Chapter 12. Polymers for Advanced Technologies

12.1 Membrance science and technology

Solubility and diffusivity can vary depending on the chemical structure of polymers.

12.1.1 Barrier polymers

Good barrier materias -- important for packaging film, plastic beverage bottles
and encapsulation of electronic parts.

Barrier polymers : a polymer with a permeability less than 10^{-11} cm^3-cm/cm^3-s-cmHg

PET -- attractive CO_2 barrier properties used as plastic bottles

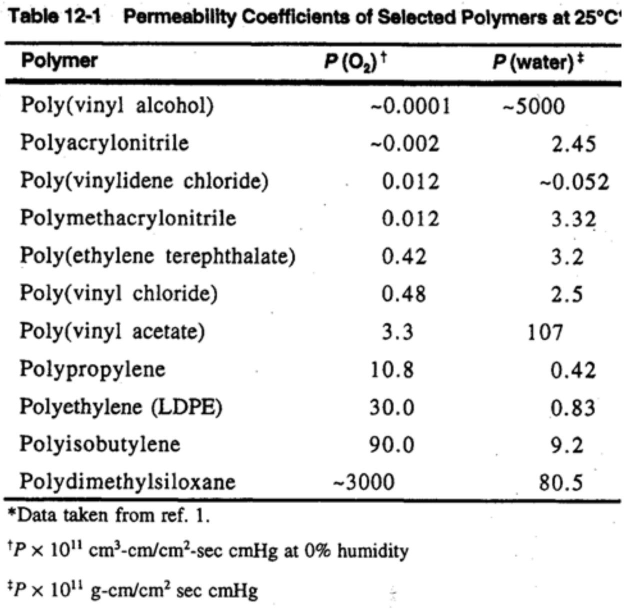


Table 12-1 Permeability Coefficients of Selected Polymers at 25°C*

Polymer	$P(O_2)$[†]	P(water)[‡]
Poly(vinyl alcohol)	~0.0001	~5000
Polyacrylonitrile	~0.002	2.45
Poly(vinylidene chloride)	0.012	~0.052
Polymethacrylonitrile	0.012	3.32
Poly(ethylene terephthalate)	0.42	3.2
Poly(vinyl chloride)	0.48	2.5
Poly(vinyl acetate)	3.3	107
Polypropylene	10.8	0.42
Polyethylene (LDPE)	30.0	0.83
Polyisobutylene	90.0	9.2
Polydimethylsiloxane	~3000	80.5

*Data taken from ref. 1.

[†] $P \times 10^{11}$ cm^3-cm/cm^2-sec cmHg at 0% humidity

[‡] $P \times 10^{11}$ g-cm/cm^2 sec cmHg

12.1.2 Membrane separations

Major uses of membranes: production of potable water by reverse osmosis (RO)
and separation of industrial gases

Other applications: filtration of particulate matter, separation of liquid mixtures,
ion separation in electrochemical processes, membrane dialysis,
controlled release of therapeutic drugs, membrane-based sensors

* Filtration

: filteration of dust, salts, bacteria and large viruses (See Fig. 12.1)

Microfilters (MF) --- membranes having pore diameter of 0.01 to 10 μ ı

Ultrafilters (UF) --- " " 10 to 1000 Å

Reverse osmosis (RO) --- to obtain potable water from salt water (5 - 20 Å

Nanofilteration (NF) --- demineralization of water, higher water flux than RO

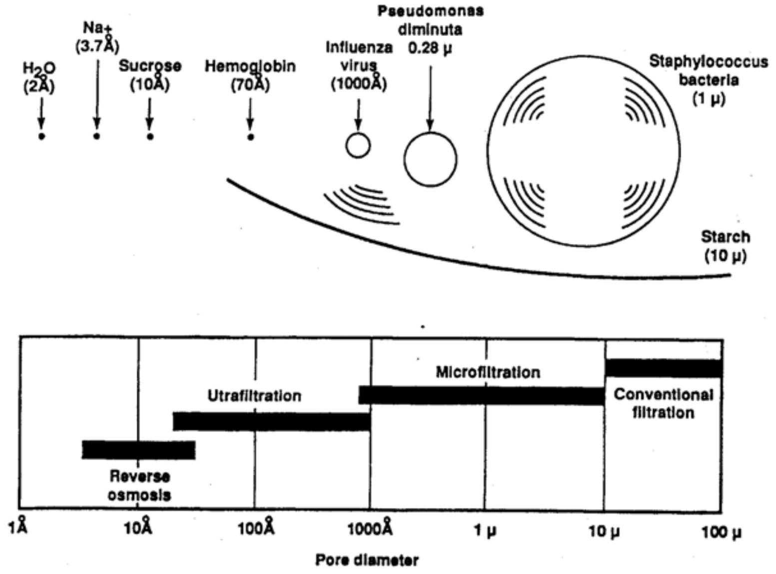


Figure 12-1 Pore sizes and terminology used in filtration. (Courtesy of Membrane Technology and Research, Inc., Menlo Park, CA).

Table 12-3 Industrial Applications for Microfiltration and Ultrafiltration Membranes

Industry	Examples
Biotechnology	Product separation from fermentation broth and blood/plasma filtration
Electrocoating	Electrocoat paint filtration
Food	Clarification of apple juice and egg-white concentration
Pharmaceutical	Cold sterilization by removal of microorganisms such as bacteria and yeast cells from aqueous solutions
Semiconductor/electronic	Production of 18 megohm or ultrapure water
Waste management	Oil–water separation and metals recovery

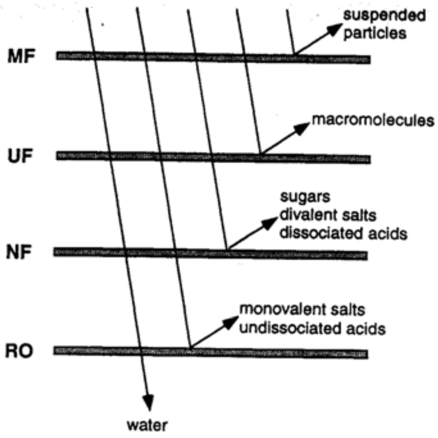


Figure 12-2 Comparison of the rejection performance of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse-osmosis (RO) membranes to solutes of different sizes and charge. (Adapted from L. P. Raman, M. Cheryan, and N. Rajagopalan, *Chemical Engineering Progress*, March, 1994, with permission of the American Institute of Chemical Engineers.)

* Gas separation

Important industrial applications:

oxygen enrichment of air, hydrogen separation from CO, removal of CO_2 from natural gas, reduction VOC in air, preservation of food, and dehydration of gases

Table 12-4 Applications for Polymeric Membranes in Gas Separations

Separations	Suitable Polymers
O_2/N_2	Silicone rubber Polysiloxane-*block*-polycarbonate Polysulfone Ethylcellulose Poly[(1-trimethylsilyl)-1-propyne] Polypyrrolone Polytriazole Polyaniline
H_2 from CO, CH_4, N_2	Polysulfone
Acid gases (CO_2 and H_2S) from hydrocarbons (e.g., natural gas and enhanced oil-recovery)	Cellulose acetate Poly(vinyl chloride) Polysulfone Polyetherimide
Hydrocarbon vapors from air	Silicone rubber

Polymer membrane: high selectivity, easily fabricated over molecular sieve carbon membrane, metallic membrane, and ceramic membranes

Driving force for gas transport: pressure drop ($\triangle p$)

Permeability -- the ratio of flux to pressure drop

$$P_A \equiv \frac{J_A x}{\triangle p}$$ where x is membrane thickness

Permselectivity -- the ratio of permeabilities for gas A to gas B

$$\alpha_{AB} = \frac{P_A}{P_B}$$

Permeability of a polymer for a gas -- increases with decreasing size and increasing solubility

The order of decreasing gas permeability:

$H_2 > He > H_2S > CO_2 > O_2 > Ar > CO > CH_4 > N_2$

(See Table 12.5)

Table 12-5 Gas Permeability and Permselectivity of Representative Polymer (at 25° to 35°C)

Polymer	$P(O_2)^*$	$\frac{P(O_2)}{P(N_2)}$	$P(CO_2)$	$\frac{P(CO_2)}{P(CH_4)}$
Rubbery Polymers				
High-density polyethylene ($\rho = 0.964$)	0.4	2.9	1.7	4.4
Butyl rubber	1.3	3.9	5.8	6.6
Low-density polyethylene ($\rho = 0.914$)	2.9	3.0	12.6	4.3
Natural rubber	24	3.0	134	4.7
Silicone rubber	610	2.2	4,553	3.4
Glassy Polymers				
Poly(ethylene terephthalate) ($X_c = 0.50$)	0.06	4.5	0.30	—
Cellulose acetate	0.68	3.4	5.5	28
Polysulfone	1.3	5.2	4.9	23
Polycarbonate	1.5	5.2	6.0	23
Polystyrene	2.6	3.3	10.5	—
Poly(2,6-dimethyl-1,4-phenylene oxide)	18	5.0	59	15
Poly(4-methylpentene-1)	29	4.4	93	—
Poly[1-(trimethylsilyl)-1-propyne]	7,200	1.7	19,000	4.4

* Permeability in barrers [10^{-10} cm^3 (STP)-cm/(cm^2-s-cm Hg)]

* Liquid separations

<-- to separate liquid mixtures in competition with traditional chemical processes, such as distillation, adsorption, and liquid-liquid extraction

Pervaporation : Liquid mixture is pumped across the membrane surface.

- crossflow operation (reduces the potential for fouling)
- dead-end operation

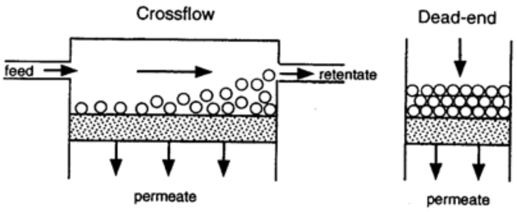


Figure 12-3 Illustration of a crossflow membrane process (left) compared to dead-end filtration (right).

Separation factor : selectivity for component A over B

$$\alpha_{AB} = \frac{y_A/y_B}{x_A/x_B}$$

Enrichment factor : ratio of concentrations of pervaporating species in the permeate and feed.

$$\beta_A = \frac{y_A}{x_A}$$

where x_A and y_A represent the conc. in the feed and permeate.

* Other separations

Table 12-6 Other Membrane Processes

Process	Applications	Driving Force	Membrane Type	Applications
Dialysis	Separation of colloids and other large particles from inorganic ions and other small particles	Concentration gradient	Hydrophilic ultrafilters	Artificial kidney Plasma purification Caustic recovery in the viscose process
Electrodialysis	Separation of ions having opposite charges	Electrical potential	Ion exchange	Concentration of electrolyte solutions Desalting
Electro-osmosis	Treatment of colloidal suspensions and sludge in effluent and waste streams	Electrical potential	Ion exchange	Dewatering

12.1.3 Mechanisms of transport

Two principal modes of transport:

① size exclusion

-- depends on the size of the pores to the mean free path

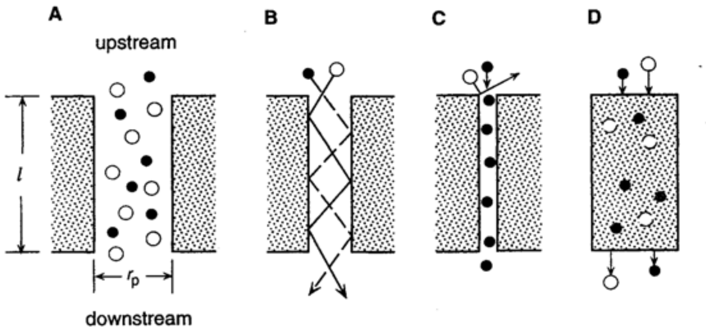


Figure 12-7 Illustration of the membrane transport of two differently sized molecules by various mechanisms. From left to right: **A** *viscous flow* through large pores of radii, r_p (no separation); **B** *Knudsen flow* (separation based upon difference in molecular weights); **C** *molecular sieving* (separation due to relative diffusive rates and surface sorption on pore walls); and **D** *solution-diffusion* through a dense membrane (separation based upon relative solubility and diffusivity).

② solution-diffusion

-- depends on the dissolution and subsequent diffusion of molecules

Permeability can be represented as the product of solubility and diffusivity.

==> $P = S D$

Solubility of gases in liquids or rubbery polymers is given by Henry's law.

==> $C = S p$

where C is the conc. of sorbed penetrant and p is pressure.

* Fundamental law for transport through a flat membrane (Fick's 1st law)

$$J = -D\frac{dC}{dx}$$ <---- Integrating & using Henry's law

==> $$J = \frac{SD}{x}(p_2 - p_1)$$ <---- Substitution of P=SD

==> $$J = \frac{P}{x}\triangle p$$

12.1.4 Membrane preparation

Dense membranes -- formed by melt extrusion, compression molding, solution casting

Microporous and asymmetric membranes -- require significant art, as well as a basic understanding of polymer morphology and solution thermodynamics.

* Microporous membranes

Table 12-9 Methods Used to Prepare Microporous and Ultraporous Membranes

Method	Description
Leaching	Extraction of solid pore formers
Phase inversion	Phase separation of a ternary mixture of polymer, solvent, and nonsolvent
Sintering	Melting of a semicrystalline polymer powder
Stretching	Combined stretching and annealing of extruded semicrystalline film
Thermally induced phase separation	Cooling a mixture of a polymer with a latent solvent to a point of thermal separation of the mixture followed by extraction of the latent-solvent phase
Track etching	Irradiation of polymer films resulting in the production of fission fragments followed by caustic etching

* Asymmetric-membrane formation

4 techniques to prepare symmetric membranes:

dry, wet, thermal, and polymer-assisted.

. Dry process : polymer, solvent and nonsolvent are mixed to be miscible --> evaporation of volatile components --> phase separation

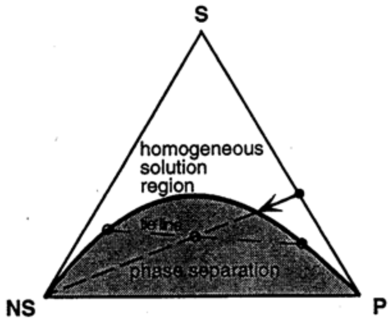


Figure 12-14 Phase diagram of a ternary mixture containing polymer (P), solvent (S), and nonsolvent (NS) at constant temperature. When a nonsolvent is added to a concentrated polymer solution whose composition is indicated by the filled circle along the S–P side, the overall composition of the mixture follows the line connecting this point and the NS vertex. When the composition reaches the phase envelope, phase separation (coagulation) begins. The composition of the two equilibrium phases is given by a tie line through the point on the phase diagram representing the overall composition of the ternary mixture, as shown.

. Wet process : Same as dry process, but coagulated in a nonsolvent

. Thermal process (or TIPS(thermally incuded phase separation)) : "latent" solvent is used --> decrease in temp. --> phase separation

cf.) Latent solvent requires a high-boiling, low MW solvent for polymer at high T but a nonsolvent at lower T.

. Polymer-assisted process : a mixture of two physically compatible but immiscible polymers in a common solvent --> casting and evaporation --> phase separation --> dissolution of dispersed-phase polymer

* Module fabrication

: For commercial membranes, large surface areas, high area-to-volume ratios are needed to meet flux requirements.

. Membrane module configurations : hollow-fiber, spiral-wound, plate-and-frame, tubular, and capillary membrane modules

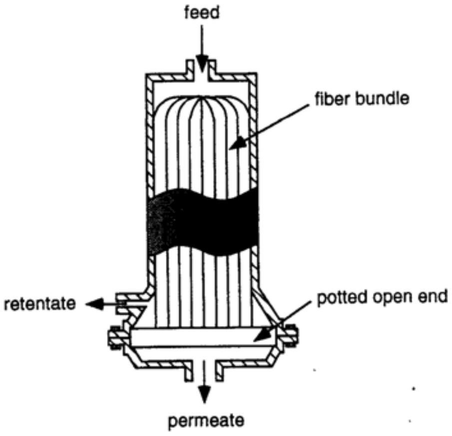


Figure 12-17 Cutaway view of a typical hollow-fiber membrane module. (Adapted from K. Scott, *Membrane Separation Technology*, STI, Oxford,1990.)

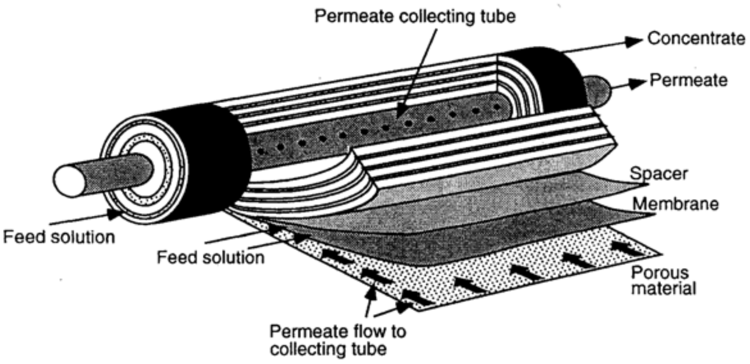


Figure 12-18 Spiral-wound membrane modules. (Adapted from K. Scott, *Membrane Separation Technology*, STI, Oxford, 1990.)

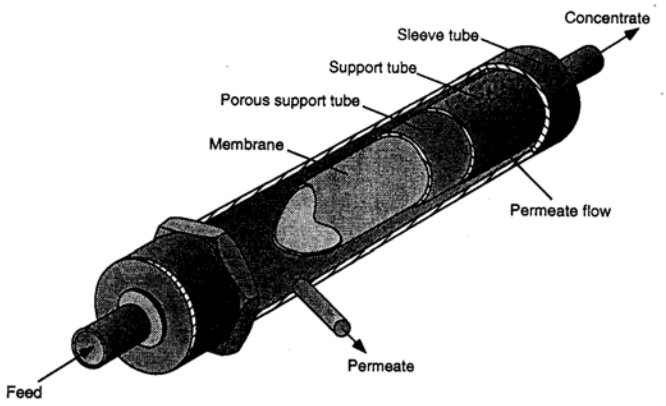


Figure 12-19 Tubular-membrane module. (Adapted from K. Scott, *Membrane Separation Technology*, STI, Oxford, 1990.)

. Module applications: reverse osmosis (RO), pervaporation (PV), gas permeation (GP), ultrafiltration (UF), electrodialysis (ED), microfiltration (MF)

Table 12-10 Preferred Module Designs for Major Membrane Separations

Module Type	Separation*
Capillary	UF, MF
Hollow fiber	RO, GP, PV,
Plate and frame	PV, UF, ED
Spiral wound	RO, PV, GP
Tubular	UF, MF

* Code: RO, reverse osmosis; GP, gas permeation; PV, pervaporation; UF, ultrafiltration; ED, electrodialysis; MF, microfiltration.

12.2 Biomedical engineering and drug delivery

Polymers for biomedical use must possess some properties including biocompatibility, selective permeability, biodegradability, and high strength or modulus.

Biocompatibility depends on the degree of adsorption of plasma proteins to polymer surface and the interaction of these proteins with cell receptors.

Polymers used in medical applications: PVC, PP, some acrylics and PS

Two examples of the biomedical uses of polymers

* Kidney dialysis -- used to remove low-to-moderate MW compounds from blood (NaCl, KCl, urea, creatinine, and uric acid)

Driving force for dialysis: conc. gradient

Polymer suitable for kidney dialysis: cellophane (in the form of hollow fibers)

* Controlled drug delivery -- to maintain a steady therapeutic conc. of drugs

ex.) delivery of contraceptives and treatment of glaucoma

Rate of drug release can be controlled by diffusion, reaction, or solvent.

Diffusion-controlled: driving force is the conc. gradient

Reaction-controlled: utilize biodegradable polymers as a means of delivery
Solvent-controlled: by water permeation through polymer (Fig. 12.20)

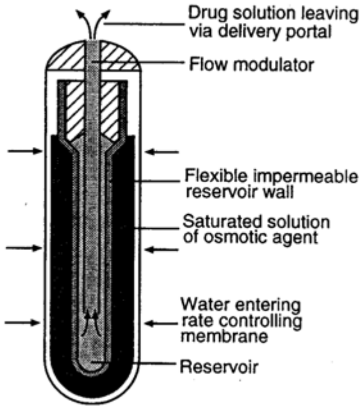


Figure 12-20 Illustration of an osmotic pump used in controlled drug delivery. (Copyright ASTM, reprinted with permission from *ASTM Standardization News*, October, 1986.)

12.3 Applications in electronics

12.3.1 Electrically-conductive polymers

In general, polymers have very poor electrical conductivity.
Electrical conductivity of an organic polymer could be increased when doped.

Table 12-11 Conductivities of Polymers and Metals

Material	Conductivity* S cm^{-1}	Specific Gravity
Silver	10^{6}	10.5
Copper	6×10^{5}	8.9
Aluminum	4×10^{5}	2.7
Polyacetylene (doped)	1.5×10^{5}	1
Platinum	10^{5}	21.4
Polythiophene (doped)	10^{4}	1
Mercury	10^{4}	13.5
Carbon fiber	500	1.7–2
Carbon-black-filled polyethylene	10	1
H_2SO_4 electrolyte	10^{-1}	2
Polymer electrolyte	10^{-4}	1
Polytetrafluoroethylene (Teflon)	10^{-18}	2.1–2.3
Polyethylene	10^{-22}	0.9–0.97

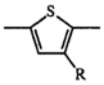
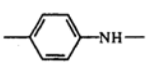
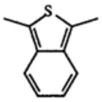
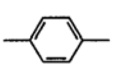
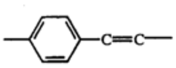
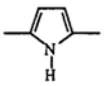
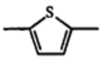
* Units of siemans (S) per cm.

Chemical structure of the repeating units of conductive polymers

(See Table 12.12)

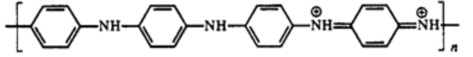
Transport of electrical charge is based on a conjugated π electron consiting of alternating single and double bonds along the polymer chain.

Table 12-12 Chemical Structures and Conductivities of Some Electrically Conductive Polymers

Conductive Polymer	Repeating Unit	Dopants	Conductivity* (S cm^{-1})
trans-polyacetylene		I_2, Br_2, Li, Na, AsF_5	10^4
Poly(3-alkyl-thiophene)		BF_4^-, ClO_4^-, $FeCl_4^-$	$10^3 - 10^4$
Polyaniline†		HCl	200
Polyisothianaphthalene		BF_4^-, ClO_4^-	50
Poly(*p*-phenylene)		AsF_5, Li, K	10^3
Poly(*p*-phenylene vinylene)		AsF_5	10^4
Polypyrrole		BF_4^-, ClO_4^-, tosylate‡	500–7500
Polythiophene		BF_4^-, ClO_4^-, tosylate,‡ $FeCl_4^-$	10^3

* Approximate maximum conductivity of doped polymer.

† Polyaniline exists in four oxidation states, of which only the emeraldine salt.



is a good conductor requiring only protonic doping of the imine nitrogen as shown.

‡ *p*-Methylphenylsulfonate.

* Polymer batteries

: light, flexible and easy to fabricate

A diagram of a typical lithium-polymer battery

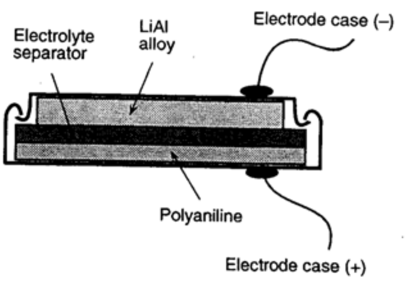


Figure 12-21 Illustration of a rechargeable battery using a polymeric cathode (polyaniline). The anode is a lithium-aluminum alloy, while the electrolyte can be a solution (e.g., propylene carbonate) of an appropriate salt or a solid polymer electrolyte (e.g., Li–PEO). (Courtesy of M. G. Kanatzidis.)

Other uses of conductive polymers

: sensors, conductive paints, semiconductor circuits, low-current wires, and electromechanical acutators.

12.3.2 Electronic shielding

Radio-freq. range (RF) emitted by electrical devices can interfere with normal RF.

Unfilled polymers provide poor EMI (electromagnetic interference) shielding capability.

To achieve EMI shielding: coating the plastic with a conductive metal, or
blending the plastic with conductive fiber or particles

Carbon- and metal-filled composites provide suitable housings for electronic devices.

12.3.3 Dielectrics

Low-k (dielectric constant) materials to replace SiO_2 (k=4.2) are a current challenge.

For the 0.1 μ ι circuit lines for the next generation computer chips, $k < 2.5$.

Polymers for low-k materials:

polyimides, heteroaromatic polymers, poly(aryl ethers), and fluoropolymers

Thermal stability requirements for low-k polymers: withstand $T > 400$ to 450 ℃

12.3.4 Encapsulation

: to provide integrated-circuit devices with a protective seal against moisture, radiation and ion contamination

. Thermosets: polyimides, epoxies, unsaturated polyesters and alkyd resins
. Thermoplastics: PVC, PS, PE, fluoropolymers, and acrylics
. Elastomers: silicone rubber and polyurethanes

12.4 Photonic polymers

Optical devices for both storage and processing of data are widely used.

CD-ROM/WORM drives for optical storage of computer data are already common.

Polymers that exhibit nonlinear optical (NLO) properties are suitable for optical technology because their optical properties vary with the intensity of the light.

* Nonlinear optical polymers

Refractive index of NLO material is not constant but a function of the intensity of the incident light.

For NLO effects to be observed, the light must be coherent and intense.

Materials that have significant NLO behavior have a small optical band gap, high concentration of easily polarizable electrons, and a large effective conjugation length.

* Light-emitting diodes

LED : a crystalline semiconductor chip that glows.

OLED (organic light-emitting diode) is made of sheets of polymer semiconductor material resembling plastic. (Fig. 12.22)

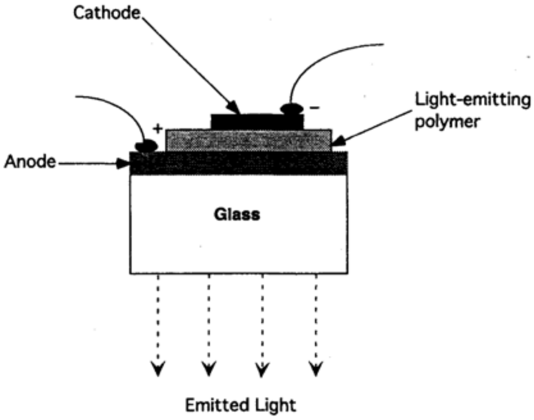


Figure 12-22 Basic design of a simple polymer LED.

LEDs can provide light at very high efficiency (up to 75% of electric consumption can be converted to light).

A variety of polymer configuration including block copolymers, side-chain polymers, and dendrimers provide opportunities for LEDs.