polyamides (6F-PA), fluorinated copolyamides (6F-CoPA), fluorinated poly(amide-imides) (6F-PAI), fluorinated copoly(amide-imides) (6F-CoPAI), SIXEF polyimides, SIXEF copolyimides, fluoro-poly(ether imide) (6F-PEI), fluoro-copoly(ether imide) (6F-CoPEI), molecular designing of polyimides and co-polyimides, CERAMER (cearmic-polymer) nanocomposites, METAMER (metals-polymers) nanocomposites, METACER (metals-ceramics) nanohybrides, fluoro-poly(ether imide)/MMT Clay nanocomposites, Ceram-Imide (polyimide-nanostructured particle) nanocomposites technology, synthesis of polyimides, monomers for polyimides, 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydrides (6FDA), 1,2,4,5-benzenetetracarboxylic anhydride, that is, pyromellitic dianhydride (PMDA), 3,3,4,4-biphenyltetracarboxylic dianhydride (BPDA), 3,3,4,4-benzophenonetetracarboxylic dianhydride (BTDA), 3,3,4,4-oxydiphthalic anhydride (ODPA), 2,2-bis(3-amino phenyl) hexafluoropropane (3,3-6F-Diamine), 2,2-(3-amino phenyl)(4-amino phenyl) hexafluoropropane (3,4-6F-Diamine), 2,2-bis(4-amino phenyl) hexafluoropropane (4,4-6F-Diamine), 2,2-[bis(3-amino-4,5′dimethyl)phenyl]hexafluoropropane (3,3′-Diamino-4,5-Dimethyl 6F-Diamine), 2, 2′-bis [4,-(4′-aminophenoxy) phenyl] hexafluarapane (BDAF), 4,4′-bis(3-aminophenoxy) diphenyl sulfone (m-SED), 4,4′-bis(4-aminophenoxy)diphenyl sulfone (p-SED), 4,4′-bis(4-aminophenoxy)diphenyl propane (BPADE), 1,2′-bis(4-aminophenoxy) benzene (o-BAPOB), molecular designing of polyimides and co-polyimides, polyimides by polycondensation polymerization, chemical mechanism of polyimide polymerization reaction, mechanism of chemical imidization reaction, processing of polyimides, wet lay-up and autoclave molding, filament winding, compression molding, pultrusion, film fabrication methods, resin transfer molding (RTM), characterization techniques, elemental analysis, viscosity measurement, rheology, FT-IR, GPC/SEC, density of polymers, solubility of polymer films, hydrolytic stability, mechanical properties, thermal properties, DSC, fox equation, estimation of glass transition (Tg) of copolymers, fox-vora equation for calculation of molar concentration of monomers for linear, random and block copolymers, TMA, DMA, CTE, thermal stability, TGA, thermal degradation kinetics, thermo-oxidative stability (TOS), electrical properties, low-dielectric polyimides, Lorentz-Lorenz's Theory, Vogel's theory, vora-wang Equations, DEA, estimation of dielectric constant, XRD, WAXD, SEM, EDX, surface properties, applications of polyimides, photosensitive polyimides, separation membranes, SIPN imide blends, semi-interpenetrating polymer network (sipn), galvanic corrosion, lightning strike protection polymers.

Introduction

Historical Background of Research and Development of High-Performance Polymeric Materials including Polyimides and Fluoro-polyimides and their Industrialized Products.

After World War II, rapid expansion of the aerospace industry created a need for new materials for the new high technology, which it generated. Many of these requirements could not be achieved with metallic and existing plastic materials. There was a need for newer materials which would be lightweight, oxidatively and thermally stable, have good and mechanical properties and chemical and moisture resistance and could operate in space environments.

During the past 60 years, the world has witnessed a remarkable development in structural plastics material technologies; many interesting new polymers were

discovered, which had unusually stable mechanical properties at high temperatures. Relatively few achieved commercial success, however. The successful materials were those that could overcome the challenges of manufacturing cost and the inherent difficulties to be fabricated into useful forms in large scale. Since the last 4 decades, newer nonmetallic materials such as ceramics and polymer matrix composites are replacing metals in a wide variety of industrial, aerospace, and consumer applications, ranging from highly specialized spacecraft structural components, cryogenic rocket engines, cutting tools to tennis rackets [1–7].

High-performance polymeric materials

In Aerospace applications, highly specialized spacecraft structural components, cryogenic rocket engines parts, military aircraft components, etc. are made up of light weight, mechanically stronger, and high-temperature-stable composites. These composites are made from special graphite, carbon, glass, or ceramic fiber matrix prepregs impregnated with the advanced high-performance thermoset and/or thermoplastic polymeric materials.

Such advanced high-performance polymeric materials, resin alloys, and hybrid systems possess long-term "service temperature" capabilities in the range from room temperature (RT) to >150°C. The service temperature is based upon the "Thermal Index" rating assigned by the Underwriters' Laboratories (UL) of the United States [8]. The UL relative Thermal Index is an indication of the thermal stability of a polymer. UL addresses this phenomenon with the UL Temperature Index. The temperature indices are used by UL as a guideline when they compare hot spots on devices and appliances made from these materials. Higher "Thermal Index" rating for a particular polymeric material means that it would continuously provide a long term thermal stability in terms of good mechanical strength, good environmental stability, dimensional stability, solvent resistance, and electrical properties at the elevated temperature for which it is rated. UL defines the end of service life as the aging time required to produce a 50% drop in the property compared with the initial value [8].

A typical list of high service temperature polymers (thermosets and thermoplastics) including linear, and heterocyclic types that are commercially used in current electronics, aerospace, automotive, electrical industries is given below [1–3,5–7,9–16]:

- epoxy
- polyarylate (PA)
- liquid crystal polymers (LCP)
- polycarbonate (PC)
- poly(*p*-phenylene sulfide) (PPS)
- polyethersulfone (PS)
- polyketones
- poly(ether ether ketone) (PEK or PEEK)
- polyimides (PI)
- fluoro-polyimide (6F-PI)
- bismaleimide (BMI)
- PMR-15
- poly(amide-imide) (PAI)
- polyamide
- poly(ether imide) (PEI)
- polyphenylquinoxaline (PPQ)
- polybenzoxazole (PBO)
- polybenzimidazole (PBI)
- and their copolymers
- etc.

Some of these polymers have mechanical properties typically required for high performance composites for aerospace applications (Table 10.1.1).

It is well understood that not every industry sector uses high-performance polymers for product development for their specific industry related applications. There are various factors which affect the selection of a particular polymer for a particular application or product development. These factors typically include, material selection based on final product use, product life time, polymer's properties, processibility, and of course, the cost (a main factor for most industries) of making that product using that particular polymer.

Table 10.1.2 shows the relative importance of factors that a product development engineer would take into consideration according to his/her final industry products applications and end-uses [3–7,9,11].

Thermoset resins

For aerospace composites applications, thermoset resins have shown some advantages over the thermoplastic counterpart, such as low initial melt viscosity, which provide uniform wetting, tack, and ease of handling. In addition, their good solvent resistance, good interfacial adhesion, good mechanical performance and durability and good damage tolerance also have ensured their use in the aerospace industries for over 50 years. However, it was also found that these resins had some disadvantages. For example, the application of epoxies required complex formulations, and the resins provided poor prepregs stability and required a long processing cycle which was economically costly.

In the case of BMI [16] and PMR-15 type resin [16] chemistry, the composites showed poor toughness and thermal cracking in endurance test, indicating questionable durability. However, extensive efforts were made in the development of processes for fabrication of aerospace

TABLE 10.1.1 Neat resin mechanical and fracture toughness properties of high-performance thermoplastics [1–3,5–7,9–16].

Polymer	Tensile properties @ 25°C					Fract. energy ($G_{I\ C}$)	
	Yield strength		Modulus		Strain to break		
	(Kpsi)	(MPa)	(Kpsi)	(GPa)	(%)	Lb/in^2	(kJ/m^2)
PEEK	14.5	(100)	450	(3.1)	> 40	> 23	(> 4)
PXM 8505	12.7	(88)	360	(2.5)	13	–	–
PPS	12.0	(83)	630	(4.3)	5	0.6–1.4	(0.1–0.2)
PAS-2	14.5	(100)	470	(3.2)	7.3	–	–
TORLON C	20.0	(138)	550	(3.8)	15	19.4	(3.4)
TORLON 696	13.0	(90)	400	(2.8)	30	20.0	(3.5)
ULTEM100	15.2	(105)	430	(3.0)	60	19.0	(3.3)
NR 150B2	16.0	(110)	605	(4.2)	6	13.7	(2.4)
Avimid K-III	14.8	(102)	546	(3.8)	14	11.0	(1.9)
LARC-TPI	17.3	(137)	540	(3.7)	4.8	10.0	(1.8)
$PISO_2$	09.1	(63)	719	(5.0)	1.3	8.0	(1.4)
P-1700	10.2	(70)	360	(2.5)	> 50	14.0	(2.5)
SIXEF-44[a]	13.8	(--)	405	(--)	7.8	–	–
Epoxy (3501-6)	12.0	(70)	620	(4.3)	1.2	19.4	(3.4)
BMI(HG89107)	–	–	450	(3.1)	7	19.4	(3.4)

[a] [6,11,14-16].

TABLE 10.1.2 Relative importance of factors affecting high-performance resin selection by the end-user [2,3,6,7,9,11–54].

Factor	Applications: Consumer/ Industrial	Electronics/ electrical	Aerospace	Automotive
Electrical	Low	High	Medium	Low
Environmental	High	High	High	Medium
Mechanical/ Durability	High	Medium	High	High
Processability	High	Medium	High	High
Thermal Stability	Medium	High	High	Medium
Price	High	Medium	Low	High

High Medium Low

structural components by the contractors of NASA and U. S. defense industries under Defense Advanced Research Projects Agency (DARPA) funded programs. Some of the most effective processes that came out of these development programs are now also used commercially, which has been discussed later.

Research and development trends in high-performance polymers

Since the early 1990s, there has been a definite worldwide trend toward the research and development (R&D) spending for the further development high-performance polymers, and extending such polymers' use to the electronics sector, which put forth large efforts in the application product development. This has led to the high use of performance polymers in the electronic industries increasing faster than in the aerospace and military hardware industry sector. However, due to specific favorable processing conditions, thermoplastic polymers took lead in R&D efforts over thermoset polymers.

The major trend in high performance polymer R&D efforts is illustrated in Fig. 10.1.1 [1−7,9,11−54].

Market survey showed that besides thermoset epoxies, condensation polymers having thermoplastic nature such as thermoplastic polyimide (TPI), liquid crystal polymers (LCP), polyetheretherketone (PEEK), polyetherimides (PEI), fluoropolyimide, had been used in the product development of very large scale integrated circuits, Micro-ball grid arrays packages, flex circuit substrates, etc. Of course, the development of high-temperature service applications continues to be funded by major US and foreign Government's defense industries.

Polymeric materials based on polyimide and related chemistry are also used in electrical, electronics and aerospace industries. The market has been driven by performance, and more recently by the life cycle of products, and ultimate cost considerations [6,7,9,11−54].

Polyimides

Ceramic, graphite, carbon, even glass fiber reinforced composites using polyimides as a matrix resin are increasingly being used in military engineering and aerospace applications because of their high strength-to-weight ratios and corrosion resistance. A variety of these polymers including polyimides, Fluoropolyimides, and their copolyimides, have been synthesized by NASA, DuPont, M&T Chemicals, Ciba Geigy, National Starch, Hoechst Celanese, Union Carbide, and others, as high performance materials, for example, as matrices for fiber reinforced composites, foam and fibers, electronics substrate films, packaging encapsulants, adhesives, and protective coatings [1,2,9−11,14−39].

Ongoing development of improved synthesis methods has yielded a new generation of thermosets and TPIs that offer broader processibility and enhanced physical properties. Some new high temperature polymers eliminated the tendency to brittleness and other limitations that were present in earlier products. While established market sectors continue to account for most of the volume, the newer polymers are making inroads in such fast-growing and exciting areas as microelectronics and aerospace [13].

One of the key advantages of polyimides in these markets is that they can be used in a range of −450°F (−230°C) up to 800°F (427°C), well beyond the capability of most organic plastics [2,11−13,15].

As mentioned earlier, polyimides constitute a very important class of advanced materials because of the combination of many unique chemical (good hydrolytic stability, chemical resistance, adhesion property), thermal (high stability to thermal oxidation and irradiation), mechanical (good planarization and processibility, low thermal expansion, high mechanical strength), and electrical properties (low dielectric constants, high breakdown voltage, low

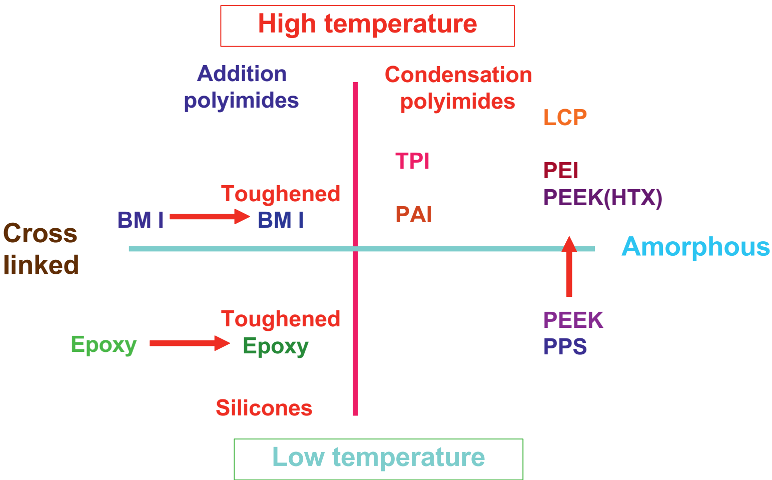


FIGURE 10.1.1 Trends in high-performance polymer development [1−7,9,11−54].

losses over a wide range of frequency) [1−3,11−16]. Polyimides can be used for applications where bismaleimides (BMIs) are no longer useful thermally.

Through the last 70 years of extensive R&D, numerous polyimides and monomers for preparing polyimides have been identified and synthesized and introduced in the market. Over 60 polyimide products, such as, Kapton [40], and Pyralin 3002 [41], Vespel [42], NR-150 [43], PMR-15, [44], LARC-TPI [10], ULTEM [45−47], Polyimide-2080 [48,49], M&T-2065 [50], SOLIMIDE-Foam [21], XU-218 [24], SIXEF-PI [25−38], THERMID-IP and THERMID-AF [23,51], Torlon [3,5,20,54], etc. to name a just few, have been successfully commercialized (Table 10.1.3) and today play a very important role in devices for aerospace, defense, and the electronics industry. However, polyimides also have some inherent problems that limit their further development. These include high monomer cost, toxicity and complex processing techniques. The synthesis of appropriate aromatic dianhydrides and diamines with suitable functional structures is not trivial, and their costs are prohibitive, resulting in the higher costs of polyimides, and a greater hurdle to commercialize novel polymers. Additionally, some of the aromatic diamines and aromatic dianhydrides are suspect

TABLE 10.1.3 Some of the commercial polyimides and their manufacturers.

Type	Company	Trade Name	References
Condensation	E.I. Du Pont de Nemours	Kapton Film	[2,16,40−44,51−67]
		Vespel	[16,42]
		Pyralin	[16,41]
		Pyre−M.L.	[16]
		Avimid-K	[3−5,9,10,16,20]
	ICI/UBE Industries Ltd.	Upilex	[68,69]
	Monsanto	Skybond 700 Series	[4,9]
	M&T Chemicals	M&T-PSI	[50,70−80]
	American Cyanamid	FM and BR Series	[2,16]
	Hoechst Celanese Corp.	SIXEF	[6,7,25−38,81−120]
	Rogers Corp	Durimide	[16,121]
Thermoplastics	E.I. Du Pont de Nemours	NR-150	[16,122]
	General Electric Co.	Ultem	[46,47]
		Silicon polyimides	[16,47]
	Amoco[a] (now Solvay, USA)	Torlone	[3,5,20,54]
	Ciba-Geigy[b]	XU-218	[16,24,45]
	Upjohn	Polyimide 8020	[16,48,49]
	Mitsui Toastsu Chemicals, Inc.	REGULUS, AURUM	[16,123,124]
	Imi-Tech/National Harvester	Solimide Foam	[21,79,80,125−128]
	Ethyl Corp.	EYMYD	[129−131]
	Chemiefaser Lenzing, AG	P84 Polyimide	[132]
	Kanagafuchi Japan	Apical PI Film	[12,13]

(*Continued*)

TABLE 10.1.3 (Continued)

Type	Company	Trade Name	References
Addition	Rhone-Poulenc[c]	Kermid	[16]
	NASA-Lewis	PMR	[122,133,134]
	NASA-Langley	LARC	[1–5,9,10,16,122]
	National Starch and Chemicals	Thermid	[23,51]
	Ciba-Geigy	XU-292	[16]
	Rhodia	Nolimid	[135]
	Boots Technochemie	COPIMIDE BMI	[136]
	Rohm & Haas	KAMAX	[137]
	High Technology Services, Inc.	TECHIMER 2001	[138,139]
Photosensitive	E.M. Industries/Merck Chemicals	Selectilux- HTR-3	[140]
	Ciba-Geigy	Matrimid	[141–144]
		Probimid	[145]
	Shova Denko K.K. (formely Hitachi Chemicals)	Polyimide-isoindoloquinazolinedione, Nonphotosensitive Precursors (PIX) seriesproducts: PIX-3400 and PIX-8103, and High Heat-resistant Liquid (HL) coating products: HL-1000 and HL- 1210 Series	[146]

Poulenc family trivia: Étienne Poulenc's oldest sons, Gaston and Emile, were key contributors to the apothecary business. The youngest son Camille (1864–1942) was a pharmacist and docteur des sciences, credited as the founder of French pharmaceutical industry. He had collaborated with Pierre and Marie Curie. Emile was the father of French composer Francis Poulenc (1899–1963), a member of the famed Les Six in 20th Century French classical music, which also included Georges Auric, Louis Durey, Arthur Honegger, Darius Milhaud, and Germaine Tailleferre (Sources: Encyclopedia Britannica, Arbre Généalogique Christophe Becker, and Société d'Histoire de la Pharmacie).

[a] *Amoco Corporation, originally Standard Oil Company of Indiana, founded by J.D. Rockefeller in 1889, was a global chemical and oil company. Amoco merged with British Petroleum (BP) in December 1998 forming BP Amoco, later renamed to BP. (Source: Personal notes and abstracted Wikipedia information).*

[b] *Originally, Ciba was a chemical company based in Basel, Switzerland, "Chemische Industrie Basel," and merged to become Ciba-Geigy since 1970. One of its latest successors, Ciba Specialty Chemicals sold the epoxy business which has become Huntsman Advanced Materials in 1997. In 2008, Ciba was acquired and integrated into BASF, and was renamed to BASF Schweiz AG in March 2010. Relevant to thermoset plastics, the vintage name Araldite (c.1946), is now a registered trademark of Huntsman Advanced Materials, referring to their range of engineering and structural epoxy, acrylic, and polyurethane adhesives (Source: Personal notes and abstracted Wkipedia information).*

[c] *Rhône-Poulenc was founded in 1928 as the merger of Société des Usines Chimiques du Rhône (Lyon, France) and Établissements Poulenc Frères, a Parisian apothecary enterprise founded by Étienne Poulenc in 1860 and renamed as EPF in 1900. In January 1999, Rhône-Poulenc merged with Hoechst AG to form Aventis. Later in 2004, Aventis merged with Sanofi-Synthélabo to form Sanofi-Aventis, and the name eventually simplified to Sanofi. In 1997, the chemicals division of Rhône-Poulenc was spun off as Rhodia. The agricultural chemicals division of Rhône-Poulenc, after the merger with Hoechst, was sold to Bayer in 2002.*

carcinogens, and their restricted sale contributes to the increased cost. This further disrupted R&D in polyimides. Processing of polyimides was another challenge for most polymer engineers. Fully imidized polyimides are often insoluble and infusible, rendering them difficult to be processed.

Although polyimides have service temperatures up to 700°F (371°C), they suffer from their poor processibility. But for certain electrical and electronic applications, due to their unique properties and performance, polyimides still continue to gain applications, and are widely used along with other polymeric materials in aerospace, electrical and microelectronic insulation and defense industries today [12–16,52,53].

The electronics and aircraft/aerospace industries are the largest current markets for such advanced polymeric materials. The military market includes fighter, attack and large transport aircrafts [2–7,9,10,13,20,52]. However, by the year 2010, large markets for ceramic and nanocomposite materials will be found mostly in microelectronics, military, aerospace, automotive, medical, and building and construction applications [2–7,9,20].

Fig. 10.1.2 illustrates the processing and performance requirements of polyimide resin alloys (blends), hybrids and nanocomposites to compete against other polymers for cost effective industrial applications [3–7,9,12–14,16–54].

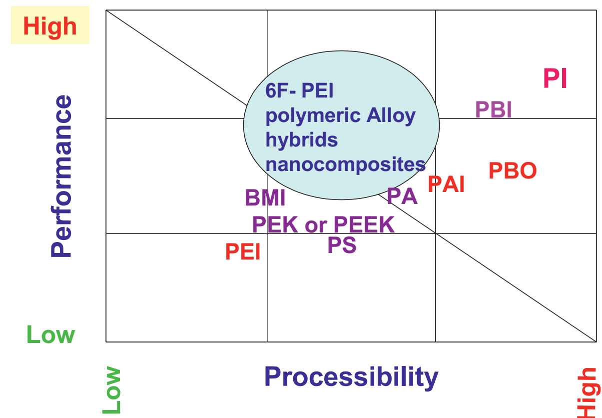


FIGURE 10.1.2 High performance polymeric materials for industrial applications [3–7,9,12–14,16–54].

FIGURE 10.1.3 Application of high temperature, high performance polymers in aerospace application [2–5,9,10].

History of commercial development of polyimides

Historically, polyimide was first reported in 1908 [1,2] when it was discarded as a useless oligomeric residue. In 1955, DuPont successfully developed high molecular weight aromatic polyimide [1,2]. The first patent for polyimide was applied by DuPont in 1959 [3]. The company also developed the first commercial polyimide, Kapton, in 1960 and marketed in 1962 [4,5]. Since then, polyimides have seen more rapid development due to the large demands of high performance polymers for aerospace projects' requirements.

In this section of history of polyimides, ***only the history of commercial development of four major types of polyimides including some of the very well-known and important polyimide products introductions are highlighted***.

Since there were over 60 polyimide products in the high performance polymer market segment by the year 1990, it is, therefore, beyond the scope of this brief introduction to include each one of them. Besides, there were several thousands of technical papers published by hundreds of academic institutions around the globe since 1955 in the polyimide area. In most cases these research works just remained as an academic interest only. However, they did enhance the overall scientific knowledge on polyimides and their properties and potential applications.

Brief history on extensive polyimide research and development and worldwide introdution of major commercial products

Early 1959–70

DuPont introduced the first polyimide product, Kapton-H based on Pyromellitic Dianhydride (PMDA) and 4,4′-Oxydianiline (ODA) chemistry. By mid 1960's DuPont had three major polyimide products: Kapton (film), Vespel (molding), and Pyre-ML (wire-enamel) and developed over a period of 10 years, a niche and sizable market for these high-performance polymer materials [2,16,40–44,51–67].

1970–75

The polyimide business grew with a rapid pace in the United States in excess of US$ 200 million in value and 12 million pounds (approx. 5.45 million kg) in volume.

- The National Aeronautics and Space Administration (NASA)'s Lewis led to the development of PMR technology, which is a class of polyimides known as PMR (for in situ Polymerization of Monomer Reactants). PMR-15 is based on dimethyl esters of BTDA, and norbornene anhydride and methylene dianiline (MDA) [133,134].
- The NASA's Langley Research Center was actively involved in polyimide R&D and developed various poly(amic acid)s thermoplastic formulations based on BTDA, and benzophenone group containing diamines. These products were referred to as LARC-TPI polymers. This technology was then made available for licensing to commercial enterprises worldwide.

Contractors of US governments' defense related projects were major customers for their uses in aerospace (Fig. 10.1.3) and defense-related applications [1–5,23].

- DuPont introduced a series of NR-150 formulation products as high temperature adhesives for high performance composites. They were thermoplastic products used as binders, adhesives and coatings for structural composites. They were designed for a broad range of aerospace applications, such as radomes, jet engines, brake lining ablative heat shields, etc. [43]

- Monsanto developed and introduced SKYBOND brand of thermoset polyimide for aerospace composite prepreg fabrication applications [4,9].
- Rhodia, Inc. of New York, based on proprietary monomers, introduced thermoset polyimide under the trade name of Nolimide-A 380 for extreme high temperature (>800°F, i.e., >426°C) adhesives intended for applications in the structural composites and construction of advanced supersonic transport and tactical fighter planes [135].

1975–80

New players came in with other types of polyimides for aerospace and electrical applications. Worldwide competition in R&D efforts expanded to a record level in the United States.

Major funding was provided by the US Government for the R&D activities in novel polyimides for defense related hardware products and application development. NASA-Lewis, NASA-Langley and DARPA of the US Govt. were few of the leading collaborators [2–7,9,10,12,13,22,52,122].

1980–85

The market expanded at an average rate of 10%–13% per year. Most of it was in electrical, aerospace, military aircraft and later in electronic applications.

R&D efforts and funding continued at a faster pace with an aim to develop new applications for microelectronic industries. More new players came in with a wide variety of polyimides and photo-polyimide products and formulations. DARPA funding increased further for the development of polyimides for advanced highly sophisticated military applications [3–5,9,12,13,15,20,22,52,122].

In 1980, Ciba-Geigy Corp. introduced XU-218 polyimides having epoxy components as encapsulants for pin-grid packages containing electronic circuitry on silicon chip. Subsequently this company introduced BMI chemistry based adhesive Matrimid series of products and Probimide a photosensitive polyimide (PSPI) formulation for photolithography in microelectronics application [3–5,9,13,20,141,142,145].

In 1980, Amoco successfully introduced Torlon brand poly(amide-imide) based on trimellitic anhydride (TMA) and MDA for commercial engineering applications [3–5,20].

In 1981, Plastics Product Division of General Electric Corp. introduced ULTEM 1000, a melt processible thermoplastic PEI resin (*T*g. 220°C) made from 4,4′-Bisphenol A diether dianhydride (BPADA) and *meta*-phenylene diamine (*m*-PDA) [3–5,9,10,13,46,47,143,144].

In 1981, M&T Chemicals, Inc. invented and introduced siloxane–imide moiety containing M&T-PSI series of poly (amic acid) and polyimide products based on a proprietary siloxane diamine, novel diether dianhydride and diamines. These products were: M&T 2065, M&T 3500, M&T 4605-40, M&T 5000, M&T 1112, M&T CNF-1114. and M&T Rely-imide. The potential applications were: protective coatings for high voltage high tension power-lines and electromagnate wires for power generation station, and coatings for space satellite's solar cells and solar sail protection from space debris, etc., high performance adhesives for Copper-Kapton film laminates, silver filled die-attached adhesives for flexible circuits and junction coatings, low temperature curing encapsulants, as well as matrix resins for light weight, high temperature stable, high performance composites for aerospace, etc. [18,19,50,70–78]. This business was later acquired by National Starch and Chemicals Co of NJ, USA in 1988.

In 1982, Hitachi Chemicals Co. Ltd. which became a consolidated subsidiary of Shova Denko K.K. in October 2020), Tokyo, Japan introduced series of heat resistant fine polymeric formulations: Polyimide-isoindoloquinazolinedione (PIQ), and High Heat-resistant Liquid (HL) coating products: HL-1000 and HL-1210, besides a series of Nonphotosensitive Precursors (PIX) products: PIX-3400 and PIX-8103, etc. for dielectric insulation and passivation of semiconductor devices [146].

In 1982, the Donald S. Gilmore Laboratory of Upjohn Company introduced polyimide and fiber under brand name of Upjohn Polyimide 2080. It was an extension of its aromatic isocyanates business. This business was subsequently acquired by Dow in 1985. The products then were marketed as Dow 2080 series of polyimides. They were based on BTDA, MDI and other di-isocyanates, for thermoplastic application in printed circuit boards, composites for structural components of aircraft and aerospace [3,4,9,10,13,48,49].

In 1985, E. M Industries' Merck Electronics Products Division introduced Slectilux-HTR3 polyimide based photoresists formulations in Germany [140].

In 1985, IMI Tech, Inc. a subsidiary of International Harvester, Co., introduced SOLIMIDE (Polyimide Foam) based on dimethyl ester of BTDA and MDA and siloxane diamine (M&T) for "Nonflammable" aerospace-craft, and military aircraft's acoustic and thermal insulation applications [3–5,21,79,80,125–128].

1986–90

For the first time in the history of polyimide, in 1986, National Starch and Chemical Corp. introduced the first series of Aminophenyl acetylene-terminated (AT) isoimide oligomer based on BTDA and Aminophenoxy benzene (APB) chemistry, under the trade name THERMID. Later in 1987, it introduced Aminophenyl acetylene terminated fluorinated isoimide oligomers based on 6FDA and APB [9,13,23,51].

In 1986, Boots-Technochemie, a subsidiary of Boots Company PLC, UK introduced another BMI-chemistry based series of thermoset resin products with the brand name of COMPIMIDE for void-free fiber reinforced laminates and molding applications in aerospace industries [136].

Rohm and Haas also introduced low cost imidized acrylic polymer foams under the trade names of KAMAX

and Rohacell for commercial industrial and aerospace insulation applications [137].

In 1986, High Technology Services, Inc. (HTS) of Troy, NY introduced poly(amic acid) and polyimide based series of products and formulations, which were made from BTDA and 3,3-diaminodiphenyl sulfone (DDS), based on NASA's LARC-DDS technology licensed from NASA and modified with siloxane containing diamines, fluoro-elastomers and epoxy, such as series 1000 polyimide adhesives, series 2000X poly(amic acid) based adhesives and series 2000X polyimide based adhesives. HTS introduced TECHIMER line of BMI and Nadimide type of thermoset product formulations based on LARC-13. Bisnadimide technology was licensed from NASA Langley Research Center. TECHIMER-2001 was meant for microelectronics application. It was a poly(amic acid) formulation which was converted to a TPI adhesive upon heating [138,139].

In 1986, the High Performance Film Group of ICI Film Division of ICI America, introduced a series of UPILEX Polyimide films (UPILEX R, UPILEX SX and UPILEX X,) having comparable thermal, mechanical and electrical properties as that of KaptonH [PMDA + ODA] and to compete with DuPont's Kapton film business for military and microelectronic applications. These products were based on biphenyl dianhydride (BPDA) and *m*-PDA or ODA. Later this business was divested to Ube Industries, Japan, which remained the sole manufacturer of the film [3−5,12,13,68,69].

DuPont also introduced AVIMID-K brand series of polyimides which were amorphous products obtained from monomer solutions by the reaction of diesterified fluorinated dianhydride and aromatic diamines, for aerospace applications [3−5,9,10,20].

In 1987, National Starch and Chemical Co. USA introduced a series of thermoset AT polyimides (isoimide type) oligomers under the trade name of THERMID IP-600 as molding compounds. These isoimide oligomers upon thermal curing converted to polyimides without releasing any volatile byproducts. This technology was acquired from Gulf Oil Co. in 1984. Later it introduced a series of fluorinated versions under the trade name of THERMID FA-700 for high temperature heat stable materials for aerospace and engineering applications [23,51].

In 1987, Hoechst Celanese Corp., RI, USA introduced SIXEF brand of series of fully fluorinated polyimides [6F-PI], poly(amide-imide)s [6F-PAI], photosensitive polyimides[6F-PsPI] and copolyimides [6F-CoPI] in powder and formulation forms as high temperature advanced high performance polymers for electronics, aerospace and gas separation membrane applications. These polymers were based on fluorinated aromatic dianhydrides (6FDA and 12FDA) and fluorinated aromatic diamines and other fluorinated, aromatic monomers [7,11,15,16,20,22,25−38,81−120,122].

From 1988 to 1991, Hoechst Celanese Corp., NJ, USA was a leading collaborator in a US DARPA Program for the development of high-temperature, high-performance composite matrix resins based on SIXEF-Polyimide [PI]/ Polybenzimidazole [PBI] blends for "*low observable*" supersonic Advanced Tactical Fighter (ATF) plane (AT-71, a.k.a F-117)'s structural components (Fig. 10.1.4), under funding from NASA (Lewis) and DARPA. This team involved scientists from major aircraft companies, (Boeing and Lockheed), as well as major military aircraft engine manufacturer, (General Electric Engine Division), major resin producer (Hoechst Celanese Corp SIXEF Polymers Group) and leading universities (University of Massachusetts, MIT, Virginia Polytechnic, University of Akron, and South West Texas State University) [25−28,30−38,81−120].

In 1987 Rogers Corp of. Chandler, Arizona and Rogers, Connecticut, USA introduced DURIMID brand high temperature poly(amic acid) and TPI formulation, DURIMID100 and DURIMID120, and powder products [121].

Ethyl Corp. introduced EYMYD brand of ultra-high 2,2-bis[4-(4-aminophenoxy) phenyl] hexafluoropropane (BDAF) based fluorinated polyimide solutions for electronic coatings. This low dielectric coating technology was originally developed by TRW, Inc. and licensed to Ethyl Corp., USA [129−131].

Mitsui Toatsu Chemicals, Inc. of Japan licensed NASA's LARC-TPI Technology, and in 1988 introduced in all the countries except the United States a REGULUS brand of polyimide thermoplastic film products whose chemistry was based on BTDA and 3,3-diamino benzophenone (a highly toxic and carcinogenic diamine). The films are biaxially oriented which could be processed by thermoforming for electrical, and electronics applications [123].

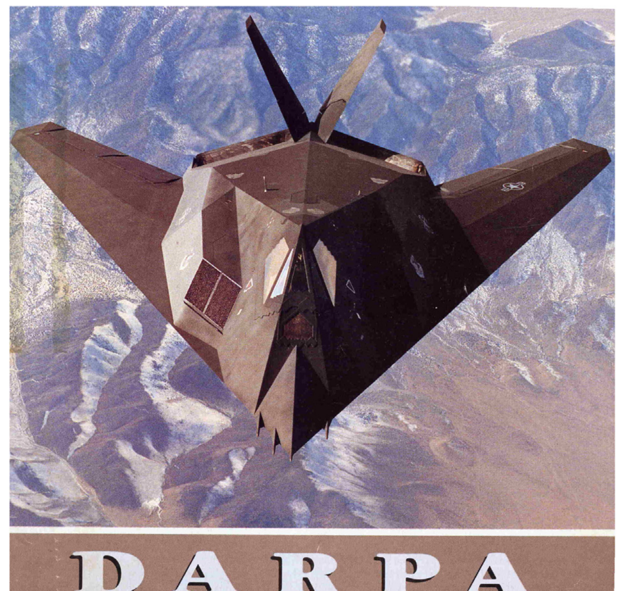


FIGURE 10.1.4 F-117, stealth advanced tactical fighter (ATF) plane developed under DARPA funding by lockheed, uses advanced polymeric materials based composites [US Air Force Photo on the Cover of Chemical & Engineering News Magazine (1992) [122]].

Chemiefaser Lenzing, AG of Austria introduced P84 Polyimide powders and strong and ultra high tenacity fibers for nonflammable, thermally stable, high performance mold and fiber braiding for aerospace composites application [132].

In 1989, Kanagafuchi Japan, and its US business partner AlliedSignal, USA introduced Apical PI Film, for electronic and microelectronic applications [12,13].

1990–95

In the United States alone, several companies introduced polyimide chemistry based products. There were 63 products in the market. Many more companies around the globe continued introducing more products and newer applications for electronic and microelectronic. Besides, many Japanese companies introduced a series of "Negative" and "Positive" acting PSPI product formulations for microelectronics applications. However, due to the end of the cold war and the collapse of Soviet Union (in early 90), the R&D efforts and funding for newer polyimides for aerospace and military applications has slowed down drastically in the United States, with several companies withdrawing their polyimide based products. Some companies went out of business altogether, and only a limited number of companies continued marketing polyimide based products. By the late 1995 in the United States, about 35 products continued to cater to markets mostly in the electronic and microelectronic and aerospace industries. However, worldwide applications development for electronic and microelectronic end-uses continued at a faster pace, and simultaneously the consumption of polyimide based products increased for that industry sector [12,13,52,122].

1995–2000

In 1996, Mitsui Toatsu Chemicals, Inc. of Japan introduced a liquid crystalline polyimide (LC-PI) resin under AURUM brand name, which was originally known as NEW TPI. It was based on another LARC-TPI Technology licensed from NASA. It was advertised as a superheat resistant TPI product whose chemistry was based on PMDA and 1,3-bis[4-(4-aminophenoxy) cumyl] benzene. The polymer can be molded into complex engineering parts, wire extrusion coatings, and film/fibers for automotive, electrical, and electronics applications [124].

Brief summary of historical polyimide market since the years 1989 and estimated growth projection to 2030

1989–90

From 1989 to 1990, approximately about 5.5 million kg of polyimide (~US $ 316.30 million in value) was produced and marketed for various market sectors such as polyimide films for electrical and electronics and commercial applications as well as small volume, high margin "photosensitive" polyimide formulations for microelectronics applications, large volume, low margin polyimide products for aerospace and consumer engineering sector [3,5–7,9,20].

1991–98

From 1991 to 1998, polyimide use overall showed rapid growth. Sale increased by about 2.55 times that of 1989–90 sale (approximately 14.062 million kg) which is by about 3.18 times in sale valued at ~US$ 1006.80 million [3,5–7,9,20].

1999–2008

Since 1999 through 2008, overall sale increased to approximately 14.783.71 million kg (~US $ 1087.08 million) in values, representing an increase in sale by about 7.97% in dollar amount from 1999 through 2008 [7,9]. The major portion of the market share (about ~40%) was covered by the electronics industry's use of specialty polyimide based films and photosensitive coatings and adhesives products, whereas the engineering and aerospace industries combined were major market for the specially formulated Coatings & Adhesives, Fibers and Foam products [7,9,16]. Among these, PEI based molding products represented in the market with sale of around 5.9 million kg valued at about ~US$ 116.00 millions. These PEI products' applications include connectors, flexible circuit board, IC-packaging, sockets, lead-chip carriers, etc. Also included were the medical appliance applications, such as humidifier manifold, surgical lights and sterilization apparatus, etc. [7].

2009–18

Worldwide demand for polyimide polymers went up. During 2009–18, the overall market grew to 23.433 million kg (US $ 2160.50 million). During this time frame, the price for large volume, low margin polyimide products for engineering applications was in the approximate range of US$ 7.50 to 115 per pound (~US$ 16.5 to 254 per kg), whereas for small volume, high margin electronic application products it was in the approximate range of US$ 161.00–480.00 per pound (~US$ 355.00–1060.00 per kg) on dry neat polymer basis [7]. For the various polyimide based products, the market sector for polyimide films for electrical and electronics and commercial applications as well as "photosensitive" polyimide formulations for microelectronics applications continued to grow at a reasonably steady rate of 5%–8% to year 2018 (Table 10.1.4) [7,16].

Sale of large volume, low margin polyimide products was doubled for aerospace and consumer engineering sector, and the sale of small volume, high margin "photosensitive" polyimide formulations and films for electrical and microelectronics applications tripled [7,16].

TABLE 10.1.4 Tentative polyimide market growth projection through year 2030.

Year	1989–90[a]		1991–98[a]		1998–2008[b]		2009–18[b]		2018–30[c]	
Polyimide products	MM kg	MM $	MM kg	MM $	MM kg	MM $	MM kg	MM $	MM kg	MM $
Film	0.590	77.0	0.868	155.0	1.284	168.0	01.856	320.0	03.01	565.0
Photosensitive	0.122	99.0	0.293	387.0	0.381	448.0	00.810	850.0	01.80	1875.0
Molding compounds	2.360	64.0	8.099	170.0	10.095	198.0	15.150	250.0	25.10	400.0
Coating and adhesives	2.313	64.0	4.546	235.0	5.559	245.0	07.851	370.0	14.50	670.0
Foam	0.045	10.0	0.124	054.0	0.210	085.0	00.557	136.0	01.15	280.0
Fiber	0.070	02.3	0.132	005.8	0.180	015.1	00.476	030.5	01.50	097.5
Total	5.500	316.3	14.062	1006.8	14.783.	1087.1	23.430.	2160.5.	74.05	3527.5

MM kg, Million kilograms; *MM $*, Million US $.
[a] [3–6,9,11,16,20].
[b] [7,11].
[c] [7,11].

Since the overall market data is not yet available for the last year 2019, it is expected that during 2019 market is grown in almost all sub-sections of polyimide-chemistry based products. The growth could be attributed to sale of large volume, low margin polyimide products such as film for electrical and microelectronics, molding Compounds due to rapid implementation of innovation 2D-printing technology in most electrical and engineering fomponents fabrication sectors, foam for Thermal Insulation applications, and fibers for FR-composites component fabrication applications for aerospace and consumer engineering sector.

2020–30

Owing to prevailing world-wide political hot spots, and due to which, potential economic downturn, the market projections were somewhat revised. The reestimate suggest that from 2020 to 2025 market will continue to grow at a slower rate. In addition, there will be moderate increase in growth in aerospace and engineering sector, however, there will be ongoing heavy pressure on the pricing of certain products, especially on film, molding compounds, Foam and Fibers due to introduction of "competing" chemistry as well as nanomaterials-based products [7].

One interesting note here to mention is that in early 1990s, NASA joined hands with Boeing Company, GE Aircraft Engines, McDonnell Douglas and Pratt & Whitney (Aircraft Engines) and "re-initiated" its High-Speed Research Program. Since 2000, the goal of this project was further revised to continue collaboration research activities and develop several the "critical" high-temperature stable and high-performance matrix polymers (including polyimides) and Ceramic Materials (including Nanotechnology-based materials such as Carbon Nanotubes, Graphene, Boron Nitride, etc. reinforced CERAMERS and METACERS Materials), and their 3D-Fabrication Process and Quick Sample Testing Technologies

FIGURE 10.1.5 Artist's concept of future hypersonic commercial Jetliner of Boeing Co. [147].

and needed for an environmentally compatible and economically viable indigenously fabricated High-Speed Defense/Civil Transport Airplane prototypes (Figs. 10.1.5 and 10.1.6). During 2010 to 2025 this program is continued to be supported on a limited priority by NASA. However, it is expected that this project will be find continue funding and hence momentum to develop enhance economically viable technology with less carbon foot-print for the world's next generation of defense and commercial aviation industries sometime during by the year 2025–30 [7].

It is therefore, believed that sometime during by the year 2025–30, overall due to increasing demand for lighter and stronger materials, which can withstand high operating temperatures, particularly in military and commercial supersonic transport planes, aerospace (rockets and space shuttles),

FIGURE 10.1.6 Artist's concept of high-speed civil transport plane of McDonnell Douglas Co. [148].

TABLE 10.1.5 Polyimide research and development area and publications and patent activities around the world in period from December 1970 to December 2018 [6,7,164–166].

Research and development area	Publications and patents (combined)
Polyimide	60,450
Polyimide/inorganic materials-based hybrids	3975
Polyimide/nanomaterials-based nanocomposites	3250

microelectronic fab processes, oil-field gas separation membranes, etc., the chemistry of polyimides will continue to compete with other chemistry such PEEK, Polysulfone [PS], etc. at the forefront of industrial polymeric materials R&D work around the worldwide [3–7,16].

Brief summary of cursory literature survey on worldwide polyimide research and development activities

It is noteworthy that extensive basic and applied R&D on polyimides is conducted around the globe at the universities and in the multinational companies. Authoritative technical papers, books, reviews, have been published on the synthesis, structure-property relationships, characterization and applications of polyimides. Fervent patent activities have ensued [2,11,14,16,44,51,58,147–159]. International technical conferences on polyimide have been held regularly since 1982 [160–163].

Cursory searches carried out at the SciFinder, a Chemical Abstracts (CAS) service of the American Chemical Society (ACS), Washington DC, USA [164], and ScienceDirect, a literature reference search service (Elsevier B.v., Amsterdam) [165], and the Google Scholar search engine, showed that since the late 1950s to December 2018 [166], over 70,000 scientific research works (technical papers and patents) on polyimides have been published. In addition, from December 1970 to December 2018, there were publications of 3975 technical papers and patents combined, on polyimide/inorganic materials-based hybrids materials; and 3250 technical papers and patents combined, on polyimide/nanomaterials-based nanocomposites materials, as illustrated in Table 10.1.5.

It is interesting to note that most technical tapers were published by academicians working at the universities, whereas most patents were filled and obtained by the research scientists/engineers working in the companies around the world.

The CA Select-Polyimide at CAS service of ACS searches revealed that for the 24 month period in 1997–98 [164] in the United States alone, 105 universities and 100 companies combined had 308 publications and 95 patents filed. Industries led in filling patents and publication of small number of technical papers, whereas, universities led in publications.

Since 1970, most publications on polyimide compositions and related chemistries were from the academic institutions. Patent filing activities, on the other hand, were fervent among US and international chemical companies, with Japan leading in both R&D on polyimides for electronic applications, and manufacturing of polyimide products for the microelectronics industry. Polyimide development has continued to be a high-value polymer business [6,7,164–166].

Since 1988 there have been increased research followed by publications and patent activities in then new emerging field of Polyimide Hybrids and Polyimide Nanocomposites [6,7,164–166]. Since late 1990s there was interesting rapid growth in these areas of research with increasing number of publications and issuance of large number of patents.

TABLE 10.1.6 Illustrative statistics of research publications and patents on polyimides (2016–18) [7,164–166].

Polyimides		
Since 1950, reported total worldwide publications and patents: 60,450		
Past 3 years statistic of published R&D activities		
Year	Publications	Patents
2016	169	101
2017	145	69
2018	110	60
Total	424	230

TABLE 10.1.7 Illustrative statistics of research publications and issued patents on polyimide and inorganic materials-based hybrids (2016–18) [7,164–166].

Polyimide/inorganic materials-based hybrids		
Since 1950, reported total worldwide publications and patents: 3975		
Past 3 years statistic of published R&D activities		
Year	Publications	Patents
2016	195	81
2017	238	99
2018	270	130
Total	703	310

During the 3 year period from January 2016 to December 2018, there were total 424 technical publications and 230 patents issued in polyimides and related R&D work. At the same time-frame, there have been 703 publications and 310 patents issued in the well-established field of polyimide/inorganic materials-based hybrids and related R&D work; and 1039 publications and 464 patents issued in similarly well-established field of polyimide/nanomaterials-based nanocomposites and related R&D work [6,7,164–166]. This trend, however, clearly suggest that since past 3 years, there has been less R&D work done on the polyimide and related chemistry-based materials in the academia and companies around the world, but at the same time interesting R&D activity growth was noted in the polyimide/inorganic materials-based hybrids and in polyimide/nanomaterials-based nanocomposites research area with increasing number of publications and issuance of patents as shown in Tables 10.1.6–10.1.8 [6,7,164–166].

During the last 15 years, there have been tremendous interest in the nanomaterials R&D and technology development. Numerous polyimide hybrids with inorganic materials and polyimide–clay nanocomposites with improved thermal and mechanical properties have been reported in the past 10 years.

TABLE 10.1.8 Illustrative statistics of research publications and issued patents on polyimide and nanomaterials-based nanocomposites (2016–18) [7,164–166].

Polyimide/nanomaterials-based nanocomposites		
Since 1950, reported total worldwide publications and patents: 3250		
Past 3 years statistic of published R&D activities		
Year	Publications	Patents
2016	318	119
2017	350	144
2018	371	201
Total	1039	464

Types of polyimides

There are three types of polyimides: (1) Condensation (Thermoplastics and Thermosets), (2) Addition, and (3) Linear oligomeric type which may or may not be terminated with crosslinking groups [14]. Examples of these polymers are given in Table 10.1.9.

The first type depends on the traditional reaction route between a dianhydride and a diamine in two steps, that is, the dianhydride reacts with the diamine to form poly(amic acid) in the first step, which is usually soluble, followed by imidization (second step) through a thermal curing at temperatures above 300°Cor by chemical means. The second type is based on the addition reaction of monomeric diimides to other compounds (e.g., monomers) terminated with vinyl groups. During these reactions there are no byproducts released. The third type is based on the condensation polyimide route to produce an oligomeric linear polyimide which then reacts with compounds terminating in a cross-linking group, an amine, or a carboxylic acid group. Such polyimides are soluble, thermoplastic, and can be cross-linked at elevated temperatures via the cross-linking groups. NASA's polyimide PMR-15 series belong in this category [122,133,134,151].

Since last three decades, aromatic polyimides [2,9,16,28], fluoro-polyimides [2,9,11,16,26–38,81–118,167–172], LC-

PIs [173], and oligomeric polyimides [174] and their blends [118] have become one of the most prominent and important polymers in the advanced polymer categories. A large number of starting monomers and polyimides with different structures have been synthesized. In this respect, an industry was created for the production of polyimide materials for various applications.

The literature search revealed that polyimide chemistry was well established, and a variety of polyimides and copolyimides was synthesized by various methods, some of which achieved commercial scalability. A brief discussion of current synthesis methods, structures, properties and applications of polyimides is given below.

Synthesis of polyimides

Polyimides are polymers containing at least one "imide" linkage either as an open-chain structure or as a heterocyclic unit in the polymer backbone (Fig. 10.1.7). Only a few articles dealing with polyimides with the open-chain imide linkage have been reported [174]. In contrast, the synthesis and characterization of aromatic polyimides have been extensively reported in the literature. Numerous papers and books devoted to synthesis and applications of polyimides with heterocyclic units have been published since the first report of polyimide in 1908 [14,16,51,175,176]. The preparation of polyimides by reaction of aromatic dianhydrides with aromatic diamines followed by thermal cyclization was reported from 1955 to 1970 [40−44,51−67,177−181].

Since the first commercial polyimide product, Kapton, was successfully introduced by DuPont in the late 1960s [2,14,16,51], varieties of polyimides have been more rapidly developed.

The chemical structure of two major form of Polyimides with its repeat unit having respective aliphatic or aromatic groups containing imide-linkage shown in Fig. 10.1.7.

In general, major commercial polyimides are aromatic compounds containing an imide with five-member ring units and aromatic rings in the repeat unit, which forms part of the most popular and important high-performance polymeric materials. As mentioned earlier, there are three major types of polyimides: condensation, addition, and linear. In addition, there are those which are terminated with chemical, thermal, photochemically "cross-linkable" groups. From the first invention of aromatic polyimides to the synthesis of new thermoset and TPIs with excellent performance, it has been shown that the successful application, processing and outstanding properties of polyimides are closely associated with the synthesis of polyimide resin. Hence, synthesis forms the cornerstone for polyimide chemistry.

TABLE 10.1.9 Types of polyimides [2,11,16,149−152].

Condensation type: • *Thermosets:* Based on • PMDA/ODA chemistry • BTDA/MDA chemistry • Nonphoto sensitive chemistry • Photosensitive chemistry
• *Thermoplastics:* Based on • Polyetherimides chemistry • BTDA/TDI/MDI chemistry • Avimide K and N chemistry • LaRC-TPI chemistry • BTDA/DAPI chemistry • Polyimide sulfone chemistry
Addition polymerization type:Based on • Crosslinkable chemistry • PMR-15 chemistry • Acetylene terminated chemistry • BMIs chemistry • Bisnadimide chemistry

Monomers

A large number of starting monomers are reported in the literature and patents [1−3,6,7,9,11,14,16,25,52,86−120,180−182]. Most of them are aromatic compounds and are available commercially in small to large quantities. Some are produced for captive consumption. The generic structures of these monomers are given in Fig. 10.1.8.

(A) (B)

FIGURE 10.1.7 Typical of polyimide structures: (A) aliphatic polyimide (B) aromatic polyimide [2,14,16].

Aromatic dianhydride

Where A = ... OR ...

Where X = Single bond, $-CH_2-$, -O-, -S-, $-SO_2-$, $-C(CH_3)_2-$, $-C(CF_3)_2-$, -CO-, -C(CF3)Ph-, $-Si(CH_3)_2-O-Si(CH_3)_2-$, ..., etc.

Where Y = X

And / or

And / or

Aromatic diamines

Where X = Single bond, $-CH_2-$, -O-, -S-, $-SO_2-$, $-C(CH_3)_2-$, $-C(CF_3)_2-$, -CO-, -C(CF3)Ph-, $-Si(CH_3)_2-O-Si(CH_3)_2-$, ..., etc.

Where Z = X

Where A1 = A2 = A3 = A4 OR A1 ≠ A2, OR A1 ≠ A3, OR A1 ≠ A4, OR A2 ≠ A3, OR A2 ≠ A4, OR A3 ≠ A4,

Where A1, A2, A3, and A4 could be H, $-CH_3$, $-CH_3(CH_2)n$; where n = 1 to 20, $-NO_2$, -OH, -I, -Br, -Cl, -F, -NCO, -COOH, -CN, -CNO, $-CF_3$, $-C_6H_5$,

FIGURE 10.1.8 Generic structures of aromatic dianhydride and diamines [11].

Figs. 10.1.9 and 10.1.10 below show the chemical structures and abbreviations of diamine and dianhydride monomers currently used in the synthesis of polyimides of interest. Most of these monomers are available commercially at a price in the range of US$ 50.00–125.00 per kg except most fluorinated monomers, as they are extremely expensive, especially the diamines (price estimated to be > ~US $ 1775.00 per kg). Electronic grade 6FDA is available at around US $ 500.00 per kg in small quantities [6,7]. In commercial quantities, the price would be much lower. However, the use of fluorinated monomers is the most effective way to obtain high performance thermally stable polyimides with low dielectric constant for electronic applications.

The purity of the monomers is very critical in obtaining polyimides with high molecular weight and good electrical properties. Most of these monomers are available with purity in the range of 98.5%–99.8% with trace impurities of sodium, potassium, iron, and chloride in ppm level. It is, therefore, typically a necessity to purify these monomers by recrystallization, vacuum distillation or by sublimation. These monomers are then kept in an inert environment and dried one or more times prior to use.

Polyimides by polycondensation

Polymerization (synthesis) reaction is a complex reaction requiring a careful control of various reaction parameters to achieve high molecular weight polymers [14,16,51,150,151]. The polymerization reaction described as below can be obtained by the condensation of two monomers in equimolar (1:1) ratios: typically a dianhydride and a diamine with the elimination of small molecules for example water as shown in Fig. 10.1.11. The reaction kinetics could be enhanced by use of a condensation catalyst. However, thermal and chemical imidization methods are predominantly used commercially.

Polyimides from dianhydrides and diamines

The preparation of polyimides from dianhydrides and diamines is the most popular and more traditional method for conventional polyimides and TPIs synthesis [2,11,14,16,51,177]. The reaction proceeds in two steps. The first step leads to the formation of the intermediate, poly(amic acid) from the reaction between a dianhydride and a diamine, which is then imidized (second step) by Chemical imidization using catalyst and/or dehydrating agents (at RT or heating at higher temperature) or by step-wise heating at elevated temperature (300°C) to remove water generated as by-product of due to condensation reaction.

The first commercial polyimide, Kapton, was produced from PMDA and 4,4′-ODA by solution polymerization and imidized by the thermal process route as shown in Fig. 10.1.12 [2,11,16,40–44,51–67,180,181].

There are a few advantages of this method when compared to other methods available for preparing polyimides. One of them is the better solubility of dianhydrides in an organic solvent than that of the tetracarboxylic acid, and the intermediate poly(amic acid) [PAA]. Besides, there are more choices of

PMDA BPDA BTDA

6FDA ODPA DSDA

Si DA IPDA

BDSDA

BPADA

FIGURE 10.1.9 Most commenly used dianhydride monomers structures with their abbreviation used for preparing polyimides [1–3,11,14,16,19,25,180–192].

dianhydrides. The drawbacks of this method are the sensitivity to moisture (water), unstable viscosity of poly(amic acid), and the release of volatile by-products, for example, water during imidization reaction. Hence, this method is only suitable for thin products such as films, fibers, and coatings, and it is not suitable for thicker dimensions, such as molding, laminating and packaging materials.

It is a common observation [11,14,16] that the viscosity of the poly(amic acid) (reflecting the molecular weights), both bulk and inherent, for example, in classical case of [PMDA + ODA] poly(amic acid) [PAA] system in NMP, would increase slightly at the RT storage initially, but would gradually decrease considerably. It was found that the poly (amic acid) (PAA) is unstable over a long period of time in solution form at RT and at an elevated temperature. Its molecular weight would decrease depending upon the condition in which it is stored, and the type of solvent used (Table 10.1.10). Viscosity also depends on the purity and the moisture content of monomers and solvent used and the interaction (bonding and debonding) of the free end groups of the polymer backbone. For example, solvent NMP complexes (hydrogen bonding) with the poly(amic acid) in the early stage of the storage. Thus a gel-like structure formation and pseudo-bulk viscosity increase is observed. As time passes, the moisture in the

mPDA

pPDA

3,3'-ODA

4,4'-ODA

3,4'-ODA

4,4'-BPD

4,4'DDS

4.4'DDSO

MDA

IPD

1,3-SiDAM

4,4'-6F-DAM

3,3'-6F-DAM

4,4-APB

4,4'-(1,3)-APB

DPTP

4,4'-BPADE

4,4'-BDAF

FIGURE 10.1.10 Most commenly used diamine monomer structures with its abbreviation used for preparation of polyimides [1–3,11,14,16,19,25,177,180–182].

FIGURE 10.1.11 Synthesis scheme for polyimide from a dianhydride and a diamine by polycondensation [2,11,14,16].

solvent hydrolyzes the weak hydrogen bond formed with NMP as well as amic acid bonds. These result in a decrease in molecular weight and a lower viscosity (Table 10.1.10) [2,11,14,16,151,173,180].

Chemical mechanism of polymerization reaction

The kinetic studies show that the reaction of formation of Poly(amic acid) [PAA] by this method is fast and exothermic, and is strongly affected by the structure and purity of monomers (dianhydride and diamine), temperature, concentration, polarity and purity of solvents and the presence of impurity (moisture and metal ion) [2,11,14,16,51,150,180,181]. Therefore the initial reaction of the formation of poly(amic acid) is always carried out below 20°C for obtaining polyimides with a higher molecular weight [2,11,180−182].

The chemical mechanism pathway of the above reactions may be explained as follows. It is well described in the literature [2,11,14,16,174,175] that about five types of concurrent reaction kinetics steps take place during and after the first few hours of poly(amic acid) synthesis.

These 5 major reaction steps [2,11,14,16,174] are:

- Acylation of amine with anhydride (chain propagation step);
- Spontaneous cyclization of amic acid groups with the elimination of water and formation of imide rings [chain growth termination and equilibration (averaging) of chain lengths];
- Hydrolysis of amide bonds and formation of free amine and free carboxylic acid groups. (chain growth termination);
- Hydrolysis of terminal anhydride groups and formation of dicarboxylic acid groups (chain growth termination);
- Cyclization with elimination of amine and formation of anhydrides ring (scission within chains) leading to di- and tetra-acids. Which reverse reaction and re-equilibration of chain lengths.

These five major polymerization reactions kinetics are illustrated in Fig. 10.1.13.

One can explain that during the early stage of reaction, both the weight-average molecular weight $\left(\overline{M}_w\right)$ and number-average molecular weight $\left(\overline{M}_n\right)$ increase rapidly, arising from chain propagation and hydrolysis of terminal anhydride groups. After this, the molecular weight decreases due to spontaneous hydrolysis of amide and cyclization of *ortho*-carboxy-amide groups with elimination of the amino group. The *ortho*-carboxy-amide group of the poly(amic acid) structure is capable of cyclization to form imide, isoimide, or anhydride rings. A carboxyl group in the *ortho*-position to an amide bond can intra-molecularly catalyze the cleavage of this bond, leading to chain scission. Intermolecular cyclization and degradation proceed spontaneously. Also the water content in the solution increases the hydrolysis of the excess anhydride, leading to the formation of excess free dicarboxylic acid groups and free amines. This then leads to chain growth termination. It is also possible that ionic bond formation occurs between the free acid groups and free amines, which may lead to instability of the viscosity. Therefore an increase in solid concentration, high purity of monomers and lowering the water content of the solvent are desirable for higher molecular weight and stable viscosity of poly(amic acid) [2,11,14,16,174,180,181].

The nature of solvent affects the conformational characteristics of poly(amic acid) especially in the weak base type solvents, for example, NMP. The *ortho*-amic acid a relatively

Pyromellitic dianhydride (PMDA) + 4,4' Oxydianiline (4,4'- ODA) diamine

5 - 20 % NV, Solvent mixture, Catalyst or high temperature

[PMDA-4,4-Oxydianiline (4,4'- ODA)] Polyamide-amic Acid [PAA]

High temperature thermal imidization of wet film on control heated large diameter rotating roller drum in a controlled environment to a total dryness (- H_2O)

Kapton® [PMDA-ODA] Polyimide Film

FIGURE 10.1.12 The polycondensation reaction scheme of production route of a very first commercial polyimide kapton polyimide film based on pyromellitic dianhydride (PMDA) and 4,4' oxydianiline (4,4'-ODA) diamine [2,11,16,40–44,51–67,180,181].

strong carboxylic acid. It is because of the electron withdrawing effect of the *ortho*-amide group and its stabilization by internal hydrogen bonding of dissociated carboxylate with amide hydrogen. The strong acid-base interaction between the amic acid and the NMP solvent is the major source of the slight increase in the exotherm of the reaction and one of the most important driving forces for the complex spontaneous reactions leading to imide rings formation and water generation. In the presence of water, the anhydride groups are hydrolyzed to give free dicarboxylic acid groups. The reaction is driven by the nucleophilicity of water in dipolar, aprotic solvent and by strong acid-base interaction of the products of these spontaneous reactions with the dipolar solvent [2,11,14,16,174].

Chemical imidization reaction

Imidization of poly(amic acid) [PAA] (second step), may be accomplished chemically or by heating at elevated temperatures (300°C).

In chemical imidization, the dehydration system of acetic anhydride-tertiary amine is a very effective system for imidization of poly(amic acid) at RT. Poly(amic acid) has good solubility in organic solvents, and in general, the polyimides prepared by chemical imidization method possess better solubility in organic solvents than those prepared by heating at elevated temperatures, because the side reactions are suppressed under the mild reaction conditions (chemical imidization) [2,11,14,16,86–120,174,180–182].

Mechanism of chemical imidization

The literature on chemical imidization kinetics is not much. But it is now established that the cyclization of n-phenylphthalamic acid of the polymer segment with acetic anhydride proceeds smoothly at RT in NMP in the presence of a tertiary amine (Fig. 10.1.14) [2,11,14,16,67,174,180–182].

Other dehydrating agents such as propionic anhydride, n-butyric anhydride, benzoic anhydride etc. may also be

TABLE 10.1.10 Effect of some internal and external factors on inherent viscosity and hence the molecular weights of poly(amic acid) [2,11,86–120,166,181][a].

Factor	Effect	Optimal choice
Monomers quality	Purity of monomer negatively affects the reaction propagation kinetics, lower inherent viscosity typically means molecular weight built-up and hence the quality of poly(amic acid)	Highest purity monomers (>99.8%) with impurities at level not more than few ppm. Predried monomer just before polymerization is highly preferred.
Reaction temperature	>25°C, MW decreases, Between 15°C–20°C, MW maximum At <10°C, MW decreases	For higher viscosity, reaction temperature must be controlled in the range of 15°C–20°C
Reaction time	Within the first 10 h. Inherent viscosity and hence the MW increases with increasing time. After 10 h. the viscosity is somewhat stabilized and MW of poly (amic acid) decreases slightly. Prolonged reaction time reduces MW drastically	Polymerization reaction time should not be longer than 15 h; optimal time at 18°C is 8–12 h.
Molar ratio of two monomers (dianhydride/ diamine)	An excess of 1% molar ratio of monomers can reduce MW by 16%–20%	1:1
Concentration of reactants	MW increases with concentration up to 25% solid, but too high concentration of monomers decreases properties of final polyimide product	15%–20%
Solvent	Dipolar, aprotic solvent dissolves monomers readily. Dry solvent with very low moisture level preferred.	Dry NMP, DMAc, BLO, DMF, or mixture thereof with low moisture content (< 0.5%)

[a]*Synthesis of [6FDA + 4, 4′-6F Diamine] poly(amic acid) was done in NMP solvent.*

(1) Acylation of amine with anhydride (chain propagation step)

(2) Spontaneous cyclization of amic acid group with the elimination of water and formation of imide rings (chain growth termination and averaging of chain lengths)

(3) Hydrolysis of amide bonds and formation of free amine free carboxylic acid groups (chain growth termination)

(4) Hydrolysis of terminal anhydride groups and formation of dicarboxylic acid groups (chain growth termination)

(5) Cyclization with elimination of amine and formation of anhydrides ring (scission within chains) leading to di and tetra - acids. Chain lengths averaging due to Reverse reaction.

Fluoro-poly(amic acid)
[in 15%-25% NV in Dipolar Aprotic Solvent]
Where **X** and **A** are defined in Figure 8

FIGURE 10.1.13 Five key polymerization reaction kinetics to consider and control during the synthesis of high molecular weight poly(amic acid) [PAA] [2,11,14,16,174].

FIGURE 10.1.14 Typical mechanism of chemical imidization of poly(amic acid) to polyimide. [2,11,14,16].

used. Typically, triethyl amine, β-picoline, pyridine, methylpyridines, lutidine, N-methylmorpholine, etc are used as tertiary amines. The amine acts as a catalyst as well as an acid acceptor. The acetic anhydride acts as a dehydrating agent. Each mole of water liberated due to dehydration converts acetic anhydride into two moles of acetic acid. The phthalimides are formed by intramolecular nucleophilic substitution at the anhydride by amide nitrogen atom. There is also the possibility of the formation of isoimides by the substitution by the amide oxygen. However, under the close analysis the mechanism of chemical imidization is found to be quite complex, and depends on the type of dehydrating agents, monomer components, solvent and reaction temperature employed [11,16,174,182]. Typical reaction mechanism steps are given in Fig. 10.1.14. It should be noted that the control of molecular weight is very important for preparing high performance polyimides. It has been shown in Table 10.1.10, for example, that the presence of moisture, impurities, side reactions, purity of monomers, reaction temperature, reaction period, monomer quantities, and the molar ratio of dianhydride to diamine are affect the molecular weights of polyimides synthesized.

It is obvious to note that, any impurities may acts such as a chain stopper in the reaction system and usually affect the kinetic chain length, while moisture (water) converts dianhydride into tetracarboxylic acid, thus reducing the reactivity of the dianhydride. In general, the higher the temperature, the lower is the molecular weight. This is associated with the formation of more reactive centers at higher temperatures, thereby leading to a shorter kinetic chain length. The reaction temperature at 20°C or below is optimal. It is very important to control the molar ratio of dianhydride to diamine, as even a slight excess of dianhydride or diamine will reduce the molecular weight to a considerable extent, as illustrated in Table 10.1.11.

Metal ion such as iron may also convert diamine to monoamine during the reaction or upon storage. Monoamine is a chain stopper and may limit the increase of the kinetic chain length.

Molar ratio of dianhydride and diamine monomers

Besides the impurity, an imbalance in the "molar ratio" of Dianhydride to Diamine monomers presence in the

TABLE 10.1.11 Effect of molar ratio of monomers on the molecular weight of a polyimide[a] [2,11,14,16,152].

Dianhydride (molar)	Diamine (molar)	Molar excess (%)	Molecular weight ($\overline{M}_n$)
1.02	1.00	2	38,500
1.01	1.00	1	48,500
1.00	1.00	0	57,000
1.00	1.01	1	46,000
1.00	1.02	2	37,000

[a][PMDA + ODA] poly(amic acid) synthesis reaction was carried out in the DMF solvent.

FIGURE 10.1.15 Possible side reactions that may occur during poly(amic acid) synthesis in NMP. [11,14,16,173,174].

polymerization reaction lead to several undesirable side chemical reactions taking place simultaneously which critically effects the inherent viscosity of poly(amic acid) [PAA] and eventual the molecular weights of the polyimides [PI].

The main side reactions in polyimide synthesis between a dianhydride and a diamine are given in Fig. 10.1.15.

Soluble polyimides can also be prepared by high temperature (140°C−250°C) solution polycondensation in a one-step reaction using *para*-toluenesulfonic acid (*p*-TSA) as condensation catalyst and halogenated aromatic solvents or mixture thereof. [18,19] Research work has revealed that the imidization reaction in-situ in solution, polyimide synthesis begins at 120°C, but is completed over 250°C. However, recovery of imidized polyimides solid encounters problem of total removal of halogenated aromatic solvents or mixture thereof.

In another method, for some polyimides [PI] cases, their poly(amic acid) [PAA] is converted to respective polyimide [PI] by thermal imidization process, in which PAA solutions are gradually heated to high temperature up to 350 until the thermal imidization is achieved as confirmed by the analysis by the Fourier-transform infrared spectroscopy (FT-IR) spectra of sample. In all cases, there

are some difficulties in controlling the molecular weight of the final product at such high temperatures.

Fluoro-polyimides

In 1988 Cassidy et al. (Southwest Texas State University, TX, USA) carried out an extensive review of fluoro-polymers with the financial support from Hoechst Celanese Corp., USA [185]. This report was extensive and had a well-documented database on fluoro-polyimides of that time reported in numerous technical papers, conference papers and patents. Even today this report would serve as a valuable resource to those who would like to venture into fluoro-polymers R&D. Because of the limitation of space in this chapter, the focus has been on only a few selected fluoro-polyimides that had been commercialized [186−214] since 1987, and are briefly reviewed and reported here.

During the past four decades, interest in the polyimide technology has increased in response to an increasing variety of applications in numerous technologies varying from aerospace to medical to microelectronics. However, due to the limited solubility of some of the conventional polyimides in common organic solvents, several well-directed R&D efforts were made by high performance polymer companies and in universities world-wide. Various polyimides with perfluoroalkyl groups have been investigated for their commercial applications.

One of the most attractive and successful attempts in attaining good solubility of conventional polyimides for easy fabrication was demonstrated by Rogers et al. at DuPont Co. in the United States [25−38,81−120,185], and Critchley at UK Govt.'s defense department research laboratories [189] through the introduction of perfluoroisopropylidene groups, for example, 1,1,1,3,3,3-hexafluoroisopropyl (HFIP), into the polymer chain backbone via dianhydride structure [25−28]. The hexafluoroisopropylidene bridged dianhydride was developed and identified as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA). Later it was also discovered that the inclusion of hexafluoroisopropylidene group in the amine portion of the polymer chain also imparted similar solubility [188,190]. The above two hexafluoroisopropylidene bridged diamines and 6FDA based, and a series of fluoro-polyimide products were developed by Vora and commercialized under the trade name SIXEF by Hoechst Celanese Corp., RI, USA [25−31,81−85,185].

- 2,2-bis(3-amino phenyl) hexafluoropropane, that is, (3,3-6F-Diamine)
- 2,2-bis(4-amino phenyl) hexafluoropropane, that is, (4,4-6F-Diamine)

DuPont also developed and marketed NR-150 formulations based on 6FDA and ODA which showed excellent high temperature adhesion properties but were difficult to process because of the presence of condensation volatiles and high boiling solvent residue [184,185]. These fluoro-polyimides exhibit high thermal stability, that is, they retain usable properties at 300°C for months and can even withstand temperature >500°C for a few minutes. Some fluoro-polyimides having hexafluoroisopropylidene groups in both monomers showed optical transparency far greater than conventional polyimides (>70%). These thermally stable polymers transmit solar radiations without appreciable degradation and find application as coating materials to protect solar cells from the solar radiation damage [186−190].

Landis [195] at Hughes Aircraft Co. (El Segundo, CA, USA) reported that acetylene-terminated (AT)-imide oligomers, synthesized from 6FDA and aromatic diamines and end capped with (aminophenyl) acetylene, have improved solubility and lower melting points. These are thermoset polymers and useful as molding compounds for military, aerospace and engineering applications [199]. Later Harris and coworkers [200] at the University of Akron, OH, USA reported a series of polyimide oligomers end-capped with thermally-polymerizable groups in a project for Gulf Oil Co [200,201]. These materials later were commercialized by National Starch & Chemical. Co. NJ, USA, under the trade name THERMID FA-700 [9,12,13,51].

Fluoro-polyimide foam has been reported by Imitec Inc., which was prepared by the reaction of 3,3,4,4-benzophenone tetracarboxylic acid dimethyl ester and 4,4-6F-diamine using microwave energy. The foams have closed cells, good heat and hydrolytic stability and vapor barrier properties [202].

New partially fluorinated monomer, 2,2′-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (BDAF) was synthesized at TRW, Inc. USA under a grant from NASA - Lewis Research Center, and thermoplastic all fluoro-PEI based on 6FDA and BDAF was reported in 1978 by Jones and coworker [129−131] and later by Scola and coworkers at United Technologies and NASA Lewis Research Center [15,203,204]. The technology was licensed by Ethyl Corp and the polyimide product was commercialized under the trade name Eymyd for high performance aerospace applications. However, it was not cost effective for the performance it provided, just like Hoechst Celanese's SIXEF series of fluoro-polyimides. Using Hoechst AG (Germany)'s technology, 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) was produced by Hoechst Celanese Corp. at its Coventry, RI (USA) plant at reasonable cost. However, because of their not so optimal yields during chemical reaction and its need for time-consuming extensive and costly purification steps. Although SIXEF products performed better in a price-to-performance in overall comparison study [3−5,9,11,15,16,205,207].

Synthesis of Fluoro-polyimides and Fluoro-Copolyimides, for example, in the case of [6FDA + 4,4-6F-Deimine] Fluoro-

Polyimide [6F-44 PI] based on 2,2-bis(3,4-dicarboxyphenyl) hexafluropropane dianhydride (6FDA) and 2,2-bis(4-amino phenyl) hexafluoropropane (4,4-6F-Diamine), as per the generalized solution polymerization reaction and chemical imidization scheme (Figs. 10.1.14 and 10.1.16) and due consideration given to the molar ratio of Dianhydride to Diamine (Table 10.1.11) requirement, accurately weighed equimolar amount of high purity, electronic grade 6FDA was added to predissolved diamine solution in freshly distilled NMP to make 15%−30% nonvolatile (NV) solid concentration solution. Reaction mixture is then stirred under an inert atmosphere at carefully selected and controlled temperature for 5−24 h to obtain high viscosity poly(amic acid) [6F-PAA].

Small samples of poly(amic acid) [PAA] always retained for viscosity measurement. Bulk of Fluoro-Poly (amic acid) [6F-PAA] imidized to form Fluoro-Polyimide [6F-44 PI] by in-situ chemical imidization route.

The chemical imidization was typically carried out in the same reactor by the addition of a predetermined mole ratio of β-picoline (catalyst and acid acceptor) base and acetic anhydride (dehydrating agent), afforded successful conversion of Fluoro-Poly(amic acid) [6F-44 PAA] in to Fluoro-Polyimide [6F-44 PI], and solid polymer is obtained by its precipitation and washing in methanol and de-ionized water and subsequent air drying for 24 h and further drying at 100°C overnight in an air-circulating oven [11,38,81−85,107,119,207−214]. Laboratory synthesized Fluoro-polyimides samples tested to determine their solution and intrinsic properties. A list of typical Fluoro-polyimides [6F-PI] and Fluoro-Copolyimides [6F-CoPI] composition is given in Table 10.1.12.

Hoechst Celanese Corp. (HCC) globally sampled these Fluoro-polyimides and Fluoro-Copolyimides to test and develop market requirement projection, which ultimately led to successful limited commercialization of a select few Fluoro-polyimides and Fluoro-Copolyimides under the trade brand name SIXEF (trade name too developed by the Vora) for their niche high-performance engineering applications in microelectronics, aerospace and defense industry sector [213,214].

Due to the excellent gas transport properties and high selectivity for the separation of oxygen over nitrogen and carbon dioxide from air, several fluoro-polyimides and fluoro-copolyimides were widely investigated by Chung for the commercial development of gas separation membranes at the HCC. To support this gas separation membranes development program at the HCC, Vora modified laboratory synthesis techniques to manufacture special in-situ formulation (dope) of fully imidized [6FDA + Durene Diamine] Fluoro-Polyimide under the brand name of SIXEF-Durene and patented for the "spinning" of hollow fibers, which were successfully used in the development of gas separation membrane modules by Chung et al. [113,120]

Chung also carried out systematic study of the blends of pairs of Fluoro-Polyimide [6F-PI] as well as pairs of Fluoro-Copolyimides [6F-CoPI] Compositions [118] and found that each respective polymer pair were miscible having single Tg as shown in Table 10.1.12.

In addition, Chen and Vora later jointly developed several Fluoro-Poly(amide imide) (6F-PAI) polymers having superior thermal properties than commercially available Torlon brand of Poly(amide imide) [PAI] products from then Amoco Corp. USA [54] for molded engineering parts applications [11,88,108,111,115−117].

FIGURE 10.1.16 Synthesis scheme of SIXEF-PI and structures of three SIXEF fluoro-polyimides. [11,81−85,149,207−214].

Processes and properties

Changes in the world economy and reduction in abundance of natural resources have contributed to the increased use of high-performance engineering thermoplastic and thermoset materials. [2−5,9,10,16,20,215−225] Currently, polyimides containing both aromatic and heterocyclic structures in the main-chain are one of the best high-performance engineering plastics. Polyimides have many unique properties among which are outstanding stability toward thermal, oxidation and irradiation;

TABLE 10.1.12 Blends of SIXEF fluoro-polyimide [6F-PI] and fluoro-copolyimides [6F-CoPI] compositions and identification code [11,25−38,81−85,118].

Dianhydride monomers			
PMDA		BPDA	
BTDA		ODPA	
6FDA			
Diamine monomers			
3,3'-6F-diamine		4,4'-6F-diamine	

Polymer Code	3,3'-6F-diamine		Polymer Code	4,4'-6F-diamine		Blend of polymers	
	Dianhydride	Tg1		Dianhydride	Tg2	Ratio-(50:50)	Tg
6F1M	6FDA	250.5	6F1P	6FDA	318.5	6F1M + 6F1P	275.0
6F2M	BPDA	267.0	6F2P	BPDA	343.0	6F2M + 6F2P	279.3
6F3M	BTDA	239.0	6F3P	BTDA	304.0	6F3M + 6F3P	252.8
6F4M	OPDA	224.5	6F4P	OPDA	305.0	6F4M + 6F4P	242.7
6FC1M	PMDA + 6FDA	270.9	6FC1P	PMDA + 6FDA	354.0	6FC1M + 6FC1P	295.0
6FC2M	PMDA + BPDA	280.0	6FC2P	PMDA + BTDA	375.0	6FC2M + 6FC2P	295.5
6FC3M	PMDA + BTDA	261.0	6FC3P	PMDA + BTDA	349.5	6FC3M + 6FC3P	273.4
6FC4M	PMDA + OPDA	233.0	6FC4P	PMDA + OPDA	347.0	6FC4M + 6FC4P	258.4

excellent mechanical properties, good electrical properties and low coefficient of thermal expansion (CTE) as well as dimension stability. Thus polyimides have found uses as high-temperature stable materials in adhesives, dielectric coatings, photoresists, aerospace composites, electronics, optoelectronics, fiber optics, for membrane separation etc. applications.

Brief introduction on processing of polyimides

The service temperature and durability are essential for modern high performance materials. The thermal stability of many aromatic polyimides can exceed 600°C in nitrogen and 500°C in air and can be used at high temperatures for a longer period of time [159].

Processing of most polyimides is not an easy task because of the characteristic high *Tg*, and high or no melting point. Besides, many polyimides are insoluble and infusible, and cannot be processed by conventional polymer processing equipment [2−5,9−11,16,20].

The processing difficulty may be the main reason why only a few high-temperature stable high-performance engineering polyimides have been successfully commercialized [2−5,9−11,16,20,177,184,185]. Therefore it is most desirable to research, design molecular architecture of new compositions followed by synthesizing new polyimides with conventional thermoplastic or thermoset characteristics but with high performance regarding thermal, mechanical and electric properties. The current processing methods for producing a few well-known commercial polyimides employed globally are reported in Table 10.1.13.

Most powder of thermoset polyimides are processed by a very few molding methods due to cross-linking mechanism upon application of heat during the processing. Some thermoset polyimides even needs specially designed and built mold and well-monitored temperature regiment during molding process to process in to shaped articles.

There are, however, several other ways solid TPIs such as poly(ether imide) [PEI], poly(amide imide) [PAI]

TABLE 10.1.13 Typical processing methods for commercial polyimides [2–5,9–11,16,20,177,184,185,215–225].

Trade name	Physical form	Main composition (dianhydride + diamine)	Processing method	Company
KaptonH	PAA solution	[PMDA + 4,4-ODA]	Film casting	DuPont
Vespel	PAA powder	[PMDA + 4,4-ODA]	Powder metallurgy	DuPont
PyralinML	PAA solution	[PMDA + MDA]	Thin film enamel	DuPont
NR-150	Solution	[6FDA + *m*-PDA]	Lamination	DuPont
ULTEM 1000	Pellet	[BPADA + *m*-PDA]	Molding	GE Plastics
ULTEM 1010	Pellet	Phthalic anhydride end capped [BPADA + *m*-PDA]	Extrusion molding	GE Plastics
ULTEM 1000	Solution	[BPADA + *m*-PDA]	Fiber spinning	GE Plastics
PMR-15	PAA	Nadic anhydride end capped oligomer of [PDA + MDA]	Lamination	NASA
LARC-TPI	PAA solution	{BTDA + 3,3-DAB]	Lamination	NASA
Polyimide2080	Powder	[BTDA + 20%MDI +80%TDI]	Molding	Upjohn Co.
UPILEXR	PAA solution	[BPDA + 4,4-ODA]	Film casting	Ube Industries
UPILEXS	PAA solution	[BPDA + *p*-PDA]	Film casting	Ube Industries
Thermid7000	Solid	Acetylene terminated oligomer of [6FDA + APB]	Molding	National Starch
SIXEF-33	Solid	[6FDA + 3,3-6F-Diamine]	Compression molding	Hoechst Celanese
SIXEF-44	Solid	[6FDA + 4,4-6F-Diamine]	Compression molding solution casting	Hoechst Celanese
SIXEF-Durene	Formulation	[6FDA + 1,4-Durene Diamine]	Hollow fiber spinning	Hoechst Celanese

and poly(siloxane imide) [PSI], etc. can be successfully processed by most conventional molding and spinning process in to shaped article and fibers, respectively. Since these type of polyimides have lower *Tg* and melting points owing to the more flexible Ether (–O–) bond and Siloxane (–Si–O–) bond respectively present in the polymer's main chains, such flexible links provides easy chain rotation/wiggling of polymer chain upon heating, hence they can be processed on conventional molding process equipment. It has been reported in literature that some PEI possess T_m as high as 400°C and *Tg* of 260°C [2,10,11,14,15,52,53,204,225].

For the processing of any of these types of polyimides within the thermoset and TPIs classes, obviously, one has to strike a balance between the minimum thermal processing temperatures to be used and polymer's thermal degradation temperatures. However, the heat resistance of such polyimides would always is reduced owing to the incorporation of flexible linkage in polymer/monomer chains [2,10,11,14–16].

Brief summary on processing technology for high-performance thermoset and thermoplastic polyimides polymers

There are several processes used in the aerospace and composites industries to manufacture large dimension and complex-shaped glass, ceramics, graphite, carbon, aramide, and even polyimide-fiber reinforced composites. Mostly thermoset resins such as BMI, polymerization of monomeric reactants [PMR], liquid epoxy, and/or mostly their special blends in semi-liquid forms or in high% solid concentration formulation in low boiling solvents, have been used as matrix resins. Now due to the need for very complex geometric requirements, several high temperature thermoplastics, such as polyaramides [PAr], polyimides [PI], poly(amide imides) [PAI], poly(ether imides) [PEI], etc. or their specially formulated blends are also widely used, allowing prepreggers to closely match the dimensions of shaped components, and also to repair the final composites products [2,7,10,11,14–16].

Typical processing methods are briefly given below:

Wet lay-up and autoclave molding

It is generally used for larger and complex aircraft composites parts. The process employs prepregs, such as tapes, mats or woven cloth forms and cured using vacuum bag under controlled heating and pressure in an autoclave [2–5,7,11,16].

Filament winding

It is generally used for the fabrication of cylindrical parts: rocket fuel tanks, helicopter blades, etc. It involves the mechanical winding of continuous fiber strands either pre- or post-resin impregnation stage [2–5,7,11,16].

Compression molding

Most TPIs are also compression molded in to sheet/plate of various thickness shaped article in the specially designed and precision engineered molds made from high quality stainless steel. The process is typically used for the manufacturing of parts from powder polyimides and compounded/formulated sheet molding compounds of polyimides under very high pressure and high temperature in controlled condition in an inert atmosphere or in vacuum [2–5,7,11,16].

Pultrusion

Precision parts of constant cross section, such as rectangular beams; tubes, angles, etc. are made by this process. Continuously pulling resin-coated fibers through a heated die results in partially or fully cured parts. The former ones are cured in the final conversion stage in an autoclave [2–5,7,11,16].

Film fabrication

For many polymeric materials which are not melt processable but soluble in organic solvents, such as in the case of many polyimides, solvent casting is the only way to prepare polymer films [2,7,10,11,14–16].

Film fabrication of polyimide can be achieved by

1. draw-down casting of wet film from its poly(amic acid) [PAA] precursor solution on to a flat smooth surface followed by thermally cured/imidized and effective removal of solvent, and water formed due to the imidization reaction to obtain dry fully-imizied polyimide [PI] film;
2. draw-down casting of wet film from a solution of fully-imizied polyimide on to a flat smooth surface followed by thermally heated to remove the solvent (in which its solution was prepared) to obtain dry polyimide [PI] film,
3. extrusion molding of Solid Polyimide resin to obtain solid film of Polyimide [2,7,10,11,14–16].

The thermal imidization process for manufacture of solid polyimide is not always economically feasible to convert bulk of the liquid and solid poly(amic acid), a precursor of polyimide in a manufacturing reactor [2,7,10,11,14–16]. Furthermore, the thermal imidization process in most cases is only good for converting bulk of solution of poly(amic acid) [PAA] in to film (i.e., wet film) into only a thin solid polyimide [PI] film, whereas compression molding of solid poly (amic acid) [PAA] in to thick film/sheet/plate. For example, the commercial manufacturing of Kapton and Upilex films, a proprietary controlled thermal imidization process is applied by DuPont and Ube Industry respectively [2,7,11,16,40,68,69].

According to the information made available [7], typical production of wide width (up to 60 inches) rolls of fully-imidized dry polyimide film (about 20–50 m long is achieved by employing several extra-highly polished multiple sets of minimum 2 m wide stainless steel calendaring drums having progressively extra-large diameter (~>2 m) set-up in a raw (somewhat like in the large-scale printing press in the major newspaper's plant) [7] with each drum rotating at certain specific predetermined speeds and each are maintained at various precalculated certain "useful" temperatures (approximately ranging anywhere from 50°C to 400°C). Typical production process involves [7], first drum receive a well-controlled flow of predetermined thickness wet film (of ~64 inches width) liquid Poly(amic acid) [PAA] formulation from Reservoir, and which is upon half-turn of rotating drum begins to behaves like gel-like film (due to some evaporation of some solvent from its surface), and carefully transferred on to other rotating drum kept at preheated and maintained at even higher temperature. Semi-dry gel-like film of PAA gels further just before the full rotation of the drum, and is again transferred (and at the same time stretched/pulled in direction of rotation) on to other rotating drum with even larger diameter and kept at preheated and maintained at further higher temperature. It is on this drum where the controlled thermal imidization reaction of semi-dry PAA begins to takes place with simultaneously and effective removal of solvent, as well as also water formed as bi-product due to imidization/condensation reaction. This semi-imidized film is further transferred on to another even larger diameter rotating drum maintained at further higher temperature where the final thermal imidization reaction takes place and the fully-imidized and mechanically uniform mono-oriented dry film of amber color polyimide [PI] film with precalculated thickness continuously rolled in to final receiving roller [7].

A typical laboratory method for the preparation of films of polyimide, polyether-imide and poly (amide-imide), etc. polymers

For many polymeric materials which are not melt processable but soluble in organic solvents, such as in the case of many polyimides, solvent casting is the only way to prepare polymer films [2,7,10,11,14–16]. Solutions of poly

(amic acid) [PAA], polyether(amic acid) [PEAA], polyimide [PI], poly(ether-imide) [PEI], poly(amide imide) [PAI], co-poly(amic acid) [Co-PAA], co-polyether(amic acid) [Co-PEAA], Copolyimide [Co-PI], co-poly(ether-imide) [Co-PEI], co-poly(amide imide) [PAI], etc. preformulation samples and ULTEM1000 can be prepared at 15%−30% solid NV concentration level in NMP or other select few solvents or solvent mixture thereof and filtered through a 0.5 μm filter under nitrogen pressure.

Filtered solutions of Polymer are then coated onto glass plates by draw-down using a "Doctor Blade" (Gardner Film Casting Knife, Model AG-4300, Pacific Scientific, USA) controlled with a micrometer with an adjustable gate clearance from 0 to 12.5 mm (0−6250 μm) gap. The coated films are dried in a Nitrogen environment in Glove-box for an hour and then heated gradually in a Lenton Thermal Design (UK) programmable oven from RT to 300°C. The stepwise curing program cycle used was 55°C (1 h), 80°C (1 h), 100°C (1 h), 150°C (1 h), 200°C (1 h), 225°C (1 h), 250°C (1 h), and 300°C (1 h) as shown in Fig. 10.1.17 [2,7−10,14−16,19,30−38,78,81−112,114−118].

During the abovementioned stepwise curing program (heating steps) for preparing corresponding polyimide (PI) film from the poly(amic acid) (PAA), a gradual evaporation of the solvent (or solvent mixture) takes place along with the water that is formed due to the ongoing thermal imidization reaction taking place.

Whereas for the preparation of film from "fully imidized" polyimide solids, their solutions are prepared in the solvent of choice [such as dipolar aprotic solvents like N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO)] or mixture(s) of these solvents. During the stepwise film drying/curing process, a gradual evaporation of only the solvent takes place. After the preprogramed heating cycle, films are allowed to cool down gradually to room temperature (RT). Self-supporting films of various polyimides with average thickness between 20 and 35 m are typically obtained. These films are then stored in a desiccator over pellets of drying agents (also called desiccants), typically calcium sulfate [$CaSO_4$, which is commercially sold under the trade name Drierite by the W.A. Hammond DRIERITE Co. Ltd., OH (United States)] until used for characterization. Just before the characterization, all films are redried in a vacuum oven for few hours at 80°C, thereby removing trace of moisture (if any) adsorbed on or absorbed in the film, and immediately used for characterization [2,7,11,16].

A typical laboratory method for the fabrication of solid film of poly(amic acid), polyether(amic acid), co-poly(amic acid), co-polyether(amic acid) for the FT-IR analysis

Using the above-mentioned procedure, filtered 20% NV Poly (amic acid) [PAA], Polyether(amic acid) [PEAA], Co-Poly (amic acid) [Co-PAA], Co-polyether(amic acid) [Co-PEAA] etc. (synthesized in N-Methyl-2-pyrrolidone (NMP) or in other select few solvents) solution coated on the glass plate using doctors blade to get a uniform thin wet film. Then the

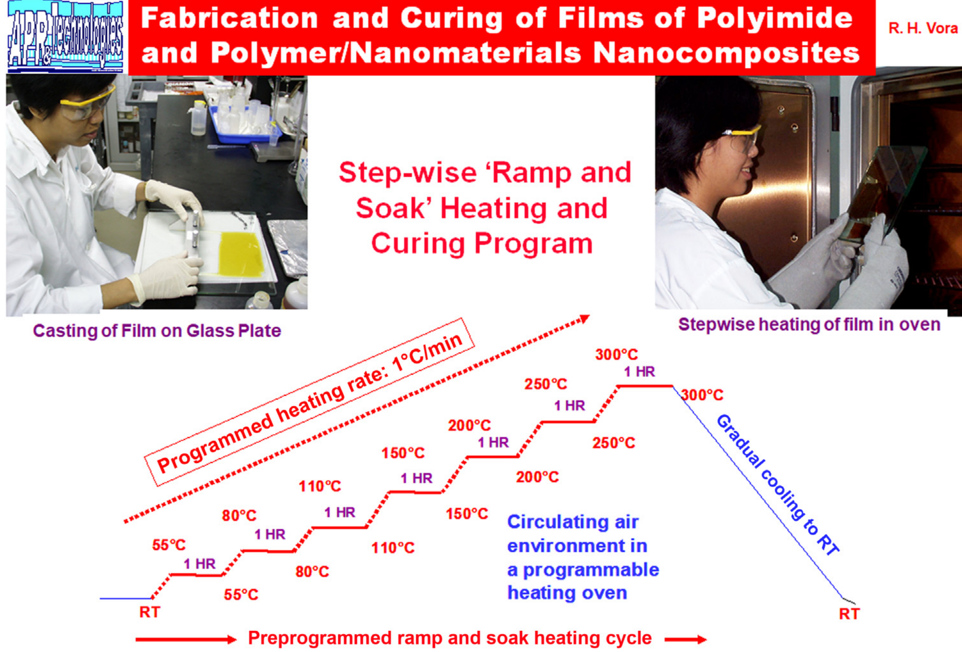


FIGURE 10.1.17 Illustration of stepwise preprogrammed ramp and soak heating and curing cycle for the preparation of films of polyimide [PI], poly(ether-imide) [PEI] and poly (amide-imide) [PAI], and polymer/nanomaterials nanocomposites etc. materials [11,226].

glass plate then carefully and gently dipped into a Pyrex (Dow Corning) glass rectangular baking tray containing de-ionized water. The color of the wet Poly(amic acid) [PAA], Polyether(amic acid) [PEAA], Co-Poly(amic acid) [Co-PAA], Co-polyether(amic acid) [Co-PEAA], etc. films changed from colorless (transparent) to Opaque pale yellow or white due to precipitation of prepolymer in water since all Poly(amic acid) [PAA] typically are hydrophobic in nature.

Solid films of Poly(amic acid) [PAA], Polyether(amic acid) [PEAA], Co-Poly(amic acid) [Co-PAA], Co-polyether (amic acid) [Co-PEAA], etc. gently lifted off the glass plate and washed with copious amount of de-ionized water for about 30 min at RT, then gently wiped dry by lint-free tissue paper (Kimwipe) and further dried in an air circulation oven at 80°Cfor 15 min to get rid of absorbed and adsorbed water inside the pores and on the surface of the film respectively. The solid film of Poly(amic acid) [PAA], Polyether(amic acid) [PEAA], Co-Poly(amic acid) [Co-PAA], Co-polyether(amic acid) [Co-PEAA], etc. stored in a desiccator over dry-rite until used for FT-IR spectroscopy study. A small amount of finely-grounded solid Poly(amic acid) (PA), Polyether(amic acid) (PEAA), etc. film mixed with KBr followed by compressed to a 1 cm round disc which was used for FT-IR analysis.

Thin polymer sheets/plates by compression molding

The TPIs are also compression molded in to thin sheet/plate form in a 10 cm × 10 cm square special steel alloy mold between heated platens of a Karver Hydraulic Press [the press fitted with 30 cm × 30 cm square platen having internal heating elements (Karver & Co, USA)] at 320°Cat 500 psi for 7 min. Almost colorless to light yellowish to yellow color transparent rectangle sheet/plate of 1.0−1.5 mm thickness obtained and then placed in a desiccator over dry-rite until used for characterization.

Characterization of polyimides

Characterization techniques

Characterization of the chemical and physical properties of polyimides is very important. Viscometry, Rheometry, FT-IR, Ultraviolet (UV)-visible spectroscopy, Nuclear magnetic resonance spectroscopy, Gas chromatography, Gel permeation chromatography (GPC)/Size exclusion chromatography (SEC), Atomic absorption spectroscopy (AAS), Mass spectrometry, Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), Thermomechanical analysis (TMA), Dynamic mechanicat analysis (DMA), Dynamic mechanical thermal analysis, Thermo-oxidative stability (TOS), DEA, Electrochemical impedance spectroscopy, Single-crystal X-ray diffraction analysis, Wide-angel X-ray diffraction analysis (WAXD, i.e., XRD), X-ray photoelectron spectroscopy, Energy dispersive X-ray analysis (EDX or EDAX), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Atomic force microscopy (AFM), Hot-stage microscopy, Goniometer, Mechanical testing, etc. among many are very useful techniques. Table 10.1.14 lists the characterization capabilities of some of these techniques in the analysis of polyimides [2,11].

A comprehensive list of characterization techniques for most Organic and Inorganic Chemical, Monomers, Polymers and Nanomaterials, Nanocomposites, Product formulation, etc. therefrom are illustrated in Fig. 10.1.18.

The details of some of the characterization methods and their respective typical analytical instrument used are provided as follows:

Elemental analysis

Number of elemental species present in Monomers and Polymers are determined by the AAS. Additionally,

TABLE 10.1.14 **Some of the typical instruments for characterization of physical properties of poly (amic acid), polyether(amic acid), polyimide, polyether-imide, co-polyamic acid, co-polyether (amic acid), copolyimide, co-polyether-imide, etc. [2,11].**

Instrument	Determination
TGA	Thermal stability, decomposition temperature, degradation mechanism
DSC	*Tg*, mp, and degradation mechanism, LCP.
TMA	*Tg*, mp. CTE
Tensile testing machine	Tensile strength, elongation, modulus
Dielectric analysis	Dielectric constant, dielectric strength, dissipation factor, resistivity
X-ray diffraction	Crystallinity of polyimides
GPC	Molecular weight
Viscometry	Viscosity and molecular weight for polyimides

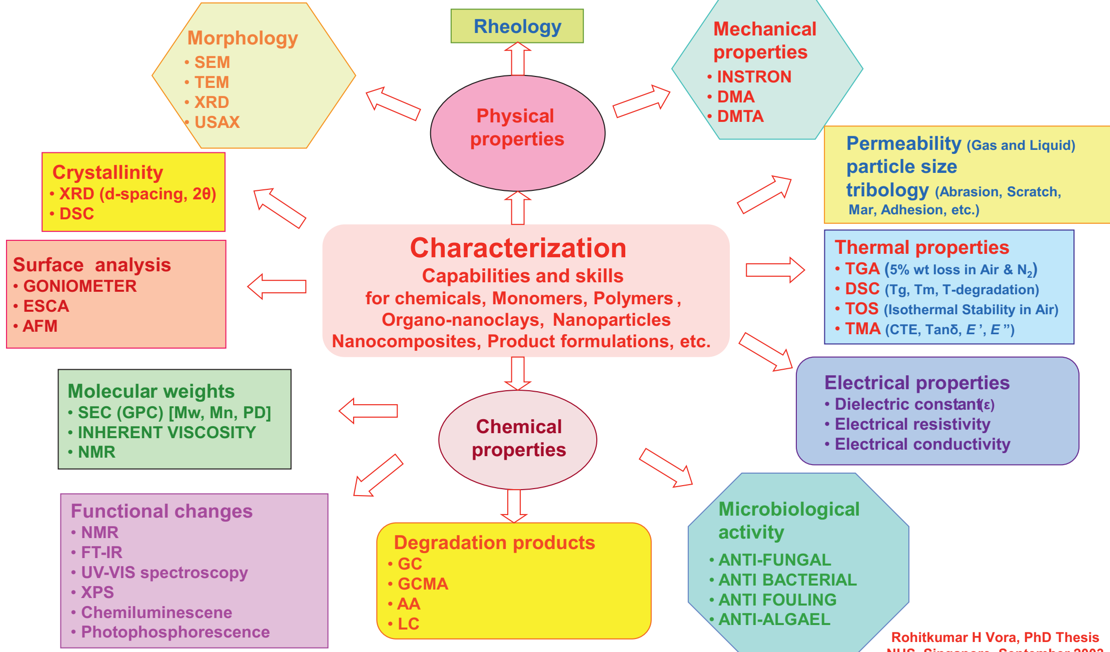


FIGURE 10.1.18 Comprehensive list of typical characterization techniques for most organic and inorganic chemical, monomers, polymers and nanomaterials, nanocomposites, product formulation, etc. therefrom [11,226].

quantification of accurate molar masses of Monomers and Polymers is determined by from the chemical mass-spectra recorded using Mass Spectrometer, for example: Micromass VG Analytical 7035 Spectrometer.

Viscosity measurement

Intrinsic viscosity [η_{int}]

The solution viscosity is a measure of the size or extension of polymer molecules in space.

The principle of viscometry is based on the determining the efflux time t required for a specified volume of polymer solution to flow through a precision capillary tube of a viscometer (Fig. 10.1.19) which has been calibrated using liquid compound of known viscosity and density, and compared with the corresponding efflux time t_0 for the solvent at identical given temperature. However, the precision of measurement varies with sample type, solvent and experimental conditions used including cleanliness of viscometer and temperature at which sample is measured. Typically precision varies from 1% to 5% [150,151,226–232].

Molecular weight is related to the viscosity of polymer solution. The molecular weights of polymers have been correlated to the viscosity at specific solvent and temperature condition at specific sample concentration. Therefore by knowing the Intrinsic Viscosity [η_{int}], one could easily determine the molecular weight of polymer by using Mark-Houwink-Sakurda [150,151,226–232] equation:

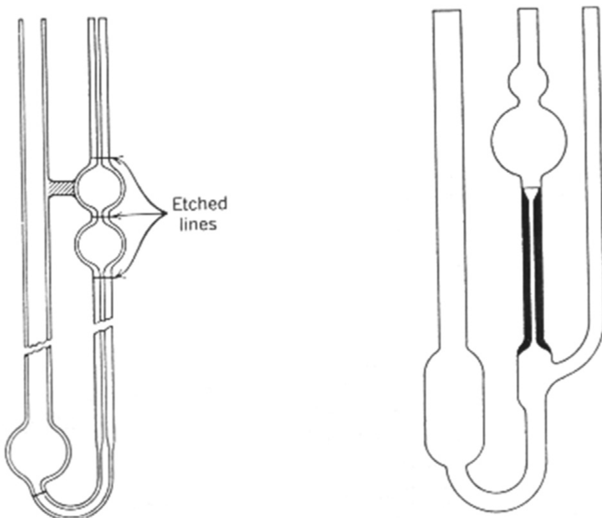


FIGURE 10.1.19 Capillary viscometers commonly used for the measurement of solution viscosities of polymers.

Mark-Houwink-Sakurda equation:

$$(\eta_{int}) = K.\overline{M}_v^a \qquad (10.1.1)$$

where $\overline{M}_v$ is the viscosity-average molecular weights.

Both K and a are empirical (Mark-Houwink) constants that are specific for a given polymer, solvent and temperature.

Inherent viscosity (η_{inh})

Inherent Viscosity [(η_{inh}), a logarithmic viscosity number] [150,151,226–232] was calculated using the following equation:

$$(\eta_{\text{inh}}) = \frac{\ln(t/t_0)}{C} \qquad (10.1.2)$$

Where t_0 is flow time of solvent, t is flow time of solution and, C is the concentration of the sample in g/dL.

For example, 0.25 g of solid polymer dissolved in 50 mL of solvent (NMP) in a volumetric flask to get a concentration of 0.5 g/dL. The solution filtered using Whatman filter (0.5 μm) paper before being filled into the viscometer.

The flow time t of the Poly(amic acid) [PAA], Polyether (amic acid) [PEAA], Polyimide [PI], Poly(ether-imide) [PEI], Co-Poly(amic acid) [Co-PAA], Co-polyether(amic acid) [Co-PEA], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. preformulation samples prepared in NMP at a concentration of 0.5 g/dL were measured according to ASTM 2515/D446 at 20°Cusing a modified Cannon Fenske viscometer or Schott-Gerate Viscometer at RT (25°C) and on an average of six readings taken for calculation. inherent viscosities (IV) (η_{inh}) of sample is then calculated using Eq. (10.1.2).

Bulk viscosity

The bulk viscosity of master batch Poly(amic acid) [PAA], Polyether(amic acid) [PEAA], Polyimide [PI], Poly(ether-imide) [PEI], Co-Polyamic Acid [Co-PAA], Co-polyether(amic acid) [Co-PEA], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. preformulation samples is determined at RT (25°C) at a fixed shear rate (5 rpm) using Brookfield Programmable Rheometer Model DV-III [with Rheocalc Software, and Brookfield Constant Temperature Water Bath (model TC-200/500)] and CP42 spindle. About 1 mL of bubble-free sample is used. Prior to analysis, sample is allowed to reach temperature equilibrium for 1 min before taking reading. Readings are automatically recorded by the Rheocalc software. Average of 6 readings taken for viscosity calculation.

Rheology

Complex melt viscosity

The Dynamic Mechanical Spectroscopy of solid polymer sample is very useful for the prediction and correlation of the time and temperature dependent stiffness, as well as for polymer melts, the viscoelastic properties under steady shear melt flow condition.

The steady shear melt viscosity and normal stress difference are measured by torsional flow between parallel plate of the Rheometric Mechanical Spectrometer. The data at low shear rates (or frequencies) are more sensitive to difference in molecular structure than are the high shear rate data obtained by capillary viscometry [233].

Rheometric Mechanical Spectrometer (model ARES) used to determine melt rheology and processing stability at 50°C above the Tg between two parallel plates having geometry of 2.54 cm, and operating frequency in the range 0.001–100 radian per second (rad/s). The system was connected to an IBM PC through interface for data acquisition. Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymer samples are first molded into disks and melted in the parallel plate test fixture of the Rheometer with minimum exposure to air. The polymer's complex viscosity is then measured as a function of time for 30 min at a frequency of 1 radian per second (rad/s) used to determine melt rheology and processing stability at 50°C above its Tg [233].

Fourier-transform-infrared spectroscopy

FT-IR is used for the identification of organic, inorganic compounds, and polymers. For organic polymers, the groups of atoms such as $-CN$, $-NO_2$, $-SO_2$, $-OH$, $-CO_2$, $-CH_3$, $-COOH$, $-C_6H_5$, $-NH_2$, etc. would absorb the energy in the infrared region at specific and predictable frequencies, thus allowing the identification of the specific functional groups within molecules relatively easy. The typical spectral analysis of the unknown spectrum is made by correlating group's absorbing frequencies, relative intensities, and comparing with the reference spectra of known compounds. In most cases this is far superior in speed and accuracy than the classical chemical methods.

The FT-IR is a very powerful tool for characterization of for the solids or films and solution samples of Organic Monomers, Poly(amic acid) [PAA], Polyether(amic acid) [PEAA], Polyimide [PI], Poly(ether-imide) [PEI], Co-Poly(amic acid) [Co-PAA], Co-polyether(amic acid) [Co-PEA], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymer.

FT-IR spectroscopy employs an interferometer to observe the spectral resolution elements simultaneously, rather than scanning through gratings and prism to disperse the infrared radiation. The advantage, resulting from such changes were increased light throughput, speed, and detection sensitivity [11,14,180–182,231,234]. The group absorption changes for chemical compounds are very easy to determine using FT-IR spectroscopy.

The FT-IR spectra of the Poly(amic acid) [PAA], Polyether(amic acid) [PEAA], Polyimide [PI], Poly(ether-imide) [PEI], Co-Poly(amic acid) [Co-PAA], Co-polyether(amic acid) [Co-PEA], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. solids are obtained using Perkin Elmer FT-IR model with Spectrum 2000 software, and a film holder and/or compressed KBr disk or NaCl crystal disk. The typical scanning range used ranged from 4000 to 400 cm^{-1}. Some useful group absorptions for Organic structural groups are listed in literature [11,14,180–182,234–238] and also for quick reference,

some useful specific absorptions band of several important organic groups including carbonyl, amide, imide, and acid and amine, etc. present in the Poly(amic acid) [PAA] and Polyimide [PI], and in the monomer (dianhydride and diamines) and Montmorrilonite MMT Clay (a.k.a. MMT NanoClay) are listed from literature [2,11,14,180−182,234−244] in Table 10.1.15.

Gel-permeation chromatography (a.k.a. size-exclusion chromatography)

To improve physical and thermomechanical properties of a polymer, it is important to control its molecular weight and the molecular weight distribution during polymerization. GPC (a.k.a. SEC) is one of the quickest methods to

TABLE 10.1.15 Some useful specific absorption bands of certain functional organic group typically present in the chemical structures of monomers, poly(amic acid), polyimide, etc. polymers. [2,14,16,180−182,215,226,232,234−244].

Organic group	Absorption band (cm^{-1})	*Intensity*	Origin
Aromatic imides	1780	*Strong*	C = O asymmetrical stretch
	1720	*Very strong*	C = O symmetrical stretch
	1380	*Strong*	C − N stretch
	725		C = O bending
Isoimides	1795 − 1820	*Strong*	Iminolactone
	1700	*Medium*	Iminolactone
	921 − 934	*Strong*	Iminolactone
Amic Acid	2900 − 3200	*Medium*	COOH and NH_2
	1710	*Strong*	C = O (COOH)
	1660	*Strong*	C = O (CONH)
	1550 amide II	*Medium*	C − NH
Anhydrides	1820	*Medium*	C = O
	1780	Strong	C = O
	720	Strong	C = O
Amines	~ 3200 two bands	*Weak*	NH_2 symmetrical structure (V_s)
			NH_2 asymmetrical structure (V_{as})
			[where $V_s = 345.53 + 0.876\ V_{as}$]
Montmorillonite (MMT) Nano Clay $[(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O]$. [233−236]			
Silanols, Water (H-O-H)	3635, 3400	*Strong*	O-H Stretching vibrations
Water (H-O-H)	1635	*Strong*	O-H Bending vibrations
	1000 − 1150 cm^{-1}		Si-O Asymmetrical stretching vibrations
	1046 cm^{-1}	*Strong*	Si-O stretching
Aluminum Hydroxide (AlAlOH)	900−950 cm^{-1}		Deformation of Aluminum Hydroxide (AlAlOH)
Hydroxy (-OH)	940, 929		Al-OH Bending vibrations
Silicate	795, 760		Si-O Stretching
Silicate	700, 420, 432		Si-O Bending vibrations
Aluminosilicate	528 cm^{-1} and	*Strong*	Si−O−Al deformation vibration, groups
Silicon	472 cm^{-1}	*Strong*	Si−O−Si deformation vibration

The text in *ITALICS* has technical significance for spectral identity and data presentation on the 'observed' FT-IR peak(s) at a given/assigned wavelength for 'very specific' organic functional group(s) in a Table in the published technical articles/chapters.

obtain relative molecular weights, and its distribution. GPC is also used to detect the number of components as well as branching in polymer sample, and to get information about polymer conformation and co-monomer distribution as a function of molecular weight.

The main use of GPC is to obtain quantitative information about oligomers and polymers having molecular weights relative to a polystyrene standard (an internal reference) within the range of a few hundred to a few hundred thousand. GPC is a method which separates molecules on the basis of their hydrodynamic volume or size (it is true only when there is no interaction between the column packing resin and the polymer sample). This is achieved by passing the polymer sample through a set of columns packed with porous resinous particles (referred to as the stationary phase) of controlled pore size. Molecules having smaller sizes will diffuse deeper in to pores of stationary phase, whereas, the larger molecules will have a lesser tendency to diffuse. As a result of this diffusion phenomenon, the order of elution is based on the hydrodynamic sizes (or molecular weights of polymer species) of the molecules. Hence, the larger molecule elutes faster. Since columns packed with different pore size resin are available, GPC is capable to investigate a wide range the molecular sizes from a very wide to narrow, depending on the appropriate selection of column. Typically, GPC is equipped with a detectors (e.g., UV/Visible, refractive index, etc.), which when interfaced to a differential viscometer. A universal calibration curve correlating the product of the intrinsic viscosity and molecular weights with retention time can be obtained for a set of preselected polystyrene standard [245,246].

Some of the fully thermo-imidized polyimides usually do not dissolve in common organic solvent as they are solvent resistant. Besides, the GPC measurement of polyimides were further complicated by strong interaction between polar polymer, solvent and also with stationary phase due to presence of "polyelectroclyte" effect [247−249]. However, such effect can be minimized or suppressed by adding electrolytes salt such as LiBr or H_3PO_4 into mobile phase and polymer sample dissolved in such eluent mixture [248,249].

The relative molecular weights [$\overline{M}_n$, $\overline{M}_w$ and the polydispersity (PD)] of solid Poly(amic acid) [PAA], Polyether(amic acid) [PEAA], Polyimide [PI], Poly(ether-imide) [PEI], Co-Poly(amic acid) [Co-PAA], Co-polyether(amic acid) [Co-PEA], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymer solids determined using a Waters GPC system containing Waters 2690 separation module and Waters 2487 UV detector and three Gelpack GL-S300MDT-5 (Hitachi) columns of size 8×300 mm, packed with polystyrene gel having a size exclusion limit of 2×10^8 connected in series, and housed in an oven maintained at 40°C.

The GPC system is always calibrated using at least 10 narrow molecular weight distribution polystyrene (Polysciences Corporation, USA) standards having a wide molecular weight range from 4000 to 2000,000 (Table 10.1.16). Mixture of THF: DMF (1:1) containing 0.06 mol LiBr and 0.06 mol H_3PO_4 used as mobile phase to suppress the "polyelectrolyte" effect typically observed for Poly(amic acid) [PAA], Polyether(amic acid) [PEAA], Polyimide [PI], Poly(ether-imide) [PEI], Co-Polyamic Acid [Co-PAA], Co-polyether(amic acid) [Co-PEA], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. type of polymers [15−19,32−38,70−78,81−113, 117−120,219−221,250−277]. The mobile phase is filtered through 0.2 μm PTFE filter (Millipore). The UV detector instead of IR detector, simply because, for the above mobile phase mixture UV detector is very sensitive and provides high resolution, and also a stable base line. Conditions used were wavelength 270 nm, flow rate 1 mL/min, injection volume 200 μL and sample concentration 1 mg/mL. The polymer samples are predissolved in above eluent mixture and filtered through 0.45 μm PTFE-PP 13 mm filter (Lida Manufacturing) just prior to injection. Data is acquired from the Waters 2487 UV detector using Millennium 32 software. Relative molecular weights [$\overline{M}_n$, $\overline{M}_w$ and PD] are calculated against the above polystyrene standards as per the procedure reported in the literature [11,32−37,245−249].

Density of polymers

The densities of dry polymer thin plates were measured by AG204 Delta-Range Mettler Toledo with a density

TABLE 10.1.16 Molecular weights of polystyrene standards used for GPC calibration. [11,32−37,245−249].

GPC calibration	
Calibration standards (polystyre)	Mol. Wt.
1	2000,000
2	900,000
3	488,000
4	400,000
5	320,000
6	200,000
7	80,000
8	30,000
9	12,900
10	4000

determination kit using the displacement technique [251]. The samples were cut into 30 × 20 mm. Before the measurement, the samples were dried in a vacuum oven overnight at 120°C to remove absorbed water. At the RT of 20°C, the weight of dry sample was W_1, whereas the weight of the dry sample immersed in ethanol solvent was W_2, and ethanol solvent density at 20°C was 0.78934. The polyimide sample density was obtained from the equation:

$$\rho = \frac{W_1}{(W_1 - W_2)/0.78934} \tag{10.1.3}$$

The densities ρ (g/cm^3) of polymer samples are determined and tabulated for reference.

Solubility of polymer films

The solubility of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymers films at RT was determined by dipping approximately 1 × 1 cm square film samples in capped vials containing selected solvents and 0.1 N fuming sulfuric acid solution in DI water, and kept on IKA Laboratechnik Horizontal Shaker (Model No. K3501 (digital) from IKA Werke GmbH & Co. KG Staufen, GERMANY) at RT [226]. The levels of solubility of samples were visually checked after 24 h, and the observed solubility is tabulated in for each polymer.

Hydrolytic stability

% Moisture absorption measurement of thin film samples of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymers calculated from the difference in weights of the “predried” (at 100°C for 1 h) film sample (W_0) and the “wet” film sample (W) of approximately 1 × 1 cm square measured with Sartorius Ultra Microbalance (Model YDP-03-OCE, with weight reading range of 0.001 mg to 5.1 gm. Predried and weighed film samples were dipped completely in de-ionized water in glass vials. The vials are immediately sealed and maintained at 50°C for 100 h. After 100 h of wetting, film samples taken out of the vials and quickly patted dry using lint-free tissue papers and re-weighed immediately.

$$\%\ \text{Moisture absorption} = \frac{W - W_0}{W_0} \times 100 \tag{10.1.4}$$

Mechanical properties

The physical properties of a solid polymer are determined under a variety of loading and test environmental conditions. Continum mechanics provides mechanical testing with an analytical tool for understanding polymer’s behavior and performance which are interpreted in terms of stress-strain states. The polymer film or bar specimens are loaded at a constant rate of deformation and stress-strain data are collected continuously. Most polymers exhibit viscoelastic behavior. Thus the stress-strain data are time and temperature dependent and therefore, also dependent on rate of loading. From the analysis of these data mechanical properties such as Young’s modulus (which is a measure of rigidity), ultimate stress at break (a measure of strength), ultimate deformation (elongation) at break and other properties can be calculated [252,253].

Mechanical properties of films or compressed sheet/plate of solid powder of an average thickness 1 mm of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymers determined using a fully-computerized Instron Mechanical Analyzer System (model 5548 from Instron Corp. Canton, MA, USA) using 0.2 cm wide and 4.00 cm long samples with a clamp distance of 2.00 cm [226] as per the ASTM Method-D 882-95a [252].

Thermal properties

Thermal transition in polymers

The thermal transitions, such as: Meting Point (mp) and Glass Transition (Tg) can be measured by the DSC, Thermo-Mechanical Analyzer (TMA), and DMA. The most convenient and simple method is the DSC.

Polymer scientists pays close attention to the relationship between the polymer chain structure (repeat unit) and the Tg, and try to understand the morphology (crystalline, semicrystalline, amorphous nature of the polymeric materials, and use DSC for determining the onset temperature at which thermal transition occurs which, thereby also help to understand and establish correct softening and melting temperature of a given polymeric materials.

Polymer engineers uses thermal transition information derived from the DSC data of the given polymeric materials to establish the correct and cost-economical processing parameters at which such polymeric materials can be melt-processed by the conventional molding methods (such as, injection molding, extrusion molding, thermoforming, fiber-spinning, compression molding, etc.) into the shaped articles for industrial and consumer use applications.

Differential scanning calorimetry

DSC is a technique for studying the thermal behavior of materials as a function of temperature. They undergo

physical or chemical transformation with absorption or evolution of heat or with a change in heat capacity. A glass transition (Tg) will be recorded as a more or less sudden increase in heat capacity. Melting and crystallization are recorded as endothermic and exothermic peak, respectively. Integration of these peaks permits quantification of the transition. Glass transition is the property of only the amorphous portion of a semi-crystalline polymer in which the polymer undergoes transformation from rubbery to glassy phase [2,11,14,16,259].

Meting point (mp) of monomers and polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly (ether-imide) [Co-PEI], etc. polymers solid and/or film determined by a DSC model DSC-2920 from TA Instruments with Pyris Software. Sample temperature and heat flow rate are calibrated using a tiny crucible made of pure Indium metal as a standard. Temperature Scans is run at a heating rate of 10°C/min always in flowing nitrogen (10 mL/min). Sample is first heated from the RT to 425°C in the first heating cycle, and allowed cool down gradually from 425°C to 50°C in the cooling cycle to remove the previous heat history of the sample. Such sample is again heated for the second time at a heating rate of 10°C/min from 50°C to 425°Cand thermal transition data is simultaneously collected and plotted. Tg of given polymeric material solids and/or their films are determined from the second heating cycle of DSC. However, in some cases, the Tg transition is not so clear in DSC curves, making the accurate determination more difficult. (Tg) transition can also be clearly determined from the dimensional change of this polymer by thermomechanical analysis (TMA).

Estimation of glass transition (Tg) of copolymers

The Tg (i.e., Tg_{Co}) of a given copolymer determined by the DSC can also be roughly predicted and correlated from the DSC data calculated using the **Fox Equation** given as follows: [255]

$$\frac{1}{Tg} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2} \quad (10.1.5)$$

where W_1 = Weight fraction of homopolymer 1; W_2 = Weight fraction of homopolymer 2; Tg_1 = Glass transition temperature of homopolymer 1; Tg_2 = Glass transition temperature of homopolymer 2.

The weight fractions of homopolymer 1 (W_1) is calculated using the following equation:

$$W_1 = \frac{m_1 M_1}{(m_1 M_1) + (m_2 M_2)} \quad (10.1.6)$$

where m_1 and m_2 are molar fractions of homopolymer 1 and 2, and M_1 and M_2 are the molecular weights of homopolymer 1 and 2 respectively.

Or

The weight fractions of homopolymer 2 ($W2$) is calculated using the following equation:

$$W_2 = \frac{m_2 M_2}{(m_1 M_1) + (m_2 M_2)} \quad (10.1.7)$$

where m_1 and m_2 are molar fractions of homopolymer 1 and 2, and M_1 and M_2 are the molecular weights of homopolymers 1 and 2 respectively.

It is important to note that if properly synthesized, the newly designed copolymer compositions would show only a single glass transition temperature (Tg_{Co}) in the DSC curves instead of two or more Tg transition corresponding to the Tg of individual homopolymer-1 and homopolymer-2 (if) present unreacted in the new copolymer.

In addition, DSC data is also used to find proper approaches to determine correct molar composition of the monomer reactants necessary to synthesize newly designed polymer and copolymers with having a preselect lower or higher Tg values, and thereby making the newly synthesized polyimides more tractable and processable without sacrificing their other outstanding properties [2,14,16,256].

Thermomechanical analysis

TMA is a technique in which the deformation (dimensional change) of a polymer film sample is measured under nonoscillatory (static) load as a function of controlled temperature change rate. Stress can be applied to the sample during analysis. The TMA can be run with penetration (or compression) or an expansion probe. In compression mode under controlled temperature change rate, due to its high sensitivity to dimensional change, the Tg is more accurately determined for film sample as compared to Tg measured by DSC for the identical sample [254–256].

Coefficient of thermal expansion

The CTE values reported as μm/m°C or ppm/K unit and **CTE** Tg of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymer films determined by a thermal mechanical analyzer (TMA) [model TMA-2940 from TA Instruments] at a heating rate of 5°C/min in air. (ASTM method D 696). TMA also used to determine Tg of KaptonH film.

Dynamic mechanical analysis

DMA is used to measure the dynamic modulus and damping of polymer material under oscillatory load as function of temperature. The DMA uses the principle of forced

amplitude for measuring the viscoelastic properties of sample as a function of temperature. Most polymers show viscoelastic behavior in which a portion of the deformation energy is dissipated in other form of energy such as heat. The DMA compensates for this energy loss by an in-phase drive signal which keeps the sample in a continuous natural frequency oscillation, and maintain a constant amplitude. The size of the force needed for constant amplitude is a measure of sample's energy dissipation (damping). The other measured parameter is the resonant frequency. From these data, the storage modulus G', Tan δ and loss modulus E" of polymer film samples can be determined [254,256].

The storage modulus E' or G', damping coefficient (*tan delta*, i.e. (tan Δ)) and loss modulus G" or E" of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymer films or compressed thin sheet/plate from solid powder of an average thickness 1 mm determined by dynamic mechanical analyzer (DMA) [model TA-DMA-2980 from TA Instruments]. Polymer film samples of size 10 mm in length and 2 mm in width were subjected to temperature scan mode at a heating rate of 3°C/min. in air at a frequency of 1 Hz, and amplitude of 0.2 mm is used during the measurements.

Thermal stability

Knowledge of thermal stability of materials is an important aspect in determining their continuous thermal performance at a given upper-use temperature limit [250,254,256,257].

There are the three major thermal analysis techniques are used for determining thermal degradation and stability of given Materials in in Air or Inert gas environment, as follows:

1. Dynamic thermogravimetric (D-TGA, a.k.a. TGA) (carried out in air or inert gas (e.g. Nitrogen) environment) method;
2. Isothermal thermogravimetric (I-TGA) analysis [carried out in air or inert gas (e.g. Nitrogen) environment] method, and
3. Long-term isothermal aging weight-loss measurement by TOS (carried out in air environment) method,

Of these three techniques, for the most materials sample, thermal analysis by TGA [carried out in air or inter gas (e.g. Nitrogen) environment] is the widely used method because it requires a very quantity of small sample (Liquid, Powder, Particles, Film, Fiber) and the entire study is completed in a few hours.

I-TGA analysis for long-term weight-loss (in air or inert gas environment) is used to establish thermal stability of given polymeric materials for practical long-term continuous use application at a given maximum use temperature. However, this method ties-up TGA equipment for a very long time until the completion of study, and in addition, it only allows one sample at a time (i.e., in other words, multiple samples requires multiple equipment for simultaneous long-term isothermal aging weight-loss measurement study. Hence, for a long-term isothermal aging weight-loss measurement of a series of materials, the use of I-TGA analysis is not at all very practical use of TGA equipment.

Therefore the third very practical analysis technique, long-term isothermal, TOS method (carried out in air environment), is widely used which is carried out in the laboratory setting using a conventional forced air-circulating and time-temperature and heating rate graphemeable oven, and a very sensitive micro-balance.

Thermogravimetric analysis

Thermogravimetric Analysis (TGA) technique determines the change in polymer sample weight as a function of temperature (Dynamic TGA) at a constant heating rate in a given environment [air or inter gas (e.g. Nitrogen)]. As stated above, TGA can also be used to study the change in sample weight as a function of time at a constant temperature by the Isothermal TGA method.

For the thermal degradation temperatures of solid or film samples of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymers determined using dynamic TGA [Perkin Elmer model TGA-7 with Pyris software]. Scans are run at a heating rate of 10°C/min in flowing air or Nitrogen gas atmosphere (10 mL/min). Since Polyimides are organic materials, its totally disintegrates/burned-up by the time temperature in TGA furnace reaches as high as 1000°C. Therefore the% char yield is determined only in flowing nitrogen atmosphere (10 mL/min) at a heating rate of 10°C/min from 100°C to 1000°C [254].

Typically the temperature at which the maximum 5% wt. loss of a given sample occurs is reported and uses for the comparative studies of 5% wt. loss of several polymeric materials to identify which materials lost the least weight at the highest temperature at a constant heating rate set in the given gas [air or inert (e.g., Nitrogen)] environment for all the samples during the D-TGA analysis.

The activation energy by thermal degradation kinetic study using TGA method

In addition data generated from dynamic thermogravimetric analysis (D-TGA), for the thermal degradation [in air or inert gas (e.g. Nitrogen) environment] can be confirmed with those data obtained from use of one of simplest methods among the five kinetic methods, such as Coates and Redfern method [258–260] available for

calculating the thermal activation energy (Ea) needed for the thermal degradation in materials.

The Coates and Redfern method [259] as defined by Eq. (10.1.8):

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\left(\frac{AR}{\phi}\right)\left(1-\left(\frac{2RT}{E_a}\right)\right)\right] - \left(\frac{E_a}{RT}\right) \tag{10.1.8}$$

where α is the fraction decomposed at temperature T, ϕ is heating rate, Ea is activation energy, R is universal gas constant, A is Arrhenius frequency factor.

The activation energy (Ea) can be calculated by multiplying the universal gas constant with the slope of the plot of ln $[-\ln(1-\alpha)/T^2]$ versus $1/T$

This method assumes: (1) that only one reaction mechanism operates at a time; (2) that the calculated activation energy for degradation (E_a) is for this mechanism; and (3) that product disappearance can be expressed by the following basic rate equation

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{10.1.9}$$

For the thermogravimetric analysis, the fraction decomposed α is defined as the ratio of actual weight loss to the total weight loss corresponding to the degradation process, that is,

$$\alpha = \frac{(M_0 - M)}{(M_0 - M_f)} \tag{10.1.10}$$

where, M is the actual weight of the sample, M_0 is the initial weight of the sample, M_f is the final weight of the sample

"k" can be expressed in terms of "T" by the Arrhenius type equation:

$$k = Ae^{-E_a/RT} \tag{10.1.11}$$

For the linear heating rate ϕ (deg/min)

$$\phi = dT/dt \tag{10.1.12}$$

If the reaction order (n) can be assumed to be one, then the plot of ln $[-\ln(1-\alpha)/T^2]$ versus $1/T$ gives a straight line with slope equal to $-E_a/R$

Rao and Bijmoll [260] used the above equation for the determination of activation energy for the thermal degradation of polyimides derived from ether ketone diamines.

The super-imposed Plots of ln $[-\ln(1-\alpha)/T^2]$ versus $1/T$ for each polymeric materials films (tested in air or inert environment) are plotted for the graphical illustration and clear visual presentation of data. And the activation energies (E_a) for thermal degradation for each polymeric materials films (tested in air or inert environment) calculated by multiplying the universal gas constant with the slope of the plot of ln $[-\ln(1-\alpha)/T^2]$ versus $1/T$. and tabulated for comparative analysis.

Thermo-oxidative stability

The oxidative degradation takes place at much faster rate in the air environment than in most inert gas environment at the elevated temperature. As stated above, most the long-term isothermal, TOS study is carried out in the laboratory setting using a conventional forced air-circulating and time-temperature and heating rate-programmable oven, and a very sensitive micro-balance.

Long-term isothermal, TOS study is carried of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymers, and Polymer/Nanomaterials Nanocomposites, etc. materials solid or film samples determined in air for 300 h at 300°C using a Lenton Thermal Design, UK programmable forced air oven. Percent weight loss of accurately preweighed thin film samples was calculated from the difference in their weights after heating at the regular interval (24 h) of time from the original weights measured with Sartorius Ultra Microbalance (Model No. YDP-03-OCE with a weight reading range of 0.001 mg to 5.1 g from Sartorius AG, Göttingen, GERMANY).

X-ray diffraction

Single crystal X-ray diffraction analysis

The single crystal X-Ray diffraction analyses of monomers carried out using Bruker AXS Smart CCD three-cycle diffractometer with a Mo Kα radiation wavelength λ of 1.54 Å. ORTEP [261,262] and SMART [263] software used for collecting frames of data, indexing reflections and determining crystal structures. The details of crystal data and structural refinement data are tabulated for the record. Also Ridge Thermal Ellipsoid Plot illustrations [261] of single crystals of monomers are recorded.

Wide-angle X-ray diffraction

The X-ray diffraction can qualitatively provide information on the crystallographic nature (structure), molecular packing and orientation of polymer chains in bulk samples, fibers and films. It is one of the best techniques to determine the crystalline-amorphous nature of polymer sample. The degree of crystallinity of polymer sample is measured as the ratio of the crystalline component to total scattering from both the crystalline and amorphous components. A beam of monochromatic X-rays with wavelength λ is incident on to the polymer sample, and by virtue of the crystallographic atomic arrangement in the polymer, the X-rays are diffracted at various discrete angles (2θ) when the Bragg condition is satisfied. The crystallographic interlayer spacing (d-spacing) solely depends on the lattice structure and the unit cell size. The

intensity of the peak depends on the atomic arrangements within the cell [264].

The WAXD measurements of sample of solid Poly (amic acid [PA], Polyether(amic acid) [PEAA], and that of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], etc. polymer in the form of films or compressed disks of solid powder of an average thickness 1 mm carried out at RT in reflection mode in order to better understand the structure (i.e. chain orientation and order) effect on the solubility and glass transition property.

An X-ray diffraction unit (Philips model PW 1729-10) fitted with Cu − Kα radiation (30 kV, 20 mA) with wavelength λ of 1.54 Å. The scan rate of 0.5°/min. at ambient temperature in the spectral window ranged from $2\theta = 1°$ to 10° and/or $2\theta = 10°$ to $2\theta = 40°$. The diffraction patterns of intensity versus two theta (2θ) were automatically recorded with computer software. The corresponding *d*-spacing value was calculated from the diffraction peak maximum, using the Bragg equation:

$$d = \frac{\lambda}{2\sin\theta} \qquad (10.1.13)$$

Dielectric analysis

Most unmodified polyimides are excellent insulator of electric current due to high resistivity and practically no conductance as shown in Fig. 10.1.20 [265].

Various factors influence such resistive behavior of polymer. These factors are chemical structure, polarization of groups in polymer chain, polymer morphology and porosity, hydrophilicity or hydrophobicity, temperature, impurity or contaminant within and on its surface. The electrical properties that have to be considered when selecting a polymeric material for electrical or electronics insulation coating applications are dielectric constant, dielectric strength, volume resistivity, surface resistivity, dissipation factor, and arc resistance [265]. It is also understood that these properties are affected by the external factors such as temperature, operating frequency and voltage electric field, and other environmental variables.

First let us understand the importance of response of polymeric materials under an applied electric field. When a polymer film is placed between the parallel plates of the DEA instrument and the electric filed is applied, the net result of which causes polarization of polymeric materials through displacing the positive and negative charges within the atoms in the molecules of the polymer in the opposite direction, and thus the whole materials consequently become electrically polarized [266,267].

The electric polarization of polymeric materials is in fact an electric dipole moment per unit volume, and is defined as

$$P = Np \qquad (10.1.14)$$

where P is dipole moment per unit volume of polymer (measured as coulombs per square meter), N number of atom per unit volume, p is the dipole moments of individual atoms per unit volume

The dielectric constant (ε') can be expressed as

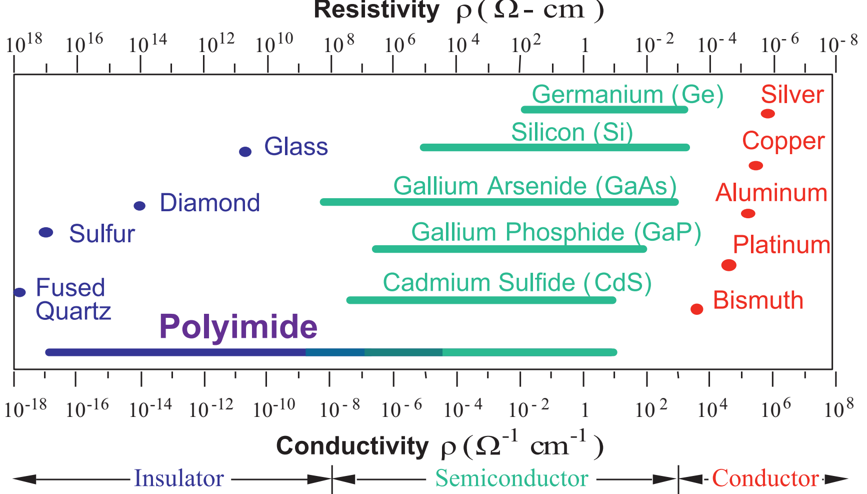
$$\varepsilon' = P/\xi \qquad (10.1.15)$$

where ξ is the applied electric filed, and is defined as the voltage applied per unit meter [266,277].

For practical purpose, the dielectric constant of a polymeric material is also defined as the ratio of capacitance C_p of a capacitor having given polymeric material to the capacitance C_v of the same capacitor in vacuum.

$$\varepsilon' \text{ or } \kappa = C_p/C_v \qquad (10.1.16)$$

where ε' or κ is dielectric constant or also known as permittivity [266,277].



FIGURE?10.1.20 Typical ranges of electrical conductivity of polyimide and other inorganic metal and semiconductors [265].

The dielectric constants of polymers are due to their electronic polarizability and the presence or absence of polar groups in polymer's molecular structure. Polymer with polar groups have larger dipole moments and large dielectric constant since their dipole are able to orient in the applied electric field. The dielectric analysis of polymer is therefore based on the interaction of polar groups on the polymer when subjected to a high and/or low electric filed. For insulation applications, polymers without polar groups are preferred. As mentioned above, the good insulator exhibits very high resistivity, that is, the current passing through them is extremely low.

The volume resistivity is calculated from the voltage, current and geometric configuration of the polymer film sample, and the electrodes used. [265] The dielectric constant of polymers varies with the applied frequency and would increase or decrease depending upon the molecular structure, and the presence of any additives or fillers.

The dissipation factor of a polymeric material is defined as the ratio of the current of the resistive component to the current of the capacitive component and it is equal to the tangent of the dielectric loss (tan δ) [268].

The dielectric strength of a polymer is its ability to withstand high voltage current field without breakdown. It is defined as the maximum voltage below which no breakdown occurs. Whereas, the breakdown voltage is defined as the maximum voltage above which actual failure occurs [267].

For the dielectric property measurements of film samples of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], KaptonH, ULTEM1000 and Upilex-S, etc. polymers, their films were sputter coated with ultra-thin gold layer via vacuum evaporation deposition for 40 s using JFC-1200 Fine Coater (model fitted with FC-TM10 Thickness Monitor from JEOL, Akishima, JAPAN) on both sides.

The gold-coated film then placed between upper and lower parallel plates thin film sensors of a Dielectric Analyzer [model DEA-2970 from TA instruments] furnace. To insure proper electrical contacts, 450N (newton) force was applied on the sample. In order to avoid the moisture effect on the dielectric property, a new approach was used to evaporate off any moisture condensed on the sample by heating it in the DEA furnace to a higher temperature around 150°Cin flowing nitrogen. After which it sample cooled down to 25°C (RT) and then measurement made at a frequency of 1 and 1000 Hz (1 kHz) from RT to 225°C (with furnace heating rate set at 3°C/min) under a flowing nitrogen (at 500 cc/min) gas atmosphere condition. The dielectric constant (ε') was automatically calculated and recorded by the machine as a function of frequencies [256,269,270].

Surface characteristics and properties

Surface characteristics by scanning electron microscopy analysis and energy-dispersive X-ray spectroscopy analysis

The besides TEM and AFM, SEM also produces images of high resolution (a higher magnification >3000 times to actual size of a given sample) using electrons rather than monochromatic light [215,239–244]. In addition, the EDAX a.k.a EDS coupled with SEM system provides detection of major and minor chemical elements at a given spot on the surfaces of sample materials composition, thereby allow not only each element's highly reliable identification but also% amount present at that spot [209,239–244].

The scanning electron microscope

SEM method provided detailed images which allow on real-time basis continuous close visual examination of characteristic feature of bulk of sample of polymers, nanomaterials, etc, for example, in the Sodium Montmorillonites Nanoclays, the bunch of tactoids of Nanoclays gallery aggregated as well as a selected single tactoid present at any given spot on the bulk of sample materials composition. SEM provides direct observation of not only the characteristics and morphology [i.e., crystalline form (if any)] of the mineral, but the size tactoids/particles, and the type of packing of the stacks of platelets present within a single tactoids and their size measured in Nanometer (nm) [215,239–244].

The samples preparation for SEM analysis is relatively easy since most SEM require the sample to be conductive [215,239–244]. SEM sample is prepared by pouring nonconducting dry sample, for example, a select few particles of solid samples of neat Kunipia-F Na-MMT Nanoclays or the Diamine-modified MMT Nanoclays materials, etc. in to special conducting carbon sheet holder, which is then placed in the chamber of SEM (model FEI QUANTA 200) and ultra-high vacuum is pulled to evacuate the chamber of SEM of any floating contaminants and air. A narrow electrons beam from electron gun which typically has an energy ranging from 0.2 to 40 keV, is further focused by one or two condenser lenses to a spot of about 0.4 to 5 nm in diameter on a sample's topography to scan it. The back scattered and deflected electron beam in the x and y axes is detected by the backscatter electron detector which produces low to high magnification and achieve images of microstructure present on and within the sample with resolution better than 1 nm. The SEM images of sample are recorded for the surface as well as when possible in sectional view [215,239–244].

Energy-dispersive X-ray spectroscopy a.k.a EDS coupled with the SEM system

The EDAX a.k.a EDS coupled with SEM system provides a real-time visual and printed image from the SEM allows examination of microstructure characteristic present on and within the surface of a given sample of polymers, nanomaterials, etc at magnification from a low resolution (magnification $= \sim 100\times$) to a higher resolution (magnification $> 3000\times$), are obtained by the SEM analysis [209,239–244]. In addition, the spectra from the EDAX system coupled with same SEM allows determination of presence of the various chemical elements in the sample and calculation of% content of each chemical elements [metal ions (if any)] as well [209,239–244].

Surface properties

Adhesion of polyimides to various inorganic interfaces, such as silicon, silicon oxide, aluminum, and copper must be well defined in the construction of IC devices. Good adhesion is a must not only at low temperature, but also after exposure of up to several minutes at higher temperatures in the range of 200°C–400°C [226,271–274]. Results of polyimide adhesion studies on various substrates have shown that polyimides adhere well to aluminum surface (i.e. aluminum oxide) and reasonably well to other metal surfaces [226,271–274].

Since last several years there has been significant interest generated for the novel uses of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly (ether-imide) [Co-PEI], KaptonH, ULTEM1000 and Upilex-S, etc. polymers, and their applications as high temperature thin film protective materials, such as high barrier and shielding coatings for microelectronics and telecommunication devices. Study of surface properties of such coating materials therefore would provide some meaningful information of material's adhesion behaviors on and/or de-lamination from given substrates due to changes in their surface energies.

It must be emphasized that polymer adhesion is a complex phenomenon and the effective adhesion is only partly determined by interfacial properties [275]. Similarly, the surface energy (γ_S) of polymer solid can only be measured by indirect methods. Several methods have been developed over a time. One of these methods consists of contact angle (θ) measurement of various liquids on a given solid polymer surface [276–281]. As the contact angle is a measure of the surface energy of the polymer, higher polymer surface energy results in lower contact angle, or greater change in wettability. Contact angle measurement is also an important method, which provides true surface information to show the types of functional groups present at the surface and evaluate the chemical structural effects on the surface properties of the polymer.

The surface energies of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], KaptonH, ULTEM1000 and Upilex-S, and other polymers, films determined by using One-Liquid method and Two-Liquid method.

One-liquid method

The well-known Good-Girifalco equation [282,283] is expressed as;

$$\gamma_S = \left[\gamma_{LV}(1+\cos\theta)\right]^2/4\phi^2 \tag{10.1.17}$$

where, θ is the contact angle, γ is surface energy, the subscripts S, L and V refer to solid, liquid and vapor respectively, ϕ is a constant between solid and liquid interface.

By knowing the value for ϕ for testing liquid and solid polymer pair, one can calculate the surface energy (γ_S) from the contact angle data using Eq. (10.1.17). However, in the zeroth order approximation, Good and Girifalco suggested that value of ϕ was equal to unity [282,283].

Two-liquid geometric method

Owens and Wendt and Kaelble [284,285] generalized the Fowkes' Equation [286,287].

$$\gamma_{SL} = \gamma_S + \gamma_{LV} - 2\left(\gamma_S^d \cdot \gamma_{LV}^d\right)^{1/2} - 2\left(\gamma_S^p \cdot \gamma_{LV}^p\right)^{1/2} \tag{10.1.18}$$

By combining it with modified Young equation

$$\gamma_{LV}\cos\theta = \gamma_{SL} - \gamma_{LV} \tag{10.1.19}$$

thus obtained a useful and workable equation

$$\gamma_{LV}(1+\cos\theta) + 2\left(\gamma_S^d \cdot \gamma_{LV}^d\right)^{1/2} + 2\left(\gamma_S^p \cdot \gamma_{LV}^p\right)^{1/2} \tag{10.1.20}$$

where γ_{LV} is surface tension of liquid in equilibrium with its own vapor, γ_{SL} is interfacial tension between liquid and solid surface, γ_{SV} is surfaced tension of solid in equilibrium with the saturated liquid vapor, θ is the contact angle.

The superscript *d* refers to a dispersion component and *p* refers to a nondispersion component, including all typical interactions established between the liquid and polymer surface, such as dipole-dipole, dipole-induced dipole and hydrogen bonding, etc [287,288].

Eq. (10.1.18) was used in the calculation of surface energy (γ_S) of nanocomposite films as by Owens and coworker's Two-Liquid Geometric method. In this method, two liquids (in our study, deionized water and formamide) with known surface tension component values ($\gamma^d{}_L$) and ($\gamma^p{}_L$), are used for contact angle (θ) measurement. Then

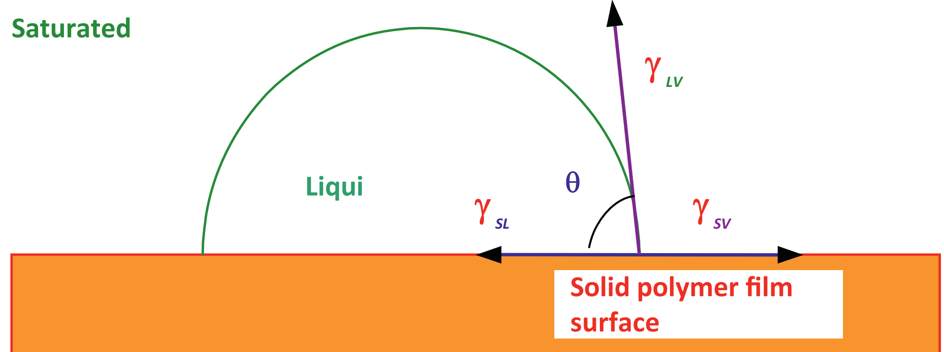


FIGURE 10.1.21 An immobile droplet of liquid on a solid polymer film surface showing a three phase force line.

TABLE 10.1.17 Surface tension parameter in (mJ/m^2) of testing liquids [285,289–291].

Parameter	Water	Formamide
γ (or γ_{LV})	72.8	58.0
γ^P (or γ^P_{LV})	51.0	18.7
γ^d (or γ^d_{LV})	21.8	39.5

one could easily calculate the surface tension component values ($\gamma^d{}_S$) and ($\gamma^p{}_S$) for polymer solid surface by solving simultaneously the following two equations

$$\gamma_{LV1}(1+\cos\theta_1)+2\left(\gamma^d_S\cdot\gamma^d_{LV1}\right)^{1/2}+2\left(\gamma^p_S\cdot\gamma^p_{LV1}\right)^{1/2} \quad (10.1.21)$$

$$\gamma_{LV2}(1+\cos\theta_2)+2\left(\gamma^d_S\cdot\gamma^d_{LV2}\right)^{1/2}+2\left(\gamma^p_S\cdot\gamma^p_{LV2}\right)^{1/2} \quad (10.1.22)$$

where θ_1 and θ_2 are the contact angle for DI-water and formamide, respectively.

Since it is known that when a liquid drop is in contact with a smooth, planer homogeneous solid surface, it exhibits an equilibrium contact angle as shown in Fig. 10.1.21. Therefore surface energies of Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], KaptonH, ULTEM1000 and Upilex-S, etc. polymers, films calculated from contact angles using Eq. (10.1.23) as follows:

$$\gamma_S=\gamma^d_S+\gamma^p_S \quad (10.1.23)$$

where surface energy γ_S is the sum of surface tension component contributed from dispersion and nondispersion parts, and the value of ($\gamma^d{}_L$) and ($\gamma^p{}_L$) of reference liquids, water and formamide provided by Kaelble [289] and Good [290], and given in Table 10.1.17.

The contact angles data and their standard deviation for six films for DI-water and formamide are listed in Table 10.1.17.

For surface properties determination, Contact Angle Measurements carried out at RT by the Wilhelmy method [271] and the Advancing and Receding Contact Angles on the Polyimide [PI], Poly(ether-imide) [PEI], Copolyimide [Co-PI], Co-poly(ether-imide) [Co-PEI], KaptonH, ULTEM1000 and UpilexS, etc. polymers, films measured. An electro-balance (Krüss Tensiometer model K14 from Krüss, Germany) with a reversible elevator used to measure contact angles. A film sample (0.3–0.6 mm in width and 4–5 mm in length) suspended from the arm of the electro-balance. A beaker containing the test liquid (De-ionized Water or Formamide) raised by reversible elevator so that liquid surface reached 2–3 mm higher than the lower edge of the polymer film (*immersion*). Then the beaker moved down to the original position (*emersion*). Weight of sample recorded continuously during an "immersion-emersion" cycle at an interfacial moving rate of 0.3 mm/min. This process repeated thrice and the weight recorded to confirm the reproducibility within statistical deviation. The contact angle calculated from the wetting force using the Wilhelmy equation [271].

Applications of polyimides

Typical applications of polyimides

In order to achieve higher reliability and better quality of electronic and other high value-added products, it is necessary that the polymers used in these applications possess good dielectric properties, outstanding thermal stability, high strength, low CTE and good adhesion to metals (e.g., Cu, Al), wafer and substrate. Polyimides typically possess most of the above properties in addition to good planarity with less pin-hole density. As a result, polyimides are especially suitable for applications in electronics and microelectronics. The main applications of polyimides in this area are as follows:

Films

The first commercial polyimide was KaptonH film, which was developed by DuPont using the casting method in 1960

[2−4,14,16,20,150,151]. Since then, the applications of the KaptonH film, because of its outstanding thermal stability, and mechanical and reasonable dielectric properties has been rapidly extended into the aerospace, defense and electronics industry.

The main applications of polyimide films are as electrical insulators in military hardware, aerospace, wire, cable and as insulator slot in electric motors and generators [2−7,9,14−16,20,227−229,267,268,274,292,293]. The benefits of using polyimide films for insulation slot are multiple. It permits better packing with a lighter weight and a 1.5−2.0-fold enhancement in the efficiency of electric motor and improvement in their dissipation property because of a 2−3-fold decrease in insulator thickness. In addition, the service temperature is increased to 300°C for a longer period and at 480°C for a shorter period because of the high strength and thermal stability of polyimide films. The nonflammable property of polyimides makes the film insulators widely applicable in aerospace, airplanes, automobiles, and in building industries. Recent research shows that the fluorine-containing polyimides possess superior insulation properties, than the conventional polyimides. And therefore have aroused a great deal of interest in both academics and industry [2−7,9,14−16,20,159−163].

Molded plastics

It has been reported that DuPont's Vespel brand of polyimide can be directly molded, not by conventional molding processes, but by a process similar to a powder metallurgy method [2,14,16,20,150,151]. In this case, it requires higher temperatures and special equipment. Other TPIs, such as ULTEM (PEI), and LARC-TPI may be processed by conventional extrusion and molding equipment. Polyimide is also a good matrix for carbon or glass fiber reinforced composites which are widely used in aerospace applications. Thermosets polyimides, for example, PMR-15 series and those with photosensitive groups have been developed by NASA are excellent successful examples [2−5,14,16,20,150,151,294−296]. These materials not only possess good mechanical properties (toughness), but also have good interfacial properties (surface energy and adhesion). Due to their outstanding thermal stability, nonflammability and high strength, polyimide foams are suitable lightweight materials for high temperature insulation applications, and for sound barriers in aircraft and rocket construction [2−7,9,10,14,16,20,294−296].

Fibers

The preparation and performance properties of polyimide fibers were first reported in the 1960s by DuPont [2]. These fibers were derived from PMDA and aromatic diamines ethylene bridge group [2−5,14,16,20]. The synthesis process was involved two steps. In the first step, the fibers are spun from a solution of polyamic acid by traditional "wet" or "dry" spinning, which in the second step undergoes a thermal imidization at elevated temperatures along with mechanical treatment to yield the final polyimide fibers. The mechanicals and thermal properties of some heat resistant organic polymers are tabulated in Table 10.1.18.

A few types of polyimide fibers are manufactured on a pilot plant scale in the United States and Russia [2−5,14,16,20,132]. The main advantages of polyimide fibers are their high thermal stability and strength, good electronic properties, nonflammability and radiation resistance.

It can be used in the temperature range between 275°C to 500°C. All these characteristics indicate that polyimide fibers belong to a class of high performance fibers. They are primarily being used in the weaving of high temperature insulating and noncombustible fabrics for fire fighters and astronaut's space suits. However, owing to the problems of high cost, toxicity of monomers and processing difficulty, polyimide fiber is difficult to compete with other high temperature organic fibers such as Kevlar (DuPont) which can be used to a temperature up to 300°C, without losing their superior strength and modulus.

TABLE 10.1.18 Properties of some heat resistant organic fibers [2−5,14].

Fiber	Thermal stability (K)	Tensile strength (kPsi)	Tensile elongation (%)	Modulus (Gpa)	573K[a] (250 h)	673K[a] (100 h)	773K[a] (10 h)
Aromatic polyamides	633	350	3−20	150	60	40	10
Aromatic polyimides	673	200	8−10	130	60	45	30
Ladder polymers	>673	40	3−5	50	95	70	50

[a]The strength retention of fiber at different temperature for given time, in%.

Adhesives and varnishes

Polyimide varnishes have been used as binders for glass, plastics and laminates, thermally stable adhesive compositions, and as high temperature coating materials [2−7,9,10,14,16,20,48,296,297]. In 1961, DuPont introduced varnishes under the trade name Pyre-Ml whose composition is between 14% to 17.5% polyimide obtained from PMDA and aromatic diamines [2,16]. Other high temperature TPI adhesives are LARC-TPIs [10], developed by NASA, and have been

Printed circuit board and packaging materials

In microelectronics, polyimides are used as the substrate for the printed circuit board, photosensitive dielectric insulation layer, packaging encapsulant materials. The major competitor of polyimides is epoxy. Approximately 50%−60% of the electronics applications use epoxy resins. Nearly 70% of the printed circuit boards manufactured are made from epoxy resin. This is due to the fact that epoxy resins are cheap and easy to process. However, IC boards made from epoxy resin can be used at maximum temperature in the range between120°C−150°C only. Therefore polyimides with good thermal stability are more suitably used such application. The flexible printed circuit boards made of polyimides are functional up to 300°Cwithout loosing it flexible characteristics. Beside that polyimides have been widely used in microelectronics as essential materials for the fabrication of semiconductor devices. They are used as a protective overcoat, an interlayer dielectric for multilevel device, an alpha-particle barrier, and an ion-implant mask. Polyimides provide the following advantages:

- Polyamic acid and a few polyimides can be solution spun-coated upon a silicon wafer to create a relatively planar surface that is suitable for the next level metallization for multilevel IC packaging.
- The thin film layer of PSPI and/or polyamic acid formulation spun coated can be further exposed, and etched with current processing equipment to yield different patterns and micro texture images and circuitry.
- The cured polyimide coatings are tough, resilient, and provides an excellent dielectric properties.

Therefore even though epoxy resin may still be the predominant packaging material [292], the future prospect of specialized polyimides, for example, polyimides modified by silicone, or fluorine containing groups, and fluoro-PEI is very promising. These polymers show exciting properties for packaging applications. These modified polyimides possess good dielectric properties, lower moisture absorption, low CTE, excellent thermal stability, high strength, and flexibility, etc. However, it is unlikely that polyimides in general can displace epoxy resins in all microelectronics applications in the near future owing to the problems of their high cost and processing difficulties.

Photosensitive polyimides

In the microelectronics industry, photosensitive resins are widely used in preparing intricate patterns of IC and for multi-chip module fabrication [2,16,274,292,294,298,299]. These materials contain photo-crosslinkable groups which can be cross-linked under irradiation of energy of certain wavelengths, thereby provides the capability of yielding patterns or image of IC on the wafer. However, current photo-sensitive formulations have some disadvantages, such as, low thermal stability, low strength, and some limitations in withstanding harsh processing conditions during microelectronics wafer-fab operation [2,16,274,292,294,298,299].

Most polyimides tend to have superior thermal stability, excellent strength, good dielectric properties, and good planarity with less pin-hole density, thus making them to be most suitable material for such application R&D.

Since 1990s, the main applications of PSPI are as stress buffer or protective coatings for IC devices and as interlevel dielectrics for multichip modules. The use of PSPI's is an emerging trend for microelectronics. Table 10.1.19 gives the list of worldwide major business players as of since late 1990s to 2005 and their various types of PSPI products for microelectronics applications.

Fluoro polyimide-based separation membrane technology

Membrane separation is one aspect of modern technology to separate and purify liquid chemicals and gases. The polymer membranes made of polysulfone, cellulose acetate, and polyamide are among the most prospective and widely used owing to their low cost, ease of processibility and high efficiency. However, since the last decade of 20th Century, the polyimide based membrane has been considered to be a new generation membranes, because polyimides not only offered outstanding thermal and mechanical properties, but also provided an excellent gas separation performance [2,16,81−109,113,118,120,149, 181,207,214,226,300−318].

For the successful development of polyimid based gas separation membrane products and to achieve very effective and high-yield gas separation membrane module system, due considerations are given to various technical factors, such as, selection of chemical structure of polyimide material(s) composition, types of membrane structure formations, and design of module system and preparations consisting of select number of membrane bundles enclosed, and over all gas production plant design

TABLE 10.1.19 Major players in photopolyimides research and development and business world-wide since late 1980s to 2005 [2,3,6,7,16,20,145,164–166,298,299].

SUPPLIER Market share (%)	TRADE MARK	FORMULATION REFERENCE	TYPE	REMARKS
OCG (12%)	Selectilux	HTR3	Covalent	
	Probimide		Covalent	
	Probimide		Intrinsic	
HITACHI-Du PONT MICROSYSTEMS (44-50%)	Pyralin-PD	PL 2700 D	Covalent	
		PL2720	Covalent	G-line
		PL2730	Covalent	Low Stress
		PL2740	Ionic	Low Stress
		PL2750	Ionic	I-line
		PL1045 (NEG)	Ionic	G-line, Low CTE
		PL1708 (NEG)	Ionic	I-line, Low CTE
		PL2135	Ionic	Low CTE
		PL3708 (NEG)	Ionic	I-line, Low CTE
		PL4235	Ionic	Low CTE
		PL5035 (NEG)	Ionic	G-line, High Resol.
		PL6008 (NEG)	Ionic	I-line, High Resol.
		PL8009 (POS)	Ionic	G & I line (Aqu.Alk)
		PL9009 (NEG)	Ionic	G & I line (Aqu.Alk)
TORAY INDUSTRIES (10%)	Photoneece	UR 3100	Ionic	Standard
		UR 3600	Ionic	High Resolution
		UR 3800	Ionic	G-line
		UR 4100	Ionic	Low Modulus
		UR 5100	Ionic	Low stress
ASHAI CHEMICALS (14%)	Pimel	G	Covalent	Standard
SUMITOMO (5%)	Sumiresin	CRC - 6081	Ionic	Standard

G- and I- lines corresponds respectively to the 436 and 365 nm lines of the photo stepper Mercury lamp.

based on given feed mixture of gases at the source location, and its commercial field operation parameters and conditions for the separation of given set of gases [109,113,120,149,226,300–307,312–318].

Fig. 10.1.22 illustrates typical technical and economic considerations given to the factors affecting key polymeric material selection, membrane's inner and outer structers formation based on hollow fiber spinning method and its operation parameters, and module and system design for successful development of polyimide polymer(s) based gas separation membrane products.

Fig. 10.1.23 inllustrates schematics of typical polyimide hollow fibers spinning set-up systems, and, basic hollow fiber orecipitation path during spinning process and schematic of comparison between the inner structures of traditional asymmetric hollow fiber composite membrane and a new microporous hollow fiber composite membrane including a SEM image showing the actual inners microporous structures of a hollow-fiber composite membrane spun from the solution (dope) of a fluoro polyimide [6FDA + Durene Diamine] by a selected hollow fibers spinning method [109,113,120,149,226,300–307,312–318].

In general, polyimides possess high selectivity, but low permeability. Obviously, with the critical experimental studies and fundamental understandings derived about the of most key parameters effecting gas separation mechanism in the membranes as illustrated in Fig. 10.1.24 for achieving high-throughput of separation of key gas from the mixture of gases passing through gas separation membrane module system, one can judiciously adjust the permeability of given gas by adjusting a combination of chemical structural compositions such as dianhydride and diamine in the given polyimide polymers or copolymer composition(s) [109,113,120,149,226, 300–307,312–318].

Additionally, high selectivity and permeability of polyimide membranes could be achieved by blending polyimide with other compatible polymers or by multi-layer composite techniques. Chung, Vora and their

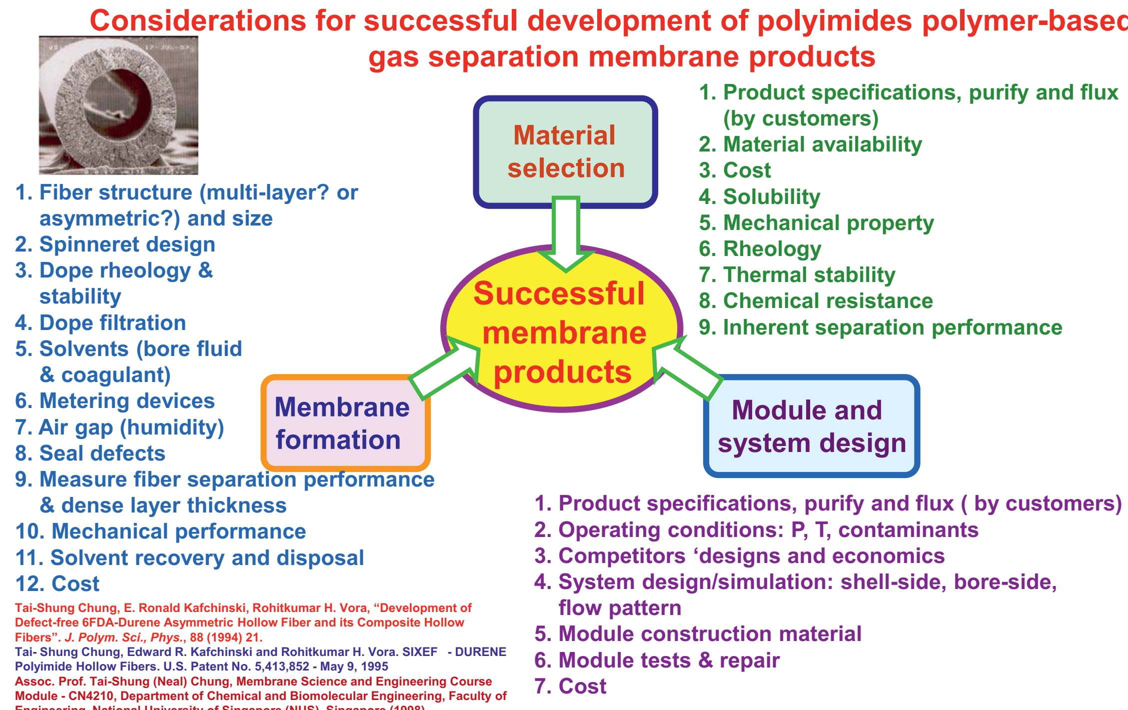


FIGURE 10.1.22 Typical technical and economic considerations given to the several important factors affecting the selection of key polymeric material, selection of hollow fiber spinning process system, key requirements for the formation of desired stable inner and outer structers of membrane, and module construction and effective gas flow operation system design for the successful development of polyimide polymer(s) based gas separation membrane products [109,113,120,149,226,300–307,312–318].

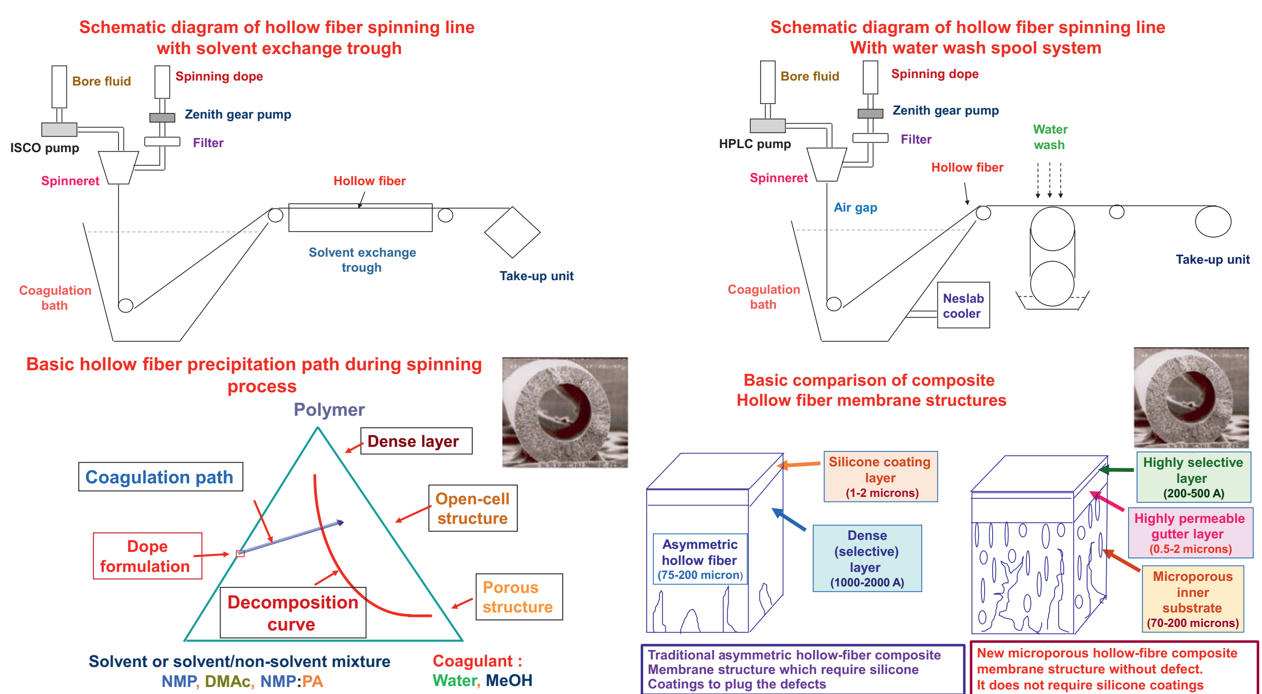


FIGURE 10.1.23 Schematics of two typical polyimide hollow fibers spinning set-up systems, basic hollow fiber orecipitation path during spinning process and schematic of comparison between the inner physical structures of traditional asymmetric hollow fiber composite membrane and a new microporous hollow fiber composite membrane [109,113,120,149,226,300–307,312–318].

FIGURE 10.1.24 Fundamental of key process condition/parameters effecting a gas separation mechanism for achieving high throughput of separation of a given gas from a mixture of gases passing thrugh the gas separation membranes system, and a magnified SEM image showing the actual inners microporous structures within a hollow-fiber composite membrane spun from the solution (dope) of a fluoro-polyimide [6F-PI] SIXEF Durene [6FDA + Durene Diamine] [109,113,120,149,226,300−307,312−318].

TABLE 10.1.20 Gas separation properties of membrane made from fluoro-polyimide [6f-pi] sixef durene polyimide having chemical composition of [6FDA + Durene], and a fluoro-copolyimide [6F-CoPI] having chemical composition of [6FDA + (50%) Durene + (50%) mPDA] [109,113,120,149,226,300−307,312−318].

Gas	Fluoro-polyimide [6F-PI] SIXEF durene [6FDA + Durene]	Fluoro-Copolyimide [6F-CoPI] [6FDA + (50%) durene + (50%) mPDA]
	Gas permeance (GPU[a])	Gas permeance (GPU[a])
CO_2	456	120
CH_4	28.3	3.77
Selectivity (α)	16.1	31.8

[a]*Where GPS = Gas Permeance Unit in Barr.*

coworkers have developed various fluoro-polyimides based separation membrane technology since 1990s [109,113,120,149,226,300−307,312−318].

The typical gas separation properties for the individual gas from a CO2/CH4 mixture passing from the gas separtion membranes which are made from fluoro-polyimide [6F-PI] SIXEF Durene having a chemical composition of [6FDA + Durene], and a fluoro-copolyimide [6F-CoPI] having chemical composition of [6FDA + (50%) Durene + (50%) mPDA] are reported in Table 10.1.20.

Tables 10.1.21 and 10.1.22 show the effect of the diamine and dianhydride structures present in the polyimide on the gas transport and separation properties of membranes.

Today, fluoro-polyimide membranes have been employed to separate and purify hydrogen with high degree purity up to 99.99% from syngas, enrichment of natural gas and synthesis of ammonia. These membranes are also find use in the separation of helium, carbon dioxide and acid gas, petroleum refinery and hydrocarbon vapors [300−318].

Due to strong hydrogen bonding interaction between carbonyls in the imide structure and proton in the water, polyimide membranes tend to possess high permeability for water and a high separation factor for water/organic compounds. Thus they are good candidates for the removal of water from organic solvents. Table 10.1.23 lists the separation properties of polyimide membranes for alcohol-water systems.

TABLE 10.1.21 Effect of diamine structure on permeability of polyimides expressed in barrer [109,113,120,149,226,300–307,312–318].

	Permeabiliy P (expressed in barrer) Where 1 barrer = 10^{-10} (cm^3 @STP.cm)/(cm^2.s.cm-Hg) Measured at temperature 35°C Gas				
Diamine	H_2	O_2	N_2	CO_2	CH_4
p-PDA[a]	9.4	0.60	0.105	2.75	0.064
p-ODA[a]	10.7	0.69	0.15	3.31	0.170
DATPA[b]	11.6	0.76	0.117	2.88	0.085

[a]*reacted with Silicone-bridged dianhydride (SiDA).*
[b]*reacted with ODPA as dianhydride.*

TABLE 10.1.22 Effect of dianhydride structure on permeability (expressed in barrer) and selectivity of polyimide membranes produced from ODA (diamine) and variuos dianhydrides [109,113,120,149,226,300–307,312–318].

	Permeabiliy P (expressed in barrer) where 1 barrer = 10^{-10} (cm + @STP.cm)/(cm^2.s.cm-Hg) measured at temperature 35°C				Selectivity $\alpha = \frac{\text{Permeance of Gas A}}{\text{Permeance of Gas B}}$		
	Gas				Gas mixture		
Dianhydride	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4	CO_2/N_2
PMDA	0.22	0.049	1.14	0.0265	4.5	43	23.23
BPDA	0.19	0.026	0.64	0.01	7.3	64	24.62
BTDA	0.19	0.024	0.63	0.01	7.9	63	26.25
SiDA	0.69	0.15	3.31	0.170	4.6	19	22.10
6FDA	3.9	0.73	16.7	0.341	5.3	49	22.88

TABLE 10.1.23 Separation properties of membrane for water-ethylalcohol system [109,113,120,149,226,300–307,312–318].

Membrane	Permeation flux rate per unit area and time (Q) (kg/m^2/h)	Selectivity (α) (H_2O/EtOH)
Polyetherimide- ULTEM1000	0.03	507
Asymmetric poly(ether imide)	1.29	57
Chitosan	0.29	36
Perfluorinated ion-exchange membrane	2.45	2

Applicability of resin transfer molding processing

Reduction of cost in processing and manufacturing is a major directive to enhance the use of composite technology in aircraft primary structures and protective housings and cowls for the turbine engines, as well as in hot regions of the aircraft, such as the fairings. Expedient and effective processing techniques shorten production cycles, simplify production procedures, accommodate complex parts fabrication, and enhance the performance of composite structures. RTM has been recognized as a process that provides the technical advantages listed below [308]:

- energy savings
- low emissions
- AST part production
- relatively low tooling cost
- encapsulation of ribs and inserts
- short tooling lead times
- no air entrapment
- all sides of part smooth
- all sides can be gel-coated
- close dimensional tolerances maintained
- versatility

Earlie, RTM was almost exclusively considered a process specific for the highly processible polyester resins. The ever-expanding requirements of the end user and constant development of new resin formulations to fit these requirements have seen epoxies and even BMIs being designed for the RTM process.

Similar RTM processing approaches for imide-based composites at higher temperature (550−800°F, or 288°C−427°C) are logical extensions. Advanced composites suitable for high-temperature durable airframe and engine applications are produced from high-performance polymer materials with a high level of fracture toughness, high modulus and strength, and environmental durability. State-of-the-art technologies indicate that high-performance polymers meeting the high-temperature requirements are mostly polyimides.

Specific to the processing challenges of polyimides, low molecular weight AT and phenylethynyl-terminated (PET) isoimide oligomers of the [BTDA + APB], [IPDA + MPDA], and [BTDA + DAB] constituencies were shown to have melt viscosities in the 10^0 to the low 10^1 range, which approach the desired viscosity range of 10^{-1} to 10^0 for RTM applications.

The low viscosity exhibited by liquid cyanate ester resins suggests that Semi-interpenetrating polymer networks (SIPNs) incorporating cyanate-terminated imide and isoimide oligomers could achieve low melt viscosities to allow hot-melt prepregging and RTM applications.

A SIPN is defined as a combination of one thermoplastic polymer and one thermoset polymer in network form, one of which is synthesized and/or crosslinked in the immediate presence of the other.

Industrial effort in resin transfer molding-able aerospace resins

Resin transfer molding has been used successfully for manufacturing fiber-glass parts for many years. The main manufacturing advantages are the reduction of cycle time and reproducibility in high volumes, which accommodates molding of complex parts. Advanced resins of higher use-temperatures which have been applied to RTM processes to mold aerospace components are epoxies, BMIs and polystyrylpyridines [309]. The liquid, monomeric dicyanate AroCy L-10 resin which has a 25°C (77°F) viscosity of 140 MPa/s (cps) or 1.40 poise and achieves the cured Tg of approximately 259°C (498°F), typical of the polycyanurates. It has been applied as a low-viscosity reactive solvent for compatible high-temperature thermoplastics such as polyimides, polysulfones, and polyarylates [310]. In the 260°C−371°C (500−700°F) service range, commercial choices are limited to LCPs, PBIs and the polyimides (inclusive of BMIs) [311]. A proprietary BMI-based RTM-able resin, FE-70,000, has been developed for transfer molding of electronic parts and for encapsulation of electronic elements by Nippon Polyimide Company (a Mitsui Petrochemical Company and Rhône-Poulenc S.A. joint venture) [312].

BP demonstrated their RTM-able BMI resins with Toray T300B fibers in a complex flywheel component [319]. Processing of Compimide BMI resins (Technochemie, GmbH) by RTM processing compares favorably to other processing techniques such as wet- and tow-preg filament winding and low pressure autoclave molding [320]. DSM’s Desbimid BMI resin is RTM-able and has been successfully applied to manufacturing the rear cowling beam of the Fokker 50 airplane [321]. Most of the attention has been given to issues of the materials availability, processing technology, automation, producibility [322] and economic advantages over metals. Applications have been successful in airframes and automobile bodies [323]. The thermal expansion resin transfer molding technique combines the technologies of epoxy RTM and rigid polyimide-based foam core prefabrication with a selective mold heating system, expanding the foam to varying densities in different regions [324−326]. Beyond these efforts little has been done to RTM polyimide resins.

Increased understanding of interfacial interaction and improved materials processing techniques potentially yield better interface, which leads to better composite

performance and durability. Optimization of interfacial interactions is extremely important toward facilitating fiber impregnation and total wet-out during resin injection.

Process control and engineering methods are relevant tools for optimizing the processes [327−329], dielectric spectroscopic methods being the most versatile approach to monitor cure.

Relevance of polyimides to resin transfer molding processing

Aromatic polyimides are known to be useful over a broad range of temperatures, even to beyond 700°F (371°C) for hundreds of hours. Isothermal weight loss studies at 700°F in air indicated that polyimides fare significantly better than other processible, nitrogen-containing polyheterocyclic polymers. Their well-defined chemistry and a vast literature data base allow many possibilities for structural modification. Many such polyimide systems have demonstrated usefulness as structural matrices, adhesives and coatings. The inherent poor processibility of aromatic polyimides is due to their high viscosity, volatilization (when processed in the amic acid form) during cure and insolubility in common low-boiling solvents. However, polyimides are also amenable to isoimide modification to enhance their melt processing latitude [330−335].

Low molecular weight aromatic polyisoimides end-capped with reactive groups are potentially useful as high-temperature-resistant RTM-able resins because of their qualifying attributes, including low melt-viscosity, and eventual TOS, but most significantly, the volatile-free cure from isoimide to imide. AT-isoimides/imides have been widely used as high-temperature composite matrices and structural adhesives. They impart higher TOS and toughness than BMIs to laminates and adhesive joints [336]. More development is needed to further reduce the melt viscosity to conventional RTM requirement of about 1 poise.

In principle, low molecular weight thermoset polyisoimides, with their low viscosity in the melt stage, can enable effective impregnation of the fiber filaments prior to resin advancement and cure. These isoimides undergo isomerization to the imide at 250°C (482°F) without liberation of volatiles.

The isoimidization process has been demonstrated to be easily adaptable to commercial polyimides to reduce viscosity and improve solubility [330−335].

In addition, low molecular weight polyisoimides and polyimides, end-capped with reactive phenylethynyl and cyanato end-groups, have been shown to possess low melt viscosity during processing. This approach therefore has greatly expanded the pool of candidate resins for selection as RTM-able high-temperature-resistant materials. In principle, a blending approach which involves these isoimides and a liquid polycyanurate precursor, for example,

$F_2C{=}CF{-}O{-}C_6H_4{-}C_6H_4{-}O{-}CF{=}CF_2$ → polymer (n)

FIGURE 10.1.25 Perfluorocyclobutane poly(aryl ethers) [337].

such as the AroCy L-10 dicyanate (140 cps @ 25°C), would produce RTM-able resins.

Similar blends with low viscosities and low melt temperatures have been made from of low molecular weight AT-isoimide oligomers with BMIs. Lockheed and Rohr Industries' collaborative studies have shown that these resulting blends have significantly higher toughness than BMIs, due probably to the chain-extending reaction of the AT oligomers. PET oligomers in place of the AT oligomers would result in Interpenetrating Network Polymers with higher Tg's. Complementary studies using AT-imide oligomers and BMIs were conducted at NASA-Langley [336].

Low-viscosity SIPN imide blends

Dow Chemical's perfluorocyclobutane (PFCB) poly(aryl ether) (Fig. 10.1.25) and poly(aryl-etherimide) are innovative in terms of the polymers' thermooxidative stability, potential long-term durability, and low moisture adsorption. The step-growth polymerization mechanism to allow molecular weight advancement of the prepolymer to any specified viscosity for processing would facilitate processing. This step-growth polymerization also produces no volatile by-products. High molecular weight polymers, poly(biphenyl perfluoro-cyclobutyl ether) and poly(1,1,1-triphenylethane perfluorocyclobutyl ether), were obtained from their corresponding aryl trifluorovinyl ether monomers [337].

An optimal exploitation of this step-growth technique is to form an SIPN. The step-growth mechanism advances the molecular weight from that of the (trifluorovinyl) aryl ether or −aryl etherimide monomer to a thermoplastic (MW-controlled). Introduction of this step-growth concept of molecular weight build-up can potentially improve the processing rheology of all SIPN blends.

An SIPN blend can be formulated by mixing the (perfluorovinyloxy)phenyl bis-imide monomers as the precursors of the thermoplastic component, with a thermoset component, such as an acetylene-terminated (AT)-imide/isoimide or a phenylethynyl (PET)-imide/isoimide. Since the initial mixture is of low MWs, the viscosity can be maintained low for easy control during processing (either prepregging or scrim impregnation). The thermally induced cyclodimerization of the (perfluorovinyloxy)phenyl bis-imide monomers takes place at 140°C. The MW of this resin can be advanced to a desired viscosity via its step-growth polymerization mechanism. The final curing of the prepreg or impregnated scrim placed at the bondline during consolidation completes the process. Fig. 10.1.26 depicts the design of such a low-viscosity SIPN system [338].

Galvanic corrosion resistance of polyimide composites

Imide-based composites showed evidence of galvanic corrosion in the form of nucleophilic attack of alkali on the imide structures of polyimide and BMI composites. The existence of a galvanic corrosion cell under appropriate conditions between carbon fibers and aluminum surfaces is well known [339,340]. The general dynamic experiment consisted of a graphite/BMI specimen in a tin can with 3.5 wt.% sodium chloride solution and JP5 jet fuel. The can was heated to 60°C and corrosive attack of the composite occurred within 24 h. The greatest rate of degradation occurred when the temperature and the amount of exposed graphite fibers were increased [341]. Among different metals, only aluminum exhibits cathodic control corrosion.

Mechanism of corrosion

Carbon and aluminum become "electrodes" in the presence of an aqueous electrolyte. An electromotive force (EMF) of approximately 800 mV exists between carbon and aluminum. When the carbon fiber is coated with an insulating polymer, such as a polyimide or BMI, the carbon electrode is effectively insolated, thus avoiding the creation of a corrosion cell. However, most polymers are susceptible to water adsorption and gradually behave like a "solid electrolyte," concentrating and transporting ions. If the carbon and the aluminum touch, the circuit is closed and electrochemical decomposition of aluminum occurs. Even if the carbon and the aluminum do not touch initially, some of the carbon may slough off with time, gradually forming a bridge through the polymer to complete the corrosion cell. Hydrogen and hydroxide ions are formed at the carbon electrode, and aluminum ions are produced at the counter-electrode. Highly soluble aluminum hydroxide is the product. The elevated pH due to the hydroxide ion concentration causes the polymer to degrade, exposing more of the carbon surface for further destruction. Such catastrophic corrosion can be prevented by several approaches. The corrosion cell can be rendered inactive by removal of any one of the components needed to complete the electrochemical cell [338].

Insulative coatings

Isolation of the anode can be achieved by a noninteractive coating on the carbon fibers. The use of hydrophobic polymers may insulate the anode and/or avoid the formation of a solid electrolyte. However, such polymers are prohibitively expensive, and the necessary 100% surface coverage (i.e., pin-hole free) may not be easily achieved.

Thermoplastic component

Thermoset component (as imide or isoimide)

FIGURE 10.1.26 Design for a low-viscosity SIPN polymer blend [338]. Controlled step-growth polymerization of the (perfluorovinyloxy)phenyl-end-capped bis-imide monomers generates the thermoplastic component to form an SIPN with the thermoset component during a higher temperature postcure [338].

Alternatively, the surface of the cathode may be rendered inactive by the deposition of a stable oxide layer that eliminates the high EMF. Aluminum, in fact, forms an inactive oxide layer in an acidic environment, but this layer is destabilized at high pH. The results from Lockheed and Sandia National Laboratory in conductive polymers, specifically the polyaniline variety, suggest a useful and cost-effective approach to offset the BMI corrosion problem [342].

Conductive polymer blends

Certain emeraldine salts may be blended with polyimides to render the latter conductive. Addition of protonic acids

to the polyaniline free-base produces emeraldine salts. The proton is mobile. While concentrated solutions of the salts have the green color of the protonated form (emeraldine), the dilute solutions have the blue color of polyaniline free base. High temperature also causes reversion of emeraldine to the free base form.

The emeraldine salt has been shown to blend well with the BMI or the polyimide matrix of the composite. Its presence provides a proton source which may shift the equilibrium potential and avoid the production of hydroxide ions, which chemically degrade the BMI matrix. A high hydrogen ion concentration may also have stabilized the inactive oxide layer on the aluminum. Both conditions effectively shut off the corrosion cell. The emeraldine salt at least extends the useful life of the imide-based composite by neutralizing the hydroxide ion, thus preventing fast decomposition of the polymer.

To test the effectiveness of polyaniline as an anticorrosion agent, a carbon fabric was treated with a BMI resin, such as Ciba Geigy's Matrimid, and another was treated with a blend of Matrimid and polyaniline tosylate. Pieces of these treated fabrics were placed in separate containers each with a 3% aqueous sodium hydroxide solution, along with a piece of aluminum. A conducting wire connected these two materials. The temperature, pH, open-circuit voltage and corrosion current were monitored periodically. Indicators of a positive anti-corrosion response have included the absence of an increased pH, a decreased cell potential and decreased cell current over the time of the test. Ideally, the cell current should drop to zero. Visually, very little decomposition of the polyimide matrix was observed [342].

Imide structural analogs

Imide analogs are five-membered heterocyclic amides that mimic the imide ring structurally, and follow synthetic schemes similar to those for imides. Structurally, they are much less susceptible to base-catalyzed hydrolysis as the imides by having one amide-type linkage eliminated. Polyimidines [343–346] and polybenzodipyrroledione [347,348] are representatives heat-resistant imide analogs (Fig. 10.1.27).

For example, the polyimidine does not contain adjacent amide linkages as in the case of imides. Hydrolysis still occurs at the sole amide linkage, but the entire polymer chain would not be scissioned. Polyimidines can be easily made from readily available starting materials as light-colored polymers, soluble in common organic solvents.

A relevant research project in the 1990s at PolyComp Technologies (Del Mar, California), supported by the Naval

A BTDA-based polyimidine

A BTDA-based polybenzodipyrroledione

FIGURE 10.1.27 Heat-resistant imide analog polymers [343–348].

Air Warfare Center, has included selecting some appropriate molecular-weight-controlled thermoplastic version of these imide analogs (based on a balance of processibility and fracture toughness) to be blended with a low molecular weight AT- or PET-oligomer based on the same imide analog structure to give a processible SIPN coating system [335].

High-performance polymers for lightning strike protection

Continued development of conductive polymers has eventually resulted in improvement of their environmental and thermal stability, processibility, and level of conductivity. Switching devices with electromagnetic interference shielding, and static electricity dissipation have become possible with nonmetallic conductive polymers. The electrical current capacity of lightning attachment and the accompanying shock wave generated by the ionized air column require very rapid dispersal of the I^2R electrical heating (Joule heating) lest severe damage would be sustained. Epoxy composite materials used in select aircraft and other engineering structures cannot resist the pyrolysis induced by the undissipated I^2R heating.

Lightning strike protection of composite structures involves such issues as thermal resistance, environmental resistance, repairability, and military specification (Mil. Spec.) requirements. Until a high-conductivity nonmetallic materials can be available, nonmetallic conductive materials continue to provide protection as sacrificial layers. While lightning strike damages cannot be avoided, they can be reduced to a less severe and manageable level.

High-temperature-resistant coatings

A straightforward approach is the replacement of epoxy materials with more thermal and thermo-oxidative resistant polymers such as high-temperature epoxies, BMIs, and high-Tg polyimide (and polyisoimide) materials that can perform long-term (near 10,000 h) at 204°C (400°F) or short-term (i.e., minutes) at over 650°C (1202°F) [330−335].

Polymer-ceramic materials (*vide infra*) have been shown to offer thermo-oxidative resistance much higher than available organic heat-resistant polymers. Continued development of these materials often must yield to economic changes and technological focus shifts in the aerospace industry, and achieving consistent production quantities is an arduous task [349,350].

Conductive paint and adhesive formulations

Commercial nickel-filled polyurethane sprayable or brush-on paints are easy to apply and repair. Nickel will not corrode. Urethanes are not suitable to render lightning strike protection and give way to BMIs and polyimides as better candidates because of their much higher temperature resistance. Nickel-coated graphite fibers or Kevlar structural fibers (for reducing Radar signals) are able to provide better approximation to an equipotential current density across the structures, as compared with graphite-reinforced structures [349]. Similarly, nickel-filled structural adhesives can be developed from polyimides and/or BMIs. These are known high-temperature-resistant structural materials for adhesives. Conductive adhesives are important in providing electrical continuity around the joining areas to prevent sparking and heating.

Conductive polymers based on polyaniline, polythiophene, polypyrrole and others can offer increased conductivities and improved processibility via better morphological control. The ultimate goal has been to achieve the metallic level of carrying high current density. They can be formulated as polymer blends with polyimide-type materials and used as spray coatings or paints, and as conductive composites, serving the dual role of load-bearing and electrical current dispersal.

Polymer layers of Carbon-Silicon Frameworks are relevant engineered material systems. They possess electrical conductivities $>10^6$/W cm, which compare well with metallic conductivities. They are lightweight, noncorrosive, and environmentally stable [350].

Polymer layers of interconnecting carbon frameworks and fullerene C_{60} and C_{70} molecular spheroids can potentially address the issues of conductivity and current-carrying capacity, equipotential current density, loadbearing ability, noncorrosiveness, and thermal/environmental stability. Indeed, the recent decade's R&D at IBM in interconnecting carbon nanotube frameworks have ushered in a new era of continued miniaturization of integrated circuitry [351]. Catalyst-mediated chemical vapor deposition growth of nanotubes has been shown to be compatible with the requirements of microelectronics technology, and can be exploited for carbon nanotube vias. Semiconducting single-walled nanotubes can be successfully operated as carbon nanotube field effect transistors [352]. Novel carbon-based resistive memory materials for high density NV memories have been fabricated with carbon nanotubes, grapheme-like conductive carbon, and insulating carbon. Repetitive high-speed switching and the potential for multi-level programming have been successfully demonstrated [353].

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