

## 14 Renewable Resource and Biodegradable Polymers

This chapter covers those polymers that are produced from renewable resource raw materials such as corn or that are biodegradable or compostable. This is a developing area in packaging materials and though there are a relatively limited number of polymers used commercially, they will certainly become more numerous and more common in the future.

Biodegradable plastics are made out of ingredients that can be metabolized by naturally occurring microorganisms in the environment. Some petroleum-based plastics will biodegrade eventually, but that process usually takes a very long time and contributes to global warming through the release of carbon dioxide.

Petroleum-based plastic is derived from oil, a limited resource. Plastic based in renewable raw materials biodegrade much faster and can be almost carbon neutral. Renewable plastic is derived from natural plant products such as corn, oats, wood, and other plants, which helps ensure the sustainability of the earth. Polylactic acid (PLA) is the most widely researched and used 100% biodegradable plastic packaging polymer currently, and is made entirely from corn-based cornstarch. Details on PLA are included in the following section.

Cellophane™ is a polymeric cellulose film made from the cellulose from wood, cotton, hemp, or other sources. There are several modifications made to cellulose called polysaccharides (cellulose esters) that are common including cellulose acetate, nitrocellulose, carboxymethyl cellulose (CMC), and ethyl cellulose. Details on cellophane™ and its derivatives are included in several following sections.

Polycaprolactone (PCL) is biodegradable polyester that is often mixed with starch. Details on PLA are included in the following section.

Polyhydroxyalkanoates (PHAs) are naturally produced, and include poly-3-hydroxybutyrate (PHB or PH3B), polyhydroxyvalerate (PHV), and polyhydroxyhexanoate (PHH). A PHA copolymer

called PHBV (poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)) is less stiff and tougher, and it may be used as packaging material.

Several interesting green polymers are discussed in the next few paragraphs. These are ones for which no public permeation data have been identified.

Polyanhydrides currently are used mainly in the medical device and pharmaceutical industry.<sup>1</sup> Figure 14.1 shows the generalized structure of an anhydride polymer and two polyanhydrides that are used to encapsulate certain drugs. The poly(bis-carboxyphenoxypropane), pCCP, is relatively slow to degrade. The poly(sebacic anhydride), pSA, is fast to degrade. Separately neither of these materials can be used, but if a copolymer is made in which 20% of the structure is pCCP and 80% is pSA, the overall properties meet the needs of the drug. Polyanhydrides are now being offered for general uses.

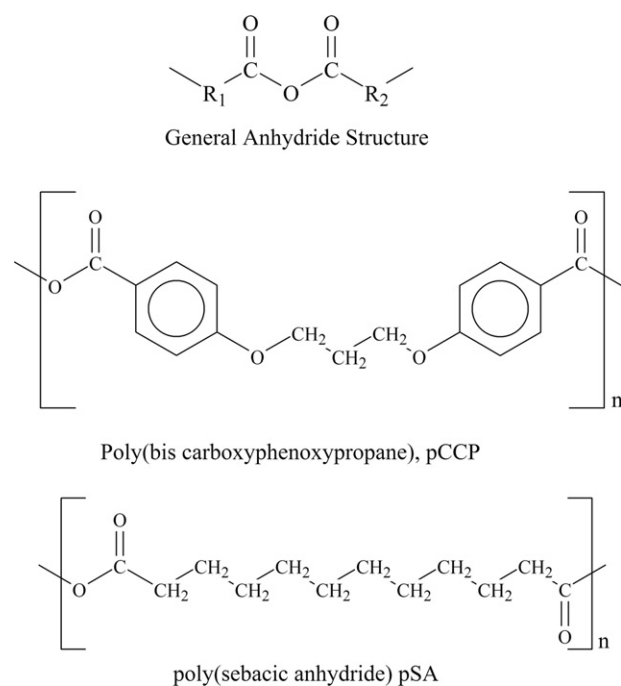
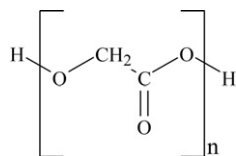


Figure 14.1 Polyanhydride chemical structures.



**Figure 14.2** PGA chemical structures.

Polyglycolic acid (PGA) and its copolymers have found limited use as absorbable sutures and are being evaluated in the biomedical field, where its rapid degradation is useful. That rapid

degradation has limited its use in other applications. There has been patent activity on PGA films.<sup>2</sup> The structure of PGA is shown in Fig. 14.2.

Interest in the “green” materials is strong as the number of commercially available materials grows. Table 14.1 lists some of the commercial materials recently available.

The following sections contain the details of several of the more common biosourced/biodegradable polymers.

**Table 14.1** A list of Some Environmentally Friendly Polymer Based Product Trade Name and Trademarks<sup>3</sup>

Trade Mark	Owner	Material
Aqua-Novon	Novon International Inc. (USA)	PCL
BAK <sup>®</sup>	Bayer AG Corporation (Germany)	Polyester amide
BioBag International AS	Polargruppen (Norway)	Mater-Bi <sup>®</sup>
Bioceta, Biocell, Biocelat	Mazucchelli, S.p.A. (Italy)	Cellulose acetate
Biofan	Gunze (Japan)	PHB/PHBV
Bio-flex <sup>®</sup>	Biotec GmbH (Germany)	Starch
Biogreen	Mitsubishi Gas Chemical Co. (Japan)	PHB
Biomax <sup>®</sup>	DuPont (USA)	PBS-co-PBST
Biomer	Biomer (Germany)	Polyester, PHB
Bionolle 1000	Showa Highpolymer Co. (Japan)	PBS
Bionolle 3000	Showa Highpolymer Co. (Japan)	PBS-co-PBSA
Biopac	Biopac Ltd (UK)	Starch
BioPar <sup>®</sup>	Biop AG Biopolymer GmbH (Germany)	Starch, biodegradable synthetic polymer
Biophan <sup>®</sup>	Trespaphan GmbH (Germany)	PLA
Bioplast <sup>®</sup>	Biotec GmbH (Germany)	Starch, PLA, copolyester
Biopol <sup>™</sup>	Monsanto Co. (Italy)/Metabolix, Inc. (UK)	PHB, PHV, and PHAs
Biopur <sup>®</sup>	Biotec GmbH (Germany)	Starch
Bioska	PlastiRoll Oy (Finland)	Starch/PVA
Bio-Solo	Indaco Manufacturing Ltd (Canada)	Starch, patented additives, PE
Biostarch <sup>®</sup>	Biostarch (Australia)	Maize starch
Bio-Stoll	Stoll Papierfolien (Germany)	Starch, LDPE/Ecostar, additive
Biotec <sup>®</sup>	Bioplast GmbH (Germany)	Thermoplastic starch (TPS <sup>®</sup> )
BioRez <sup>®</sup>	Trans Furans Chemicals (Netherlands)	Furan resin
Biothene <sup>®</sup>	Biothene (UK)	Biofuels from planted soy
CAPA <sup>®</sup>	Solvay Polymers (Italy)	PCL

**Table 14.1** (Continued)

<b>Trade Mark</b>	<b>Owner</b>	<b>Material</b>
CelGreen PH/P-CA	Daicel Chemical Industries Ltd (Japan)	PCL/cellulose acetate
CelloTherm	UCB Films (UK)	Regular cellulose (for microwave)
Chronopol	Chronopol-Boulder, CO (USA)	PLA
Clean Green	StarchTech Inc, MN (USA)	Starch-based biopolymers
Cohpol™	VTT Chemical Technology (Finland)	Starch ester
Cornpol®	Japan Corn Starch (Japan)	Modified starch
Corterra	Shell Chemicals (USA/NL)	PTT
Degra-Novon®	Novon International Inc. (USA)	Polyolefin + additives
EarthShell®	EarthShell Corp., MD (USA)	Starch composite materials
Eastar Bio	Eastman Chemical Company (USA)	Copolyester
ECM Masterbatch Pellets	ECM Biofilms (USA)	Additives for polyolefin products
Ecoflex®	BASF Corporation (Germany)	Poly(butylene adipate)- <i>co</i> -PBAT
Eco-Flow	National Starch & Chemical (USA)	Starch-based biodegradable products
Eco-Foam®	National Starch & Chemical	Foamed starch
Eco-Lam	National Starch & Chemical	Starch, PET, PP
EcoPLA®	Cargill Dow Polymers (USA)	PLA
Ecoplast	Groen Granulaat (Netherlands)	Starch
EnPol	IRe Chemical Co. Ltd (South Korea)	PBS- <i>co</i> -PBSA
Envirofil™	EnPac/DuPont/ConAgra (USA)	Starch/PVA
Enviomold®	Storopack Inc. (USA)	Polystyrene expanded products
EnviroPlastic®	Planet Polymer Technologies, Inc. (USA)	Cellulose acetate
EverCorn™	EverCorn, Inc. (USA)	Starch
Fasal®	Japan Corn Starch Co., Ltd. (Japan) Department Agrobiotechnology, Tulln, (Austria)	50% Wood wastes
FLO-PAK BIO 8®	FP International (USA)	Starch (corn or wheat)
Gohsenol	Nippon Gohsei (Japan)	PVA
GreenFill	Green Light Products Ltd (UK)	Starch/PVA
Greenpol®	SK Corporation (South Korea)	Starch, aliphatic polyester
Hydrolene®	Idroplax S.r.L. (Italy)	PVA
LACEA®	Mitsui Chemicals, Inc. (Japan)	PLA from fermented glucose
Lacty	Shimadzu Corp. (Japan)	PLA
Lignopol	Borregaard Deutschland GmbH	Lignin
Loose Fill®	STOROpack (Germany)	EPS/starch

(Continued)

**Table 14.1** (Continued)

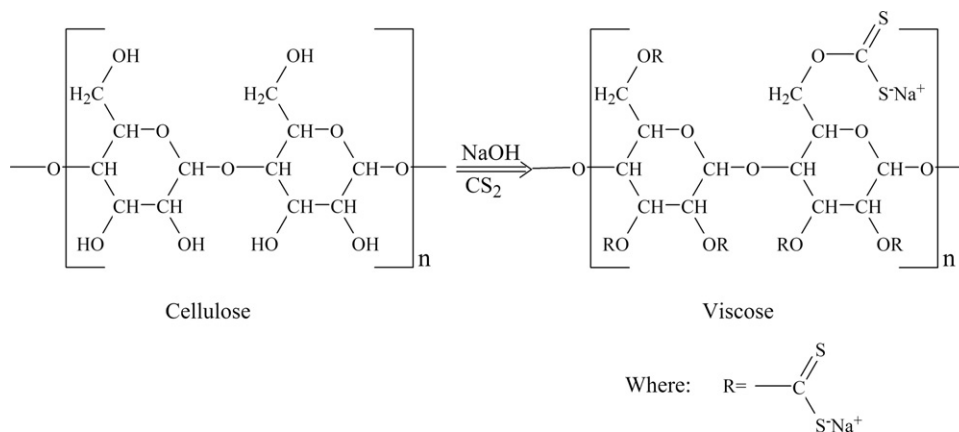
Trade Mark	Owner	Material
Lunare	Nippon Shokubai Co., Ltd	Polyethylene succinate/ adipate
Mater-Bi™	Novamont S.p.A. (Italy)	Starch/cellulose derivative
Mazin	Mazin International (USA)	PLA
Mirel™	Metabolix Inc. (USA)	Corn sugar
NatureFlex™	Innovia Films (UK)	Regenerated cellulose film
NatureWorks®	Cargill Co. (USA)	PLA
Nodax™	Procter & Gamble Co. (USA)	PHB-co-PHA
Novon®	Ecostar GmbH (Germany)	Starch
Paragon	Avebe Bioplastic (Germany)	Starch
Plantic®	Plantic Technologies (Australia)	Cornstarch materials
Poly-NOVON®	Novon International	Starch additives
Polystarch	Willow Ridge Plastics, Inc. (USA)	Additives
POLYOX™	Union Carbide Corporation (USA)	Poly(ethylene oxide)
POVAL	Kuraray Povol Co., Ltd (Japan)	PVA
Pullulan	Hayashibara Biochemical (Japan)	Starch
RenaturE®	Storopack, Inc. (Germany)	Starch
ReSourceBags™	Ventus Kunststoff GmbH	Mater-Bi
Sconacell®	Buna SOW Leuna (Germany)	Starch acetate, plasticizer
Sky-green	Sunkyong Ltd (South Korea)	Aliphatic-copolyester
Solanyl®	Rodenburg Biopolymers (Netherlands)	Starch (from potato waste)
Sorona®	DuPont Tate & Lyle (USA)	PDO
SoyOyl™	Urethane Soy Systems Co. Inc. (USA)	Soy-based products
SPI-Tek	Symphony Plastic Technologies Plc (UK)	Additives
Supol®	Supol GmbH (Germany)	Starch plant oil and sugars
TONE®	Union Carbide Corp. (USA)	PCL
Trayforma	Stora Enso Oyj (Finland)	Cellulose, food tray
Vegemat®	Vegeplast S.A.S. (France)	Starch

Abbreviations: PHBV, polyhydroxybutyrate valerate; PBS-co-PBST, polybutylene succinate copolymer poly(butylene succinate-terephthalate); PBS-co-PBSA, polybutylene succinate copolymer polybutylene succinate adipate; PHV, polyhydroxyvalerate; LDPE, low-density polyethylene; PTT, polytrimethylene terephthalate; PBAT, poly(butylene adipate-co-terephthalate); EPS, expanded polystyrene; 1 PDO, poly(dioxanone).

## 14.1 Cellophane™

Cellophane™ is a polymeric cellulose film made from the cellulose from wood, cotton, hemp, or other sources. The raw material of choice is called dissolving pulp, which is white like cotton and contains 92–98% cellulose. The cellulose is dissolved in

alkali in a process known as mercerization. It is aged several days. The mercerized pulp is treated with carbon disulfide to make an orange solution called viscose, or cellulose xanthate. The viscose solution is then extruded through a slit into a bath of dilute sulfuric acid and sodium sulfate to reconvert the viscose into cellulose. The film is then passed



**Figure 14.3** Conversion of raw cellulose to viscose.

through several more baths, one to remove sulfur, one to bleach the film, and one to add glycerin to prevent the film from becoming brittle. Cellophane™ has a CAS number of 9005-81-6. The approximate chemical structures are shown in Fig. 14.3.

The Cellophane™ may be coated with nitrocellulose or wax to make it impermeable to water vapor. It may also be coated with polyethylene or other materials to make it heat sealable for automated wrapping machines.

*Manufacturers and trademarks:* Innovia Cellophane™.

*Applications and uses:* Cellulosic film applications include tapes and labels, photographic film, coatings for paper, glass, and plastic. Medical applications for cellulosic films include dialysis membranes.

Several Innovia Cellophane™ products:

- Cellophane PØØ—Uncoated regenerated cellulose film (RCF) with no softeners incorporated.
- Cellophane P25—Uncoated RCF with high mechanical strength.
- Cellophane DM/DMS—RCF with one side coated with nitrocellulose by a solvent process.
- Cellophane LST—RCF with both sides coated with nitrocellulose by a solvent process.
- Cellophane XSB—RCF with both sides coated with polyvinylidene chloride (PVDC) by a solvent process (Tables 14.2–14.5).

## 14.2 Nitrocellulose

Nitrocellulose is made by treating cellulose with a mixture of sulfuric and nitric acids. This changes the

hydroxyl groups (–OH) on the cellulose to nitro groups (–NO<sub>3</sub>) as shown in Fig. 14.4. Nitrocellulose, also known as gun cotton and is the main ingredient of smokeless gunpowder, may decompose explosively. In the early twentieth century, it was found to make an excellent film and paint. Nitrocellulose lacquer was used as a finish on guitars and saxophones for most of the twentieth century and is still used on some current applications. Manufactured by (among others) DuPont, the paint was also used on automobiles sharing the same color codes as many guitars including Fender and Gibson brands. Nitrocellulose lacquer is also used as an aircraft dope, painted onto fabric-covered aircraft to tauten and provide protection to the material. Its CAS number is 9004-70-0.

Nitrocellulose is not usually used by itself for film applications, but more commonly is part of multi-layered film structures, especially those based on Cellophane™.

*Manufacturers and trade names:* Innovia Films Cellophane™.

*Applications and uses:* Food wrap (Tables 14.6 and 14.7).

## 14.3 Cellulose Acetate

Cellulose acetate is the acetate ester of cellulose. It is sometimes called acetylated cellulose or xylonite. Its CAS number is 9004-35-7 and the approximate chemical structure is shown in Fig. 14.5.

*Manufacturers and trade names:* Celanese Cellulose Acetate Clarifoil®; Eastman Chemical Company Tenite.

*Applications and uses:* Cellulose acetate is used as a film base in photography, as a component in some

**Table 14.2** Properties of Innovia Cellophane™ Films<sup>4</sup>

Property	Test Method	Conditions	Units	Cellophane™ Type				
				P00	P25	DM/SM	LST	XSB
Tensile strength, MD	ASTM D882		MPa	>165	124	124	117	117
Tensile strength, TD	ASTM D882		MPa	>83	69	62	62	62
Elongation at break, MD	ASTM D882		%	18	22	22	22	22
Elongation at break, TD	ASTM D882		%	32	70	70	70	70
Elasticity modulus, MD	ASTM D882		MPa	>2000	>2000	>2000	>2000	>2000
Elasticity modulus, TD	ASTM D882		MPa	>1000	>1000	>1000	>1000	>1000
Gloss	ASTM D2457	45°				95	85	55
Haze (wide angle)	ASTM D1003	2.5°	%			3.5	4	
Coefficient of friction, static	ASTM D1894	Film-to-film		0.50	0.70	0.25	0.31	0.25
Coefficient of friction, dynamic	ASTM D1894	Film-to-film		0.40	0.60	0.20	0.26	0.20

MD = machine direction, TD = transverse direction.

**Table 14.3** Permeability of Oxygen through PVDC Coated Cellophane™ Film<sup>5</sup>

Temperature (°C)	35		20	
Test Method	JIS Z1707		ASTM D3985	
Relative humidity (%)	0	65	85	100
Permeability coefficient (cm <sup>3</sup> mm/m <sup>2</sup> day atm)	0.03	0.10	0.28	0.81

Sample thickness (mm): 0.023.

**Table 14.4** Permeation of Various Gases through Cellulose (Cellophane™)<sup>6</sup>

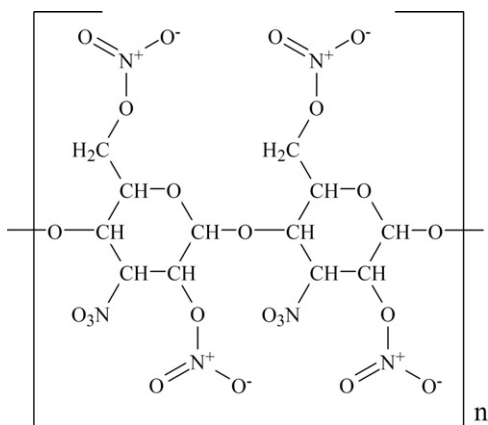
Penetrant	Temperature (°C)	Permeability Coefficient (cm <sup>3</sup> mm/m <sup>2</sup> day atm)
Helium	20	0.033
Hydrogen	25	0.427
Nitrogen	25	0.210
Oxygen	25	0.138
Carbon dioxide	25	0.309
Hydrogen sulfide	45	0.039
Sulfur dioxide	25	0.112
Water	25	12,500

**Table 14.5** Oxygen Gas Transmission Rate and Water Vapor Transmission Rate of Innovia Cellophane™ Films<sup>4</sup>

Product Code	Film Structure	Oxygen Gas Transmission Rate (cm <sup>3</sup> /m <sup>2</sup> day atm)	Water Vapor Transmission Rate (g/m <sup>2</sup> day)
DM 320	Nitrocellulose coated one side	3.0	183
DMS 345	Nitrocellulose coated one side	3.0	183
'K' HB20 (or XS)	Polyvinylidene coated both sides	3.0	12
LST 195	Nitrocellulose coated both sides	3.0	1284
MST/MT33	Nitrocellulose coated both sides	3.0	24
P00	Uncoated	3.0	>1700
P25	Uncoated	3.0	>1700

Oxygen test method: ASTM F1927, at 24 °C and 5% Relative Humidity.

WVTR test method: ASTM E96, at 38 °C and 90% Relative Humidity.

**Figure 14.4** Structure of nitrocellulose.

adhesives, and as a frame material for eyeglasses; it is also used as a synthetic fiber and in the manufacture of cigarette filters, found in screwdriver handles, ink pen reservoirs, and X-ray films.

Eastman Chemical Company Tenite:

- Tenite Acetate 105-29 is heat stabilized and has a plasticizer level of 29%.
- Tenite Acetate 105-33 is heat stabilized and has a plasticizer level of 33%.
- Tenite Acetate 105-25 is heat stabilized and has a plasticizer level of 25%.

**Table 14.6** Typical Properties of Nitrocellulose

Property	Typical Value	Units
Specific gravity of cast film	1.58–1.65	
Refractive index, principal	1.51	
<b>Electrical Properties of Unplasticized Film</b>		
Dielectric constant at 25–30 °C, 60 Hz	7–7.5	
Dielectric constant at 25–30 °C, 1 kHz	7	
Dielectric constant at 25–30 °C, 1 MHz	6	
Power factor at 25–30 °C		
60 Hz	3–5	%
1 kHz	3–6	%
<b>Mechanical Properties of Unplasticized Film</b>		
Tensile strength at 23 °C, 50% RH	62–110	MPa
Elongation at 23 °C and 50% RH	13–14	%
Flexibility of 3- to 4-mil film, MIT double folds under 200-g tension	30–500	

**Table 14.7** Permeation of Gases at 25 °C through Nitrocellulose Film<sup>7</sup>

Permeate Gas	Pressure Differential (mm Hg)	Permeability Coefficient (cm <sup>3</sup> mm/cm <sup>2</sup> day atm)
Helium	4.68	453
Nitrogen	5.21	7.6
Oxygen	4.995	128
Carbon dioxide	4.567	139
Sulfur dioxide	4.442	116
Ammonia	4.04	3749
Water	2.195	413,355
Ethane	4.92	4.1
Propane	4.57	0.6
<i>n</i> -Butane	4.34	~0

- Tenite Acetate 105-27 is heat stabilized and has a plasticizer level of 27%.

See Tables 14.8–14.10 and Figs 14.6–14.10.

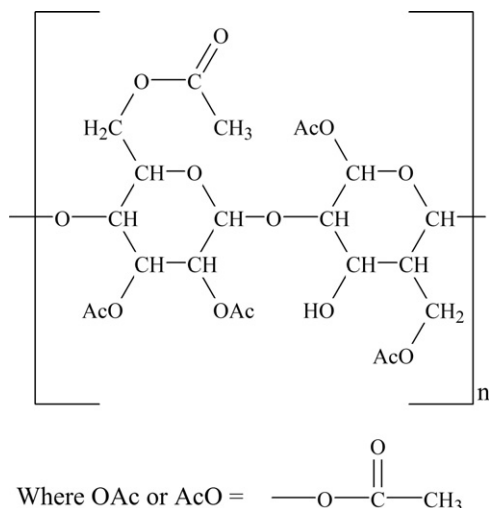
## 14.4 Cellulose Acetate Butyrate

Cellulose acetate butyrate (CAB) is a mixed ester of cellulose. CAB, commonly known as butyrate, is

resistant to ultraviolet rays, has a lower moisture absorption than cellulose acetate, and has an extremely high-impact strength. Its CAS number is 9004-36-8 and the approximate chemical structure is shown in Fig. 14.11.

*Manufacturers and trade names:* Eastman Chemical Company Tenite; Uvex<sup>®</sup>; Excelon<sup>®</sup>, and Spartech<sup>®</sup>.





**Figure 14.5** Chemical structure of cellulose acetate.

*Applications and uses:* Printing visual aids, page protection & Animation cells.

Eastman Chemical Company Tenite:

- Tenite Cellulose Acetate Butyrate 285-04 contains an odor mask and has a plasticizer level of 4%.
- Tenite Cellulose Acetate Butyrate 485-23 contains an odor mask and an ultraviolet inhibitor. It has a plasticizer level of 23%.
- Tenite Cellulose Acetate Butyrate 264-13 has a plasticizer level of 13%.
- Tenite Cellulose Acetate Butyrate 264-10 has a plasticizer level of 10%.
- Tenite Cellulose Acetate Butyrate 264-08 has a plasticizer level of 8% (Table 14.11).

## 14.5 Ethyl Cellulose

Ethyl cellulose is similar in structure to cellulose and cellulose acetate but some of the hydroxyl ( $-\text{OH}$ ) functional groups are replaced on the cellulose by the ethoxy group ( $-\text{O}-\text{CH}_2-\text{CH}_3$ ). Ethyl cellulose has a CAS number of 9004-57-3 and its structure is shown in Fig. 14.12.

*Manufacturers and trade names:* Dow Ethocel™, Ashland Aqualon®.

*Production methods:* Extrusion and solvent casting.

*Applications and uses:* Pharmaceutical applications, cosmetics, nail polish, vitamin coatings, printing inks, specialty coatings, and food packaging (Tables 14.12 and 14.13).

The physical properties of ethyl cellulose films depend somewhat on the composition of the solvent from which they are deposited. This is shown, for flexibility and tensile strength, in Figs 14.13–14.18. See also Tables 14.14 and 14.15 and Figs 14.19 and 14.20.

## 14.6 Polycaprolactone

PCL is biodegradable polyester with a low melting point of around  $60^\circ\text{C}$  and a glass transition temperature of about  $-60^\circ\text{C}$ . PCL is prepared by ring opening polymerization of  $\epsilon$ -caprolactone using a catalyst such as stannous octanoate. The structure of PCL is shown in Fig. 14.21.

PCL is degraded by hydrolysis of its ester linkages in physiological conditions (such as in the human body) and has therefore received a great deal of attention for use as an implantable biomaterial. In particular, it is especially interesting for the preparation of long-term implantable devices. A variety of drugs have been encapsulated within PCL beads for controlled release and targeted drug delivery. PCL is often mixed with starch to obtain a good biodegradable material at a low price.

*Manufacturers and trade names:* Perstorp CAPA® (previously Solvay), Dow Chemical Tone (discontinued).

*Applications and uses:* The mix of PCL and starch has been successfully used for making trash bags in Korea (Yukong Company).

Perstorp

- Capa® 6500 is a 50,000 molecular weight homopolymer which, because of its relatively low viscosity and melting point, has found considerable use in the manufacture of orthopedic casts, as an adhesive and is particularly suited for making injection molded parts.
- Capa® 6800 is a higher viscosity material having a molecular weight of 80,000 and is more suited for the manufacture of films and bottles (Tables 14.16–14.20).

**Table 14.8** Properties of Eastman Chemical Company Tenite Cellulose Acetate Films<sup>8</sup>

Property	ASTM Test Method	Units	Tenite Product Code			
			105-29	105-33	105-25	105-27
Specific Gravity	D 792		1.27	1.27	1.28	1.28
<b>Mechanical Properties</b>						
Tensile stress at yield	D 638	MPa	29.6	26.2	37.2	33.1
Tensile stress at break	D 638	MPa	33.1	29.6	40.7	36.5
Elongation at break	D 638	%	30	30	25	25
Flexural modulus	D 790	MPa	1931	1655	2344	2137
Flexural yield strength	D 790	MPa	46.9	40.0	62.7	54.5
Rockwell hardness, R scale	D 785		71	59	90	82
Izod impact strength, notched at 23 °C	D 256	J/m	203	219	160	187
Izod impact strength, notched at -40 °C	D 256	J/m	53	53	48	48
<b>Thermal Properties</b>						
Deflection temperature at 1.82 MPa	D 648	°C	68	63	77	73
Deflection temperature at 0.455 MPa	D 648	°C	79	74	86	83
Vicat softening temperature	D 1525	°C	105	100	113	109
<b>Miscellaneous Properties</b>						
Water absorption, 24 h immersion	D 570	%	2.3	2.3	2.3	2.3
Refractive index, $n_D$	D 542		1.46–1.49	1.46–1.49	1.46–1.49	1.46–1.49
Light transmission	E 308	%	>90	>90	>90	>90
Haze	D 1003	%	<8.5	<8.5	<8.5	<8.5
Specific heat at 23 °C	DSC	kJ/kg K	1.26–1.67	1.26–1.67	1.26–1.67	1.26–1.67
Thermal conductivity	C 177	W/m K	0.17–0.33	0.17–0.33	0.17–0.33	0.17–0.33
Coefficient of linear thermal expansion	D 696	/°C (mm/mm °C)	11–17 × 10 <sup>-5</sup>	11–17 × 10 <sup>-5</sup>	11–17 × 10 <sup>-5</sup>	11–17 × 10 <sup>-5</sup>
Dielectric strength	D 149	kV/mm	11.8–18.7	11.8–18.7	11.8–18.7	11.8–18.7
Dielectric constant 1 MHz	D 150		3.3–3.8	3.3–3.8	3.3–3.8	3.3–3.8
Dissipation factor 1 MHz	D 150		0.01–0.15	0.01–0.15	0.01–0.15	0.01–0.15
Volume resistivity	D 257	Ω cm	10 <sup>13</sup> –10 <sup>15</sup>	10 <sup>13</sup> –10 <sup>15</sup>	10 <sup>13</sup> –10 <sup>15</sup>	10 <sup>13</sup> –10 <sup>15</sup>

**Table 14.9** Permeability of Various Gases at 35 °C through Cellulose Acetate Membranes<sup>9</sup>

Permeant Gas	Permeability Coefficient (cm <sup>3</sup> mm/m <sup>2</sup> day atm)
Helium	656.6
Oxygen	85.4
Argon	50.6
Nitrogen	17.1
Krypton	23.0
Xenon	6.4
Carbon dioxide	413.7

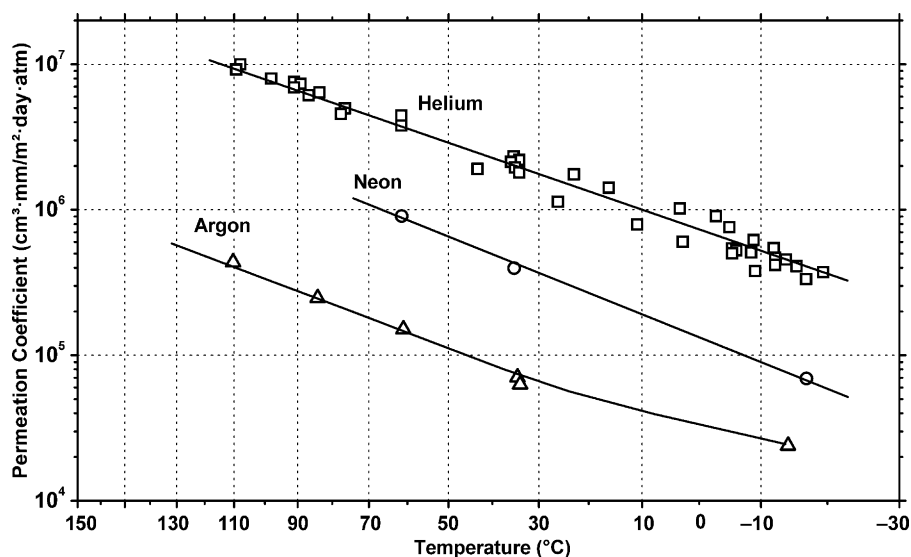
## 14.7 Poly (Lactic Acid)

PLA is derived from renewable resources, such as cornstarch or sugarcane. PLA polymers are considered biodegradable and compostable. PLA is a thermoplastic, high-strength, high-modulus polymer that can be made from annually renewable sources to yield articles for use in either the industrial packaging field or the biocompatible/bioabsorbable medical device market. Bacterial fermentation is used to make lactic acid, which is then converted to the lactide dimer to remove the water molecule that would otherwise limit the ability to make high-molecular weight polymer. The lactide dimer, after

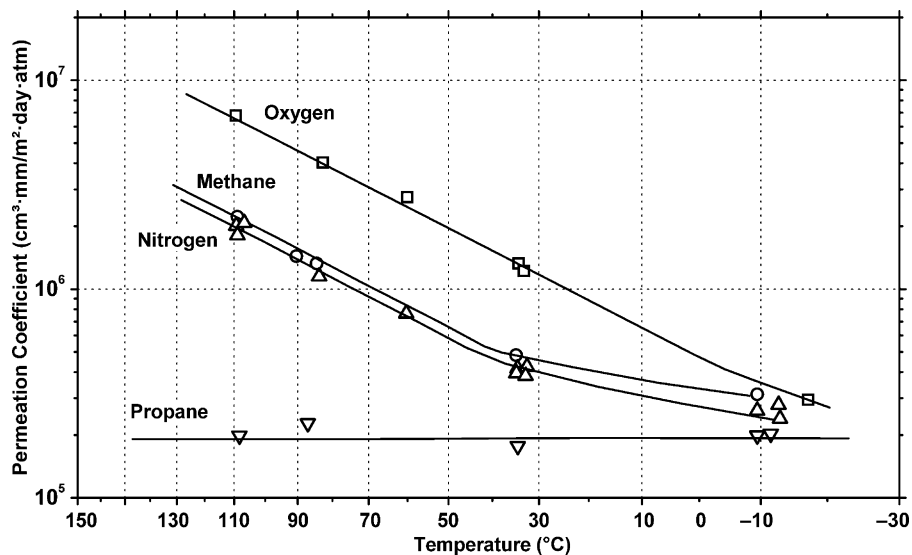
**Table 14.10** Permeability of Various Gases at 22° C through Dense and High-Flux Cellulose Acetate<sup>10</sup>

Gas	Permeability Coefficient (cm <sup>3</sup> mm/m <sup>2</sup> day atm)	
	Dense Cellulose Acetate	High-Flux Cellulose Acetate*
Helium	893	$1.84 \times 10^6$
Neon	158	$3.94 \times 10^4$
Oxygen		$1.25 \times 10^5$
Argon	21	$7.22 \times 10^4$
Methane	9.2	$4.60 \times 10^4$
Nitrogen	9.2	$3.94 \times 10^4$
Propane		$1.97 \times 10^4$

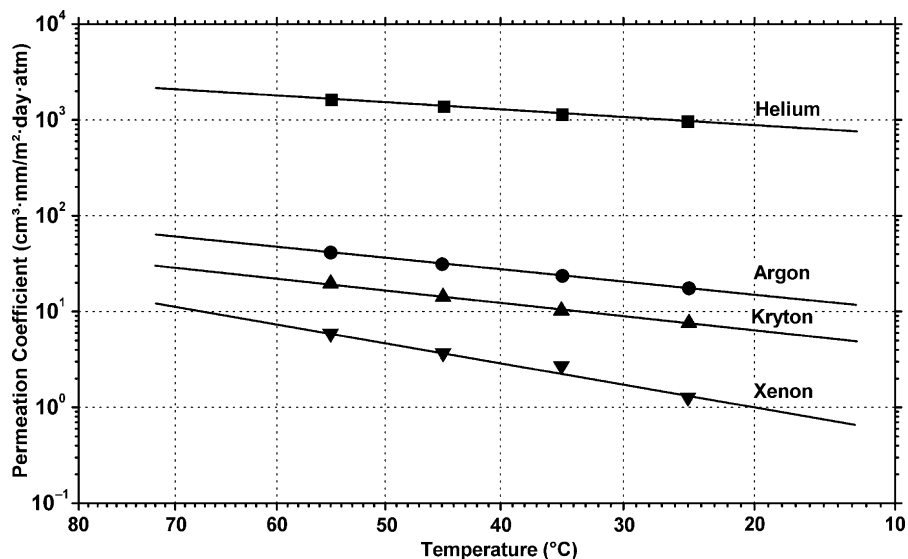
\*While the membrane thickness for fully dense membrane can be measured, the nominal thickness of high-flux material cannot be used to calculate permeability from flow rates. For this reason, permeation rates, not permeabilities, are given for high-flux sample.

**Figure 14.6** Permeation rates of noble gases at 22 °C through high-flux cellulose acetate films<sup>10</sup>. \*The nominal thickness of high-flux material cannot be used to calculate permeability from flow rates. For this reason, permeation rates, not permeability coefficients, are given.

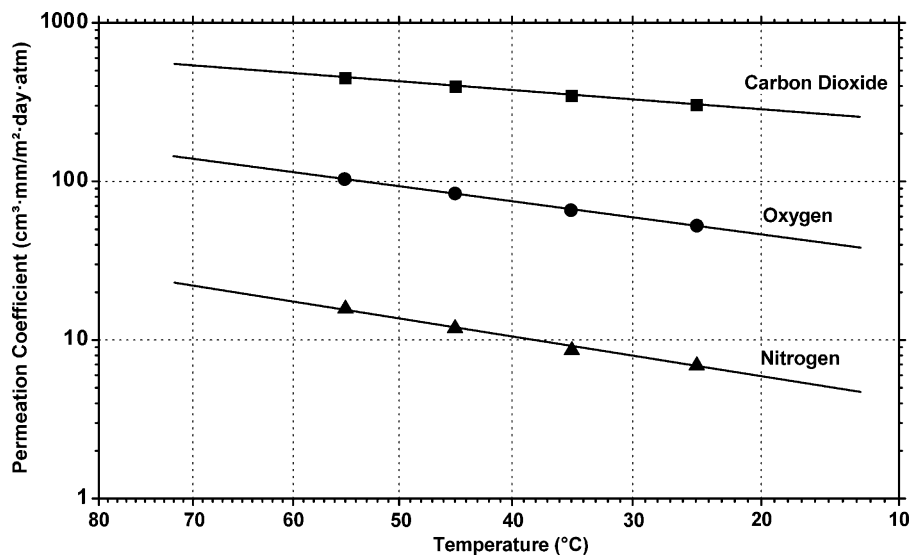
**Figure 14.7** Permeation rates of common gases at 22 °C through high-flux cellulose acetate films<sup>10</sup>. \*The nominal thickness of high-flux material cannot be used to calculate permeability from flow rates. For this reason, permeation rates, not permeability coefficients, are given.

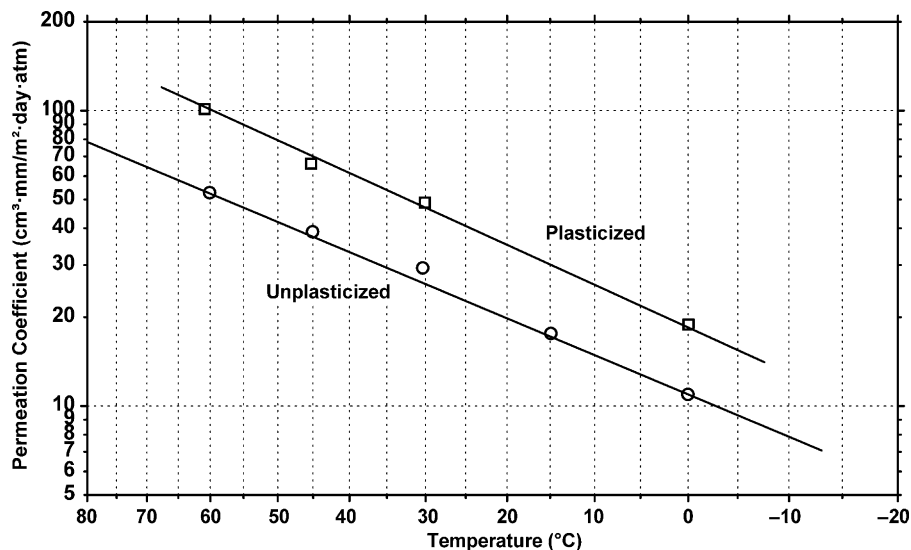


**Figure 14.8** Permeation of noble gases at 35 °C through cellulose acetate films.<sup>9</sup>

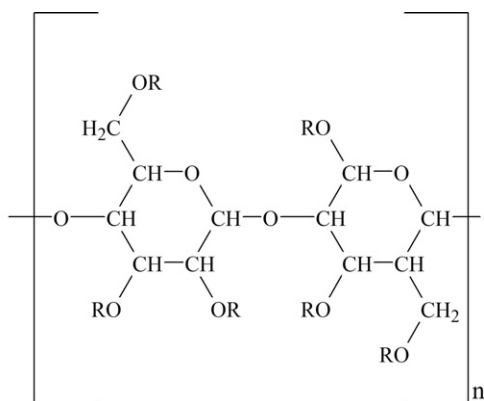


**Figure 14.9** Permeation of common gases at 35 °C through cellulose acetate films.<sup>9</sup>

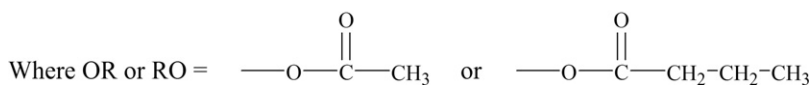




**Figure 14.10** Permeation of hydrogen sulfide vs. temperature through plasticized and unplasticized cellulose acetate films.<sup>20</sup>



**Figure 14.11** Chemical structure of CAB.



the water is removed, can be polymerized without the production of the water. This process is shown in Fig. 14.22. The PLA CAS number is 9002-97-5.

*Manufacturers and trade names:* FKur Bio-Flex<sup>®</sup>, Cereplast Inc. Compostables<sup>®</sup>, Mitsubishi Chemical Fozeas<sup>®</sup>, Natureworks LLC Ingeo<sup>™</sup>, and Alcan Packaging Ceramis<sup>®</sup>-PLA.

*Applications and uses:* Biomedical applications, such as sutures, stents, dialysis media, and drug delivery devices. It is also being evaluated as a material for tissue engineering; loose-fill packaging, compost bags, food packaging, and disposable tableware. PLA can be in the form of fibers and nonwoven textiles; Potential uses: upholstery, disposable garments, awnings, and feminine hygiene products.

NatureWorks LLC

- Ingeo<sup>™</sup> Biopolymer 4032D Biaxially Oriented Films—High heat
- Ingeo<sup>™</sup> Biopolymer 4043D Biaxially Oriented Films—General purpose (see Table 14.21)

FKur

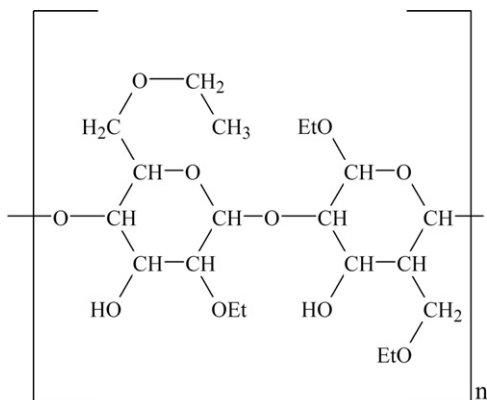
- Bio-Flex<sup>®</sup> F 1110 for film extrusion
- Bio-Flex<sup>®</sup> F 1130 for film extrusion
- Bio-Flex<sup>®</sup> F 2110 for film extrusion
- Bio-Flex<sup>®</sup> A 4100 CL for film extrusion
- Bio-Flex<sup>®</sup> F 6510 for film extrusion

See Tables 14.22–14.24 and Figs 14.23–14.26.

**Table 14.11** Properties of Eastman Chemical Company Tenite CAB Films<sup>8</sup>

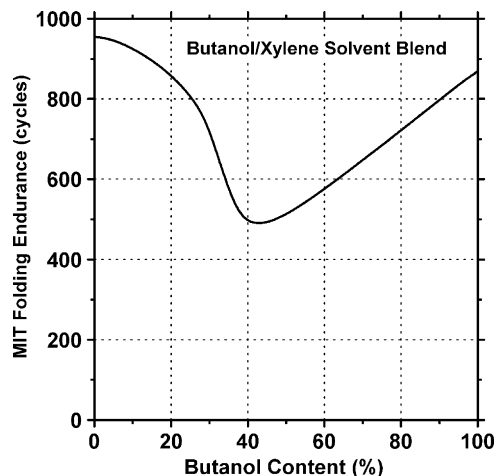
Property	ASTM Test Method	Units	Tenite Product Code				
			285-04	485-23	264-13	264-10	264-08
Specific gravity	D 792		1.205	1.16	1.18	1.19	1.20
<b>Mechanical Properties</b>							
Tensile stress at yield	D 638	MPa	43.1	17.2	29.0	33.1	37.2
Tensile stress at break	D 638	MPa	52.4	20.0	39.3	43.4	47.6
Elongation at break	D 638	%	55	50	50	50	50
Flexural modulus	D 790	MPa	1793	827	1241	1379	1586
Flexural yield strength	D 790	MPa	60	21.4	39.9	45.5	51.0
Rockwell hardness, R scale	D 785		98		59	78	88
Izod impact strength, notched at 23 °C	D 256	J/m	152	448	283	240	198
Izod impact strength, notched at -40 °C	D 256	J/m	83	123	101	96	91
<b>Thermal Properties</b>							
Deflection temperature at 1.82 MPa	D 648	°C	85	52	69	74	79
Deflection temperature at 0.455 MPa	D 648	°C	95	68	81	85	89
Vicat softening temperature	D 1525	°C	118	88	100	104	109

Miscellaneous Properties							
Water absorption, 24 h immersion	D 570	%	1.7	1.2	1.4	1.4	1.5
Refractive index, $n_D$	D 542		1.46–1.49	1.46–1.49	1.46–1.49	1.46–1.49	1.46–1.49
Light transmission	E 308	%	>90	>90	>90	>90	>90
Haze	D 1003	%	<8.5	<8.5	<8.5	<8.5	<8.5
Specific heat at 23 °C	DSC	kJ/kg K	1.26–1.67	1.26–1.67	1.26–1.67	1.26–1.67	1.26–1.67
Thermal conductivity	C 177	W/m K	0.17–0.33	0.17–0.33	0.17–0.33	0.17–0.33	0.17–0.33
Coefficient of linear thermal expansion	D 696	/°C (mm/mm °C)	11–17 × 10 <sup>-5</sup>	11–17 × 10 <sup>-5</sup>	11–17 × 10 <sup>-5</sup>	11–17 × 10 <sup>-5</sup>	11–17 × 10 <sup>-5</sup>
Dielectric strength	D 149	kV/mm	11.8–18.7	11.8–18.7	11.8–18.7	11.8–18.7	11.8–18.7
Dielectric constant 1 MHz	D 150		3.3–3.8	3.3–3.8	3.3–3.8	3.3–3.8	3.3–3.8
Dissipation factor 1 MHz	D 150		0.01–0.15	0.01–0.15	0.01–0.15	0.01–0.15	0.01–0.15
Volume resistivity	D 257	Ω cm	10 <sup>13</sup> –10 <sup>15</sup>	10 <sup>13</sup> –10 <sup>15</sup>	10 <sup>13</sup> –10 <sup>15</sup>	10 <sup>13</sup> –10 <sup>15</sup>	10 <sup>13</sup> –10 <sup>15</sup>



Where OEt or EtO =  $\text{---O---CH}_2\text{---CH}_3$

**Figure 14.12** Structure of ethyl cellulose.



**Figure 14.13** MIT folding endurance vs. butanol/xylene solvent composition of ethyl cellulose film.<sup>11</sup>

**Table 14.12** Description of Ethyl Cellulose Types<sup>11</sup>

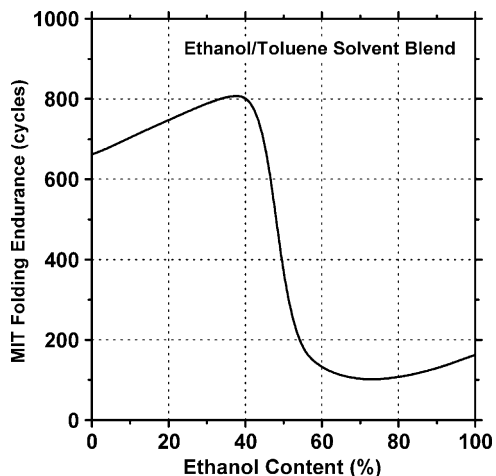
Type	Ethoxyl Content (%)	Degree of Substitution Groups per Anhydroglucose Unit
K-type	45.0–47.2	2.22–2.41
N-type	48.0–49.5	2.46–2.58
T-type	49.6–51.5	2.58–2.73
X-type	50.5–52.5	2.65–2.81

**Table 14.13** Typical Properties of a N-type Ethyl Cellulose<sup>11</sup>

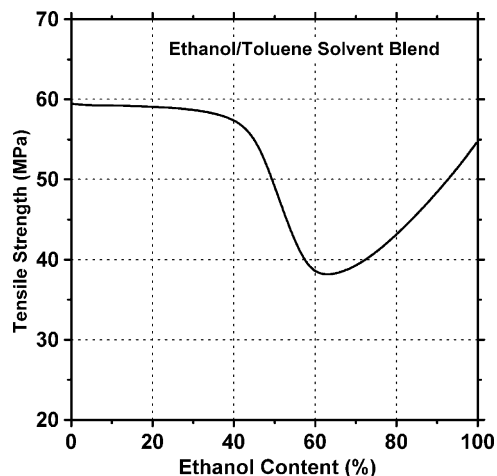
Property	Units	Typical Value
Dielectric constant at 25 °C, 1 MHz		2.8–3.9
Dielectric constant at 25 °C, 1 kHz		3.0–4.1
Dielectric constant at 25 °C, 60 Hz		2.5–4.0
Dissipation factor at 25 °C, 1 kHz		0.002–0.02
Dissipation factor at 25 °C, 60 Hz		0.005–0.02
Volume resistivity	$\Omega$ cm	$10^{12}$ – $10^{14}$
Elongation at rupture	%	7–30
Flexibility, folding endurance	MIT double folds	160–2000
Hardness index, Sward		52–61
Moisture absorption, in 24 h at 80% RH	%	2
Refractive index		1.47
Softening point	°C	152–162
Specific gravity		1.14
Tensile strength, dry	MPa	47–72
Tensile strength, wet	% of dry strength	80–85

Thickness: 76  $\mu$ m film.

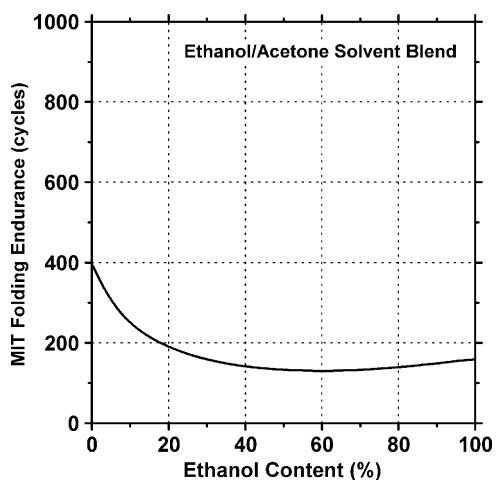




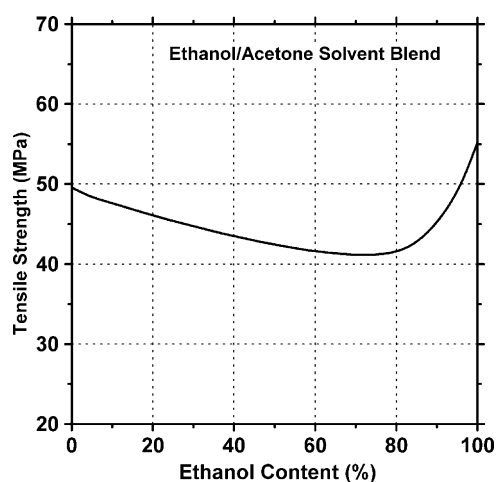
**Figure 14.14** MIT folding endurance vs. ethanol/toluene solvent composition of ethyl cellulose film.<sup>11</sup>



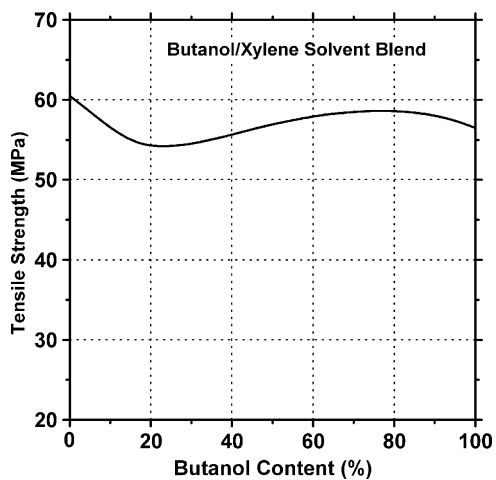
**Figure 14.17** Tensile strength vs. ethanol/toluene solvent composition of ethyl cellulose film.<sup>11</sup>



**Figure 14.15** MIT folding endurance vs. ethanol/acetone solvent composition of ethyl cellulose film.<sup>11</sup>



**Figure 14.18** Tensile strength vs. ethanol/acetone solvent composition of ethyl cellulose film.<sup>11</sup>



**Figure 14.16** Tensile strength vs. butanol/xylene solvent composition of ethyl cellulose film.<sup>11</sup>

## 14.8 Poly-3-hydroxybutyrate (PHB or PH3B)

Polyhydroxyalkanoates (PHAs) are naturally produced, and include poly-3-hydroxybutyrate (PHB or PH3B), PHV, and PHH. A PHA copolymer called poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) is less stiff and tougher, and it may be used as packaging material. Chemical structures of some of these polymers are shown in Fig. 14.27.

*Manufacturers and trade names:* FKur Bio-Flex<sup>®</sup>, Cereplast Inc. Compostables<sup>®</sup>,

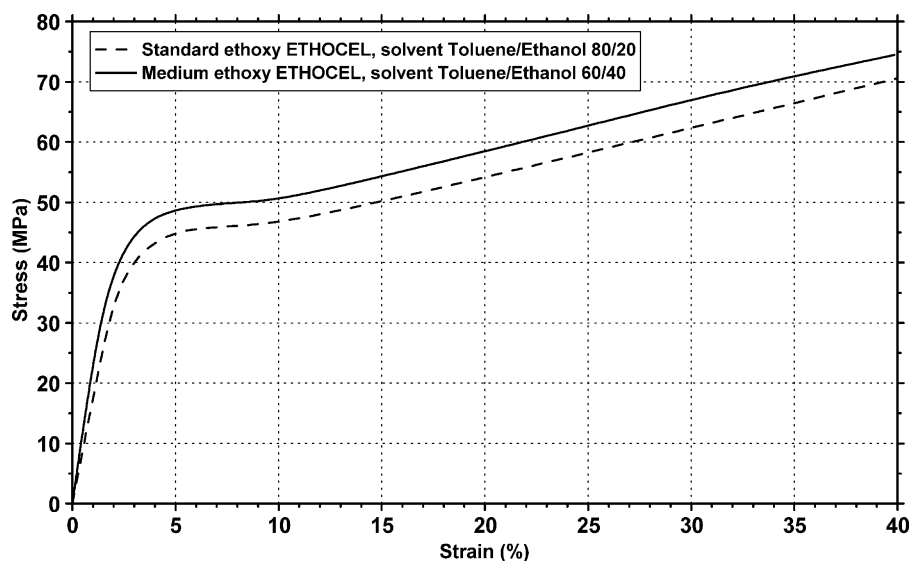
**Table 14.14** Permeation of Gases through Ethyl Cellulose<sup>7</sup>

Permeant Gas	Permeability Coefficient (cm <sup>3</sup> mm/m <sup>2</sup> day atm)
Helium	3510
Nitrogen	291
Oxygen	965
Argon	670
Carbon dioxide	7420
Sulfur dioxide	17,300
Ammonia	46,300
Water	586,000
Ethane	604
Propane	243
<i>n</i> -Butane	254
<i>n</i> -Pentane	243
<i>n</i> -Hexane	503

**Table 14.15** Permeation of Various Gases at 35 °C through Membranes made from Ashland Aqualon<sup>®</sup> Ethyl Cellulose<sup>12</sup>

Material Grade	Ethoxy Content (%)	Permeability Coefficient (cm <sup>3</sup> mm/m <sup>2</sup> day atm)				
		Carbon dioxide	Helium	Oxygen	Methane	Nitrogen
EC K-100	47.2	78	43	12.8	7.7	3.6
EC N-100	47.9	102	58	17.0	10.9	5.1
EC T-10	49.6	129	69	20.4	12.3	5.7

Pressure differential: 10 atm.

**Figure 14.19** Stress vs. strain of Dow Ethocel ethyl cellulose resins.<sup>21</sup>

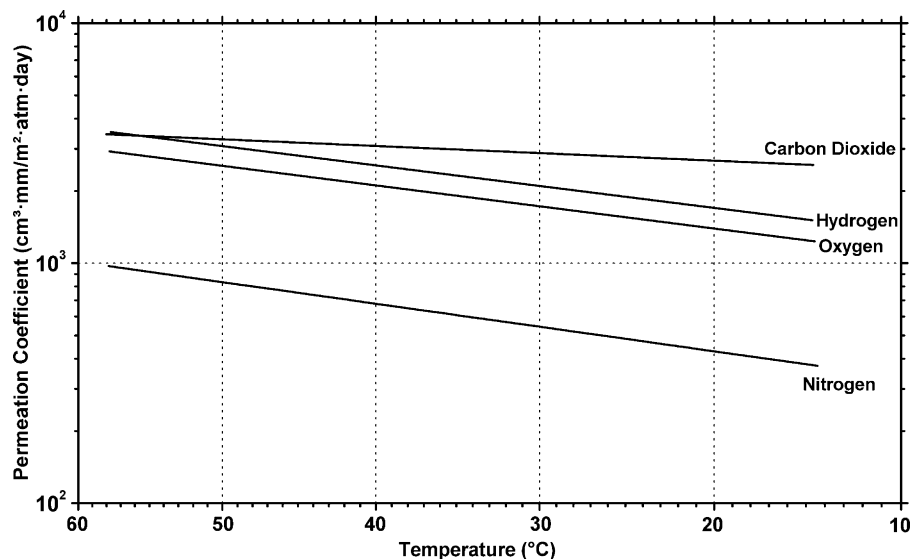


Figure 14.20 Permeation of various gases vs. temperature for Dow Ethocel™ ethyl cellulose film.<sup>22</sup>

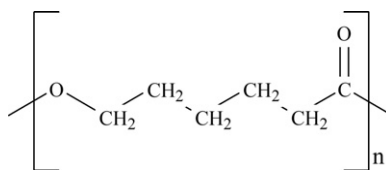


Figure 14.21 Structure of PCL.

Table 14.16 Typical Physical Properties of Capa® Thermoplastics<sup>13</sup>

Property	ASTM Test	Capa® 6500	Capa® 6800	Units
<b>Thermal Properties</b>				
Melting point	DSC	60–62	60–62	°C
Glass transition temperature, $T_g$		–60	–60	°C
<b>Tensile Properties</b>				
Yield stress, 100 mm/min	D 412-87	17.5	16	MPa
Yield stress, 500 mm/min	D 412-87	17.2	14	
Modulus, 1 mm/min	D 412-87	470	440	MPa
Modulus, 10 mm/min	D 412-87	430	500	
Stress at break, 100 mm/min	D 412-87	29	54	MPa
Strain at break, 100 mm/min	D 412-87	>700	920	%
Flexural modulus, 2 mm/min	D 790	411	nd	MPa
Hardness, shore A	D 2240	95	94	
Hardness, shore D	D 2240	51	50	

**Table 14.17** Water Vapor Permeation at 20 °C and 100% Relative Humidity through PCL Film<sup>14</sup>

Film Thickness (mm)	Orientation Speed (m/min)	Vapor Permeation rate (g mm/m <sup>2</sup> day atm)*
1.046	2.2	6485
0.051	18.5	304

\*Vapor permeation rates do not usually contain a pressure differential; see reference for description of nonstandard test method.

**Table 14.18** Oxygen Permeation at 35 °C and 0% Relative Humidity through PCL Film<sup>14</sup>

Film Thickness (mm)	Orientation Speed (m/min)	Permeability Coefficient (cm <sup>3</sup> mm/m <sup>2</sup> day atm)
1.046	2.2	96
0.051	18.5	101

Test equipment: Mocon Ox-Tran 2/20 Modular System.

Mitsubishi Chemical Fozeas<sup>®</sup>, NatureWorks LLC Ingeo<sup>™</sup>, Alcan Packaging Ceramis<sup>®</sup>-PLA, Metabolix/ADM Tirel, Tianan Enmat, Copersucar Biocycle, Biomer Biomer L, and Procter & Gamble Nodax.

*Applications and uses:* Biomedical applications, such as sutures, stents, dialysis media, and drug

delivery devices. It is also being evaluated as a material for tissue engineering; loose-fill packaging, compost bags, food packaging, and disposable tableware. PLA can be in the form of fibers and nonwoven textiles; Potential uses: upholstery, disposable garments, awnings, and feminine hygiene products (Table 14.25).

**Table 14.19** Water Vapor Permeation at 20 °C and 100% Relative Humidity through Films made from Blends of PCL, Starch and Glycerol<sup>14</sup>

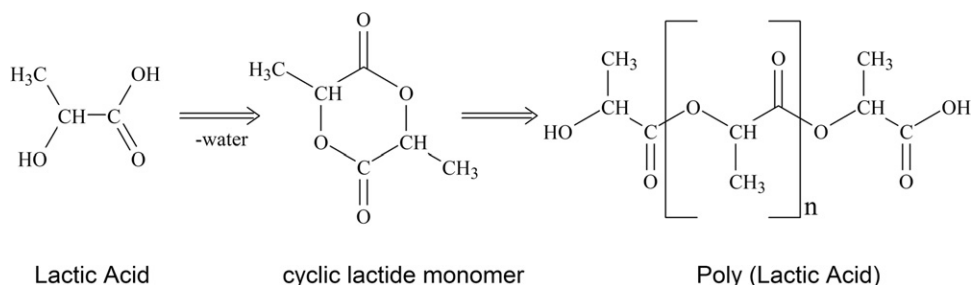
Film Composition PCL/ Starch/Glycerol (wt%)	Film Thickness (mm)	Orientation Speed (m/min)	Vapor Permeation Rate (g mm/m <sup>2</sup> day atm)*
0/60/40	0.469	0	19,300
2/58/40	0.204	0	10,100
10/54/36	0.665	0	21,800
10/54/36	0.195	3.8	10,100
20/48/32	0.208	2.2	6600
20/48/32	0.070	9.9	3040
30/42/28	0.460	0	8900
30/42/28	0.217	2.2	2600
30/42/28	0.051	8.8	1100
100/0/0	1.046	2.2	6500
100/0/0	0.051	18.5	300

\*Vapor permeation rates do not usually contain a pressure differential; see reference for description of nonstandard test method.

**Table 14.20** Oxygen Permeation at 35 °C and 0% Relative Humidity through Films made from Blends of PCL, Starch and Glycerol<sup>14</sup>

Film Composition PCL/ Starch/Glycerol (wt%)	Film Thickness (mm)	Orientation Speed (m/min)	Permeability Coefficient (cm <sup>3</sup> mm/m <sup>2</sup> day atm)
0/60/40	0.469	0	0
2/58/40	0.204	0	0
10/54/36	0.665	0	0
10/54/36	0.195	3.8	0
20/48/32	0.208	2.2	1.7
20/48/32	0.070	9.9	0.1
30/42/28	0.460	0	4.3
30/42/28	0.217	2.2	2.1
30/42/28	0.051	8.8	2.0
100/0/0	1.046	2.2	96
100/0/0	0.051	18.5	101

Test equipment: Mocon Ox-Tran 2/20 Modular System.

**Figure 14.22** Conversion of lactic acid to PLA.**Table 14.21** Properties of NatureWorks LLC Ingeo™ Biopolymer Biaxially Oriented Films PLA films<sup>15,16</sup>

Film Property	Ingeo™ 4032D	Ingeo™ 4043D	Units	ASTM Method
Density	1.24	1.24	g/cm <sup>3</sup>	D1505
Tensile strength, MD	103	110	MPa	D882
Tensile strength, TD	145	145	MPa	D882
Tensile modulus, MD	3447	3309	MPa	D882
Tensile modulus, TD	3792	3861	MPa	D882
Elongation at break, MD	180	160	%	D882
Elongation at break, TD	100	100	%	D882
Elmendorf tear, MD	0.67	0.59	g/μm	D1922
Elmendorf tear, TD	0.55	0.51	g/μm	D1922
Spencer impact	2.5	2.5	J	
<b>Optical Characteristics</b>				
Haze	2.1	2.1	%	D1003
Gloss, 20°	90	90		D1003
<b>Thermal Characteristics</b>				
Melting point	155–170	145–160	°C	D3418

**Table 14.22** Properties of FKur Bio-Flex® PLA Films<sup>17</sup>

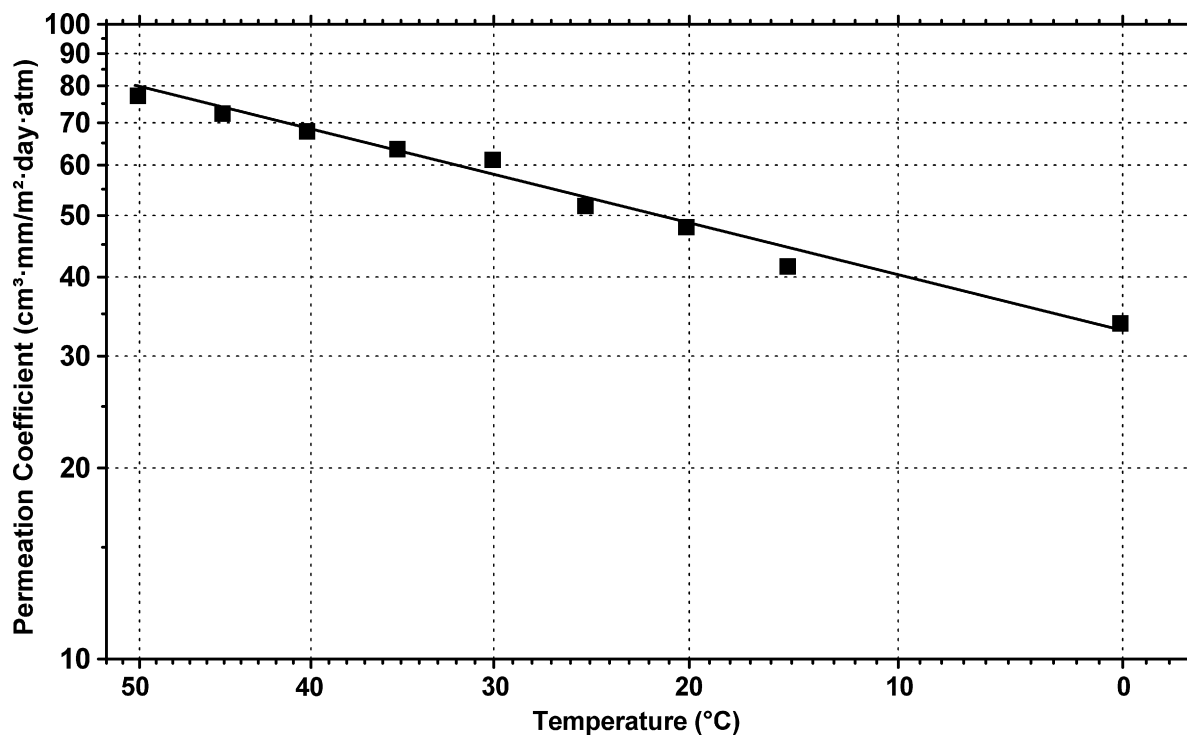
Property	F 1110	F 1130	F 2110	F 6510	A 4100 CL	Units	Test Method
<b>Mechanical Properties</b>							
Tensile modulus of elasticity	230	390	730	2600	1840	MPa	ISO 527
Tensile strength	16	17	20	47	44	MPa	ISO 527
Tensile strain at tensile strength	>300	>300	>300	4	5	%	ISO 527
Tensile stress at break no break	MPa	No break	No break	23	22	ISO 527	
Tensile strain at break no break	%	No break	No break	19	12	ISO 527	
Flexural modulus	215	370	680	2650	1770	MPa	ISO 178
Flexural strain at break no break	%	No break	No break	No break	No break	ISO 178	
Flexural stress at 3.5% strain	6	7	17	64	48	MPa	ISO 178
Notched impact strength (Charpy), RT	No break	No break	83	7	3	kJ/m <sup>2</sup>	ISO 179-1/1 eA
Impact strength (Charpy), RT	No break	No break	No break	No break	44	kJ/m <sup>2</sup>	ISO 179-1/1 eU
Density	1.28	1.40	1.27	1.30	1.24	g/cm <sup>3</sup>	ISO 1183
<b>Thermal Properties</b>							
Melt temperature	>155	>155	145 –160	150 –170	>155	°C	ISO 3146-C
Vicat A softening temperature	68	89	78	60	44	°C	ISO 306
Melt flow rate (190 °C/2.16 kg)	2–4	2–4	3–5	2.5–4.5	6–10	g/10 min	ISO 1133

**Table 14.23** Permeation Properties of FKur Bio-Flex® PLA Films<sup>17</sup>

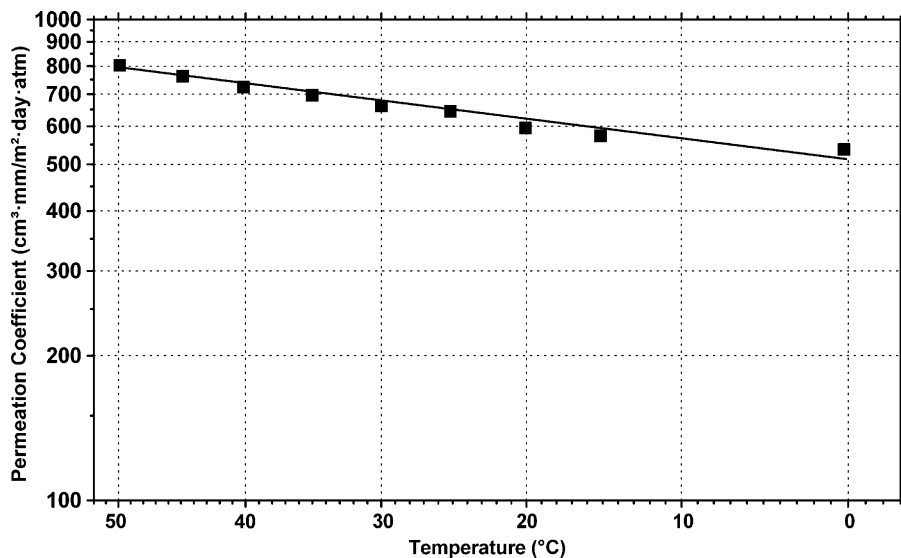
Property	F 1130	F 2110	F 6510	A 4100 CL	Units	Test Method
Film Thickness	45	30	20	20	$\mu\text{m}$	
Water vapor	70	130	130	170	$\text{g}/(\text{m}^2 \text{ d})$	ISO 15 106-3
Oxygen	850	1450	1060	130	$\text{cm}^3/(\text{m}^2 \text{ d bar})$	ISO 15 105-2
Nitrogen	160	230	150	65*	$\text{cm}^3/(\text{m}^2 \text{ d bar})$	DIN 53380-2

\*25  $\mu\text{m}$ .**Table 14.24** Permeation Properties of Cereplast Compostables® Compostable 3000 PLA Films<sup>17,18</sup>

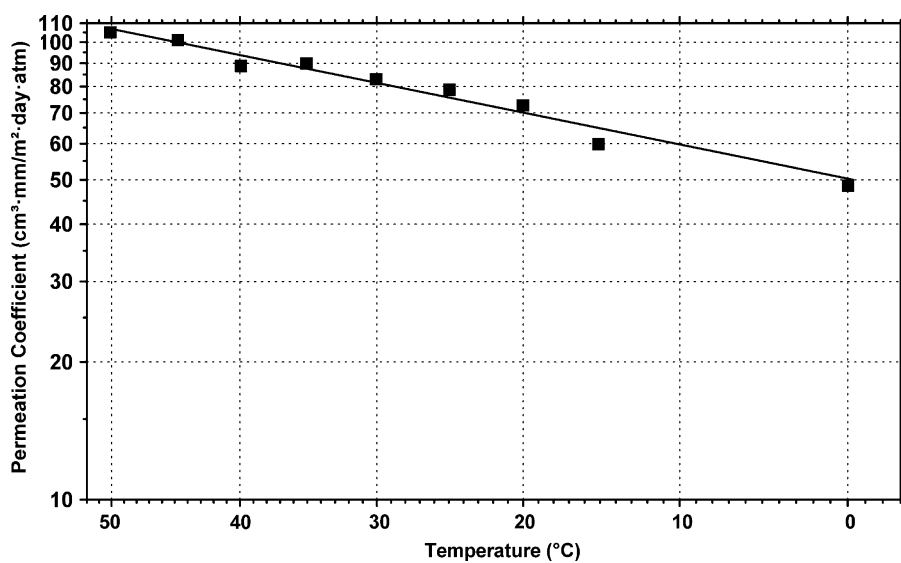
Physical Property	ASTM Test Method	Value	Units
Tensile strength at max.	D 638	26.5	MPa
Tensile elongation at break	D 638	360	%
Tensile modulus	D 638	1210	MPa
Flexural modulus	D 790	1050	MPa
Flexural strength	D 790	28.3	MPa
Gardner impact	D 5420	18+	J
Notched Izod impact strength (23 °C)	D 256	0.425	kJ/m
Melt flow index 190 °C at 2.16 kg	D 1238	3.5	g/10 min
Density	D 792 Method A	1.26	

**Figure 14.23** Permeation coefficient of methane vs. temperature through linear PLA film.<sup>23</sup>

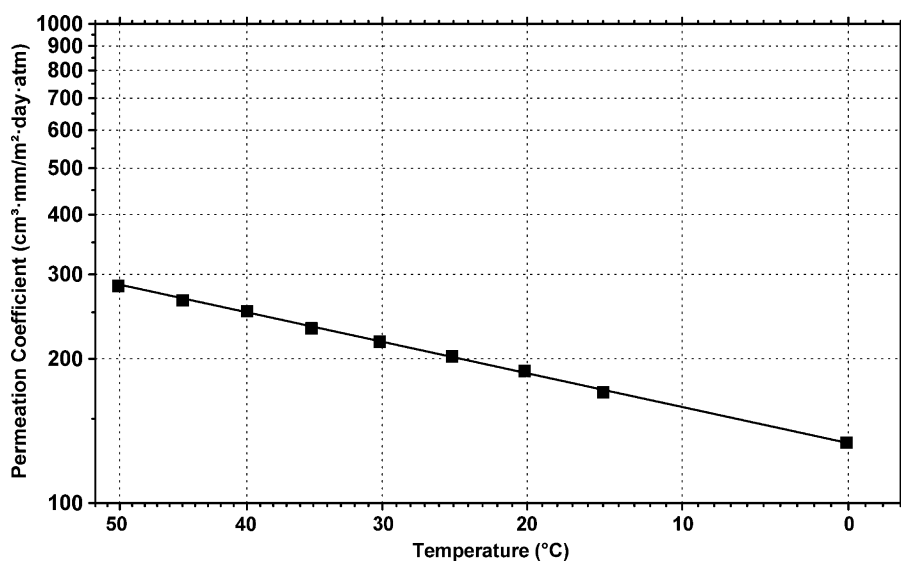
**Figure 14.24** Permeation coefficient of carbon dioxide vs. temperature through linear PLA film.<sup>23</sup>



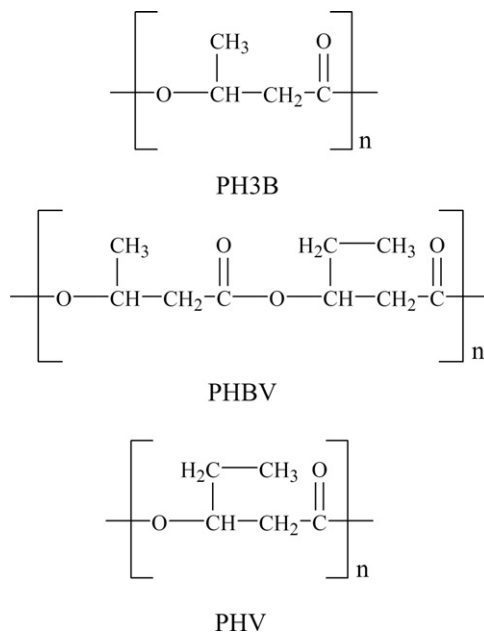
**Figure 14.25** Permeation coefficient of nitrogen vs. temperature through linear PLA film.<sup>23</sup>



**Figure 14.26** Permeation coefficient of oxygen vs. temperature through linear PLA film.<sup>23</sup>







**Figure 14.27** Structures of several PHAs.

**Table 14.25** Permeability Coefficients for Poly-3-hydroxybutyrate (PHB) Membranes<sup>19</sup>

Temperature °C	Methanol	Ethanol	<i>n</i> -Propanol	Water
	<b>Permeability Coefficient (cm<sup>3</sup> mm/m<sup>2</sup> day atm)</b>			
30	—	—	—	34,100
50	74,200	58,400	31,500	49,200
55	104,000	59,100	34,100	65,000
60	108,000	60,400	34,800	68,900
65	137,000	80,800	38,700	125,000

±5% Error.

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