SPECIALITY POLYMERS

Unit I

High temperature and fire resistant Polymers

Introduction

Compared to traditional materials (especially metals), organic polymers show extreme sensitivity to temperature.

Polymers will have high softening points if they have a high T_g and/or T_m. Thermal degradation is the first stage in the burning of polymers. In general, polymers with good thermal stability also offer good fire resistance.

Factors affecting the thermal stability and fire resistance of polymers.

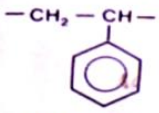
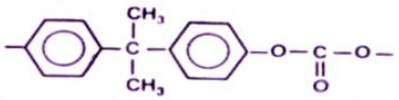
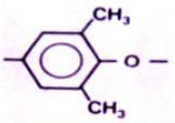
1. Tg The difference in Tg of different polymers with its structure is given below. Polymers will have high softening points if they have a high T_g and/or T_m.

2. Chemical structure -composition and bonding. Bond dissociation energy is high the thermal stability will be high. Aromatic bonds (bonds contain benzene rings) have high bond energy and stable than aliphatic. Polymers contain C=O, C=C, OH are easily degraded by heat in the presence of oxygen.

3 LOI Limiting oxygen Index is a measure of flammability. This is the minimum oxygen in an oxygen nitrogen mix to just sustain burning under specified conditions. High LOI valued polymers have flame and thermal resistance PE –LOI-18, PTFE – LOI-95

4. Presence of halogen in the polymer increases the LOI because that itself extinguishes the flame by making a halogen barrier for contacting oxygen

Table 1.1 Polymer structure and glass transition temperature

Polymer	Structural repeat unit	Stiffening agent	T_g(°C)
Polyethylene	$-CH_2-CH_2-$	—	−120
Polypropylene	$-CH_2-CH(CH_3)-$	$-CH_3$ side group	−18
Polystyrene		Phenyl ring side group	100
Polyvinylchloride	$-CH_2-CH(Cl)-$	Polar side group	80
Polymethylmethacrylate	$-CH_2-C(CH_3)(COOCH_3)-$	Di-substituted carbon	110
Polycarbonate		Benzene rings in chain	145
Polyethsulphone		Benzene rings in chain	210
Polyphenylene oxide		Substituted benzene ring in chain	220

Limiting oxygen index (LOI) of different polymers

Non self-extinguishing	LOI	Self-extinguishing	LOI
Aretal	16	Polycarbonate	27
Polyethylene	18	Polyarylate	34
Polypropylene	18	Polyethersulphone	38
Polystyrene	18	Polycthercthcrketone	40
Polyisoprcnc (natural	18	Polyvinyl chloride	42
Polymethylmethacrylat	18	Polyamide-imidc	43
ABS	19	Polyphcnylcne	44
Nylon 66	24	Po'yvinylidenc fluoride	44
Polycthylcnetcrephthal	25	Polyethcr-imide	47
Polychloroprene	26	Polybenzimidazole	48
		Polyimide	50
	'	Polyvinylidene chlo.ide	60
		Polytetrafluoroethylene	95

Methods for improving the performance of polymers for high temperature use.

STRUCTURE

1. By virtue of chemical structure polymers have high temperature resistance Example –PTFE, POLY ETHER SULPHONE
2. Modification of chemical structure of a polymer either by cross linking or by chemical reaction. Example-Radiation cross linking of PE, Chlorination of PE

ADDITIVES

3. Incorporating halogen releasing monomers as co monomers
4. Incorporating fire retardant Chemicals in compounding

Aluminum trihydroxide, ammonium polyphosphate, antimony trioxide, Brominated and chlorinated compounds. Eg. Chlorinated paraffin wax, chlorinated oils.

5. Incorporation of mineral fillers increase high temperature properties, example glass, aluminum silicate, silica ,Antioxidants

BLENDING

Blending of polymers improve high temperature properties.ABS plastic has low temperature résistance, so it can be blended with PC for high temperature properties,NR has low flame resistance ,but it can be blended with CR for high flame resistance .

Heat and fire resistant polymers

Flouropolymers

Carbon fluorine bonds have higher bond strengths (typically 485 kJ mole"') than carbon hydrogen (typically 350 435 kJ mole ') or carbon-carbon (typically 350 410kJ mole ') bonds. Fluoro-polymers are Therefore extremely resistant to attack by the free radicals involved in oxidative degradation and hence to thermo-oxidative degradation.

The most important commercial polymer is the fluoro-analogue of ethylene polytetrafluoro- ethylene (PTFE) of repeat unit—[CF_2—CF_2)n

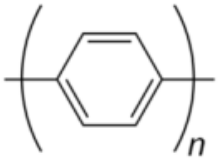
Applications .The polymer is produced in very linear high molecular weight form and has an unexpectedly high melting temperature of 327 ° C. Even above its T_m the melt viscosity is so high that it cannot be melt processed. Products are made by sintering or special extrusion techniques. However, despite its good high temperature resistance most applications utilize its extreme chemical resistance (these include pump parts, gaskets, seals, valves) or its well known non-stick properties (in coatings)

Other important fluro polymers are listed below

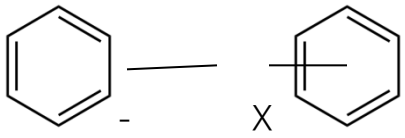
Fluoropolymer	Melting point (° C)
PVF (polyvinylfluoride)	200[8]
PVDF (polyvinylidene fluoride)	175
PTFE (polytetrafluoroethylene)	327
PFA, MFA [12] (perfluoroalkoxy polymer)	305
FEP (fluorinated ethylene-propylene)	260

Aromatic Polymers

A polymer that has aromatic ring in its structure (in its polymer chain) are called aromatic Polymers . It has combine the two main requirements for high temperature resistance .First, they have good oxidation resistance, since the C-H bonds of the benzene ring resist abstraction by the chain propagating oxidation free radicals having typical bond strengths of 435 kJ mole" ', compared with aliphatic C—H bond strengths of 350-400kJ $mole^{-1}$. It is roughly true that a polymer's susceptibility to thermal oxidation correlates with its aliphatic C-H bond content. Second.|the incorporation of the benzene ring structures into the polymer chain stiffens the chain and hence raises the 7",Jand T_m if the polymer is crystalline). However, the stiffening effect may be overdone. The polymer Consisting entirely of benzene rings linked together, i.e. poly- p – phenylene The structure is as follows



But polyphenylenes are not able to melt procesable as it melts around 500 ^{0} C and its decomposition temperature is very near to it . Therefore commercial polymers that achieve the required compromise are mostly of the type where X is a aliphatic group.

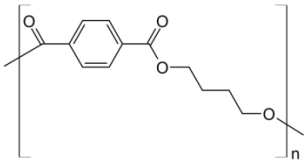


Polybutylene terephthalate (PBT)

Polybutylene terephthalate (**PBT**) is a thermoplastic engineering polymer that is used as an insulator in the electrical and electronics industries. It is a thermoplastic (semi-)crystalline polymer, and a type of polyester. PBT is resistant to solvents, shrinks very little during forming, is mechanically strong, heat-resistant up to 150 ° C (or 200 ° C with glass-fibre reinforcement) and can be treated with flame retardants to make it noncombustible.

PBT is closely related to other thermoplastic polyesters. Compared to PET (polyethylene terephthalate), PBT has slightly lower strength and rigidity, slightly better impact resistance, and a slightly lower glass transition temperature. PBT and PET are sensitive to hot water above 60 ° C (140 ° F). PBT and PET need UV protection if used outdoors, and most grades of these polyesters are flammable, although additives can be used to improve both UV and flammability properties.

Structure is



Advantages

Low water absorption, Moldability,Strength

Limitations

Affected by boiling water, Maximum use temperature is 300 degrees F (149 degrees C), Chemical resistance

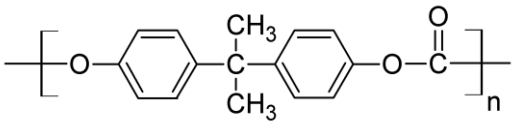
Applications

Polybutylene terephthalate is used for housings in electrical engineering, but also in automotive construction as plug connectors and in households for example in showerheads or irons. It is also found processed into fibers in toothbrushes and is used in the keycapsof some high end computer keyboards because the texture is highly resistant to wear.

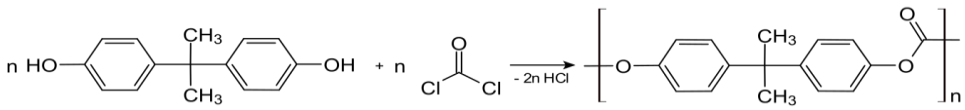
Poly Carbonate

Polycarbonates (**PC**) are a group of thermoplastic polymers containing carbonate groups in their chemical structures. Polycarbonates used in engineering are strong, tough materials, and some grades are optically transparent. They are easily worked, molded, and thermoformed. Because of these properties, polycarbonates find many applications.. Products made from polycarbonate can contain the precursor monomer bisphenol A (BPA).

Structure



The production reaction is



Bis Phenol A Epichlohyrin Poly Carbonate

Properties

Polycarbonate has a glass transition temperature of about 147 ° C (297 ° F),[7] so it softens gradually above this point and flows above about 155 ° C (311 ° F).[1] Tools must be held at high temperatures, generally above 80 ° C (176 ° F) to make strain-free and stress-free products. Low molecular mass grades are easier to mold than higher grades, but their strength is lower as a result. The toughest grades have the highest molecular mass, but are much more difficult to process.
Unlike most thermoplastics, polycarbonate can undergo large plastic deformations without cracking or breaking

Applications

Electronic components

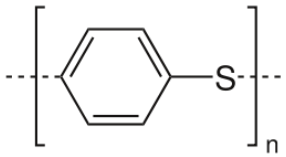
Construction materials[

The second largest consumer of polycarbonates is the construction industry, e.g. for domelights, flat or curved glazing, and sound walls.

Data storage

A major application of polycarbonate is the production of Compact Discs, DVDs, . Polycarbonate, being a versatile material with attractive processing and physical properties, has attracted many smaller applications. The use of injection molded drinking bottles, glasses and food containers is common.

Polyphenylene Sulphide



The polymer (PPS) has been available commercially for many years. It is normally crystalline (T_m 285 C, T_g about 200 C) and shows such good thermal and thermo-oxidative stability that it may be used in air at temperatures above 200 C for long periods. When heat treated in air, the polymer chain extends and cross-links, improving mechanical behavior and producing a highly insoluble and chemically resistant material.Its limiting oxygen index is 44, so it has low flammability. Injection moulded products include electrical connectors,'high temperature lamp holders and reflectors, pump parts, valves and, especially when filled for example with PTFE or graphite, as bearings. Processing temperatures are 300-350 C with mould temperatures of up to 200^0 C it is also useful in high temperature surface coating material and is

APPLICATIONS

Electrical & Electronics (E&E)

Uses include electronic components including connectors, coil formers, bobbins, terminal blocks, relay components, moulded bulb sockets for electrical power station control panels, brush holders, motor housings, thermostat parts and switch components.

Automotive

PPS boasts effective resistance to corrosive engine exhaust gases, ethylene glycol and petrol, making it the ideal material for exhaust gas return valves, carburettor parts, ignition plates and flow control valves for heating systems.

General Industries

PPS finds use in cooking appliances, sterilisable medical, dental and laboratory equipment, hair dryer grills and components.

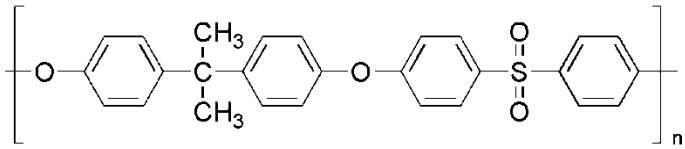
Polysulphones

. These polymers are known for their toughness and stability at high temperatures.

Polysulfones are a class of engineering polymers with high thermal, oxidative and hydrolytic stabilitiy. They are amorphous, transparent thermoplastics that can be molded, extruded, or thermoformed into a wide variety of shapes.

The high thermal stability is provided by the diphenylene sulfone group. It imparts high strength and high resistance to oxidation, but makes the polymer rigid. Flexibility in the backbone of the polymer is provided by ether linkage(s). These ether linkages also add to the thermal stability. Many commercial grades can tolerate high temperatures for a long period of time. Some grades, like polyphenylsulfone, are extremely tough and have very high impact strength, comparable to polycarbonate.
The usual grades have a good melt stability which permits fabrication by conventional thermoplastic processing methods.

The Structure



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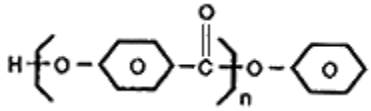
APPLICATIONS

Polysulfones have good resistance to aqueous mineral acids, alkali and salt solutions, oils and greases. Their high biocompatibility and ability to be sterilized makes them highly suitable for medical applications. Most grades can withstand long term exposure to hot chlorinated water. Several grades have received approval for food contact and drinking water.

Examples include printer cartridges, internal components of coffee machines and battery containers. Polysulfones are also used in the automotive and aerospace industries for applications where superior thermal and mechanical properties relative to conventional resins are required.

POLYESTERS

The partially aromatic polyesters, polyethylene terephthalate and polybuty leneterephthalate, are well established as plastics and fibre forming materials. However, they have limited heat resistance.(polyhydroxybenzoic acid) which is crystalline and softens only above 500^0 C, so must be processed by metallurgical techniques such as sintering and hammering. It may be used at temperatures up to 320^0 C and has found use as a bearing material. More tractable and melt processable copolymers, containing ester units from tcrcphthalic or isophthalic acid and aromatic diols), are also marketed and may be injection moulded.
Aromatic Polyester Resin Is Homopolymers Based On P-Oxybenxol Repeat Units And Are Linear Thermoplastics With Molecular Structure As Follows :



Chemical Name: POLY-P-OXYBENXOATE ; P-OXYBENXOYL HOMOPOLYESTER
It have excellent thermal stability
Decomposition Temperature : 530 ^OC
No softening below 400 ^OC
Continuous work temp. 300 ^OC

Heat moulding

Moulding conditions: 360 ^OC - 400 ^OC under pressure of 400 - 1000 KG/cm^2 for 3 -5 minutes.

With good mechinability, the molded articles could be further machined into mechanical parts. Fillers, such as Al_2O_3, short-cut carbon fabric, short - cut glass fabric, can be used to improve its strength.

APPLICATIONS

- In light industry and chemical industry
    1. Used as lubricant-free bearings, piston rings, pads, sealing packings etc. working at high temperature, or under water / or in moisture and vapor.
    2. Compounded with PTFE powder to make bridge slides.
- In electronics, electric equipment and instruments industries

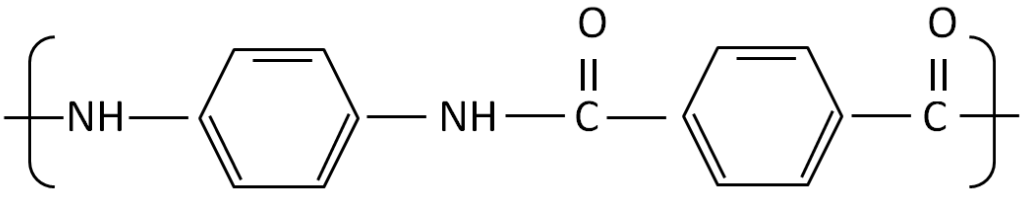
Heat-resistant plugs, sockets, spools, motor parts, printed circuit boards. Due to its excellent thermal conductivity as well as insulation properties, the parts of Aromatic Polyester powder is able to efficiently remove the heat generated in electronics' operation so that avoid damages from part overheat

- Blends of Aromatic Polyester Powder could be sprayed and form wearable coat on moving parts, which can dramatically elongate the coated parts' life and improve the working efficiency. Besides, Aromatic Polyester could be used in lubricant-free coating, anti-corrosion coating and anti-stick coating.

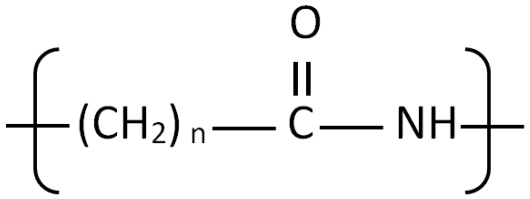
POLYAMIDES

Aramid fibers are a class of heat-resistant and strong synthetic fibers. They are used in aerospace and military applications, for ballistic-rated body armor fabric and ballistic composites, in bicycle tires, and as an asbestos substitute.

Aramid fiber is a generic term for aromatic polyamide fibers. As an example. Kcvlar fibers, composed of poly (1, 4-plienyleneterphthalamide). The polymer can be prepared by solution condensation of p-phenylene diamine and terepluhaloyl chloride at low temperature. The structure is shown



But aliphatic poly amides are



Production

Aramid fiber is produced by spinning a solid fiber from a liquid chemical blend. This causes the polymer chains to orientate in the direction of the fibre increasing strength.

It is dissolved in concentrated sulfuric acid. This is necessary to keep the highly insoluble polymer in solution during synthesis and spinning.

Major Uses of Aramid Fibers

- Ropes and cables although its severe weakening under impact limits its use on boats and climbing. It is more satisfactory in static load situations. Cables used as guy-wires for hydro tower erection for Hydro Quebec is one application of Kevlar cable.
- Sail cloth (not necessarily racing boat sails)
- Flame-resistant clothing
- Protective clothing and helmets.
- As a composite materials it is often combined with carbon fiber.
- Asbestos replacement etc,

Other Amides having high performance

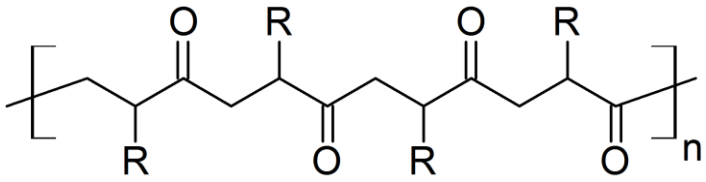
Melt processable aromatic, or partially aromatic, polyamides are produced as random copolymers, which do Cryftialline (and are therefore transparent) but are still capable of high temperature use since they have high Tg values..

Here a combination of both aromatic and aliphatic amide is formed.

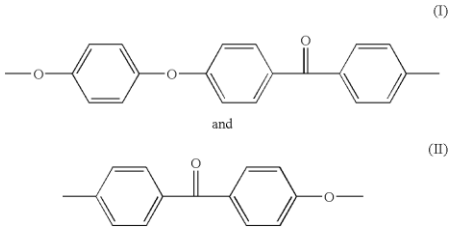
Polyketones

Polyketones are partially crystalline engineering thermoplastics that can be used at high temperatures. They also have excellent chemical resistance, high strength, and excellent resistance to burning.

Structure: general structure of poly ketones are as follows



When it comes in to aromatic the structure varies

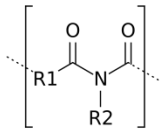


HETEROCYCLIC POLYMERS

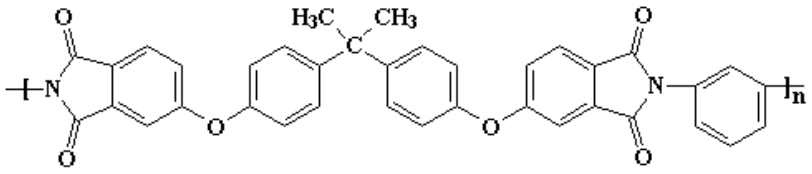
Polyimides

Polyimide (sometimes abbreviated PI) is a polymer of imide monomers. Polyimides have been in mass production since 1955. With their high heat-resistance, polyimides enjoy diverse applications in applications demanding rugged organic materials, e.g. high temperature fuel cells, displays, and various military roles.

Structure



Aromatic polyimides structure



Aromatic polyimides, have such incredible mechanical and thermal properties that they are used in place of metals and glass in many high performance applications in the electronics, automotive, and even the aerospace industries. These properties come from strong intermolecular forces between the polymer chains.

Disadvantages

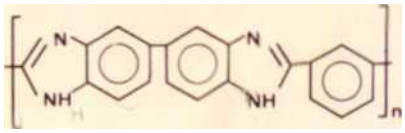
- Difficult to process, high temperatures required
- Limited resistance to hydrolysis
- High costs

Uses

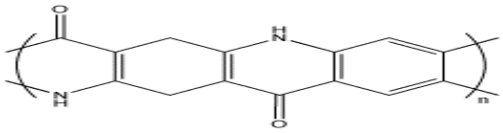
Automotive Applications , Seals , Bushings , Aerospace Applications , Pump Parts ,Gears

Other Heterocyclic polymers

Many other heterocyclic structures offer excellent thermal and thermo- oxidative stability. Among the many linear polymers, polybenzimidazoles (PBI) were developed early and are the only materials to show any real commercial promise, but they have had nothing like the success the polyimides have achieved, despite their comparable high temperature resistance. The polymer developed commercially is poly-(2.2'-w-phenylene-5,5'-bibenzimi- dazole)



(PBI)



Ladder polymers

It has been used as a laminating resin, and as an adhesive, as a reasonably tractable low molecular weight preculsor polymer. The cured product has a T_g above 400 C. Although short-teirm strength at very high temperatures is better than for polyimides, long-terrm strengths deteriorate more rapidly. Such factors, together with the high cost and toxicity of the aromatic tetramine monomers used, has limited commercial development. There is some interest in solution spun fibre for use as low flambility textiles, since the fabric limiting oxygen index is very high as 48.and it has vety lowsmoke and toxic gas generation. In principle, even higher temperature resistance may be obtained with fused ring chain polymers (double strand or ladder polymers) of schematic structure given above have high performance