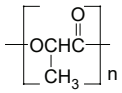
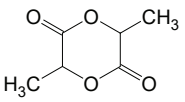
PLA poly(lactic acid)

PARAMETER	UNIT	VALUE	REFERENCES
GENERAL			
Common name	-	poly(lactic acid)	
CAS name	-	poly[oxy(1-methyl-2-oxo-1,2-ethanediyl)]; 1,4-dioxane-2,5-dione, 3,6-dimethyl-, homopolymer	
Acronym	-	PLA	
CAS number	-	51063-13-9, 26680-10-4, 34346-01-5	
Formula			
HISTORY			
Person to discover	-	Carother, W H; Dourough, G L; Van Natta F J. Filachione, E M	Carother, W H; Dourough, G L; Van Natta F j, J. Am. Chem. Soc., 54, 761-72, 1932; Filachione, E M, US Patent 2,396,994, USA, Mar. 19, 1946.
Date	-	1932, 1946	
Details	-	first synthesis by DuPont scientists; lactic acid was polymerized in the presence of p-toluenesulfonic acid	
SYNTHESIS			
Monomer(s) structure	-		
Monomer(s) CAS number(s)	-	4511-42-6	
Monomer(s) molecular weight(s)	dalton, g/mol, amu	144.13	
Monomer ratio	-	100% or less (in blends)	
Concentration of L-lactide	%	94-98	
Formulation example	-	lactic acid and tin catalyst	
Method of synthesis	-	lactic acid is heated at 150ºC to obtain oligomeric PLA (polymerization degree: 1-8). Oligomers are heated at 180ºC under vacuum for 5 hours to give PLA having molecular weight of 100,000	Bastioli, C, Handbook of Biodegradable Polymers, Rapra, 2005.
Temperature of polymerization	ºC	150-180	
Time of polymerization	h	5	
Pressure of polymerization	Pa	vacuum	
Catalyst	-	tin	
Number average molecular weight, M_n	dalton, g/mol, amu	74,000-660,000	
Mass average molecular weight, M_w	dalton, g/mol, amu	80,000-380,000; 4000-6000 (DL); 100000 (L)	
Polydispersity, M_w/M_n	-	1.5-3.79	Bastioli, C, Handbook of Biodegradable Polymers, Rapra, 2005.

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STRUCTURE			
Crystallinity	%	20-47; 25-70 (L-PLA); 10-20 (film); 65 (fiber), 20-36 (DSC); 20-44 (WAXD)	Bastioli, C, Handbook of Biodegradable Polymers, Rapra, 2005; Rudnik, E; Briassoulis, D, Ind. Crops Prod., 33, 648-58, 2011; Tsai, C-C; Wu, R-J; Cheng, H-Y; Li, S-C; Siao, Y-Y; Kong, D-C; Jang, G-W, Polym. Deg. Stab., 95, 1292-98, 2010.
Cell type (lattice)	-	orthorhombic (α), hexagonal (α'), trigonal (β), monoclinic (γ)	
Cell dimensions	nm	a:b:c=1.06:0.61:2.88 (orthorhombic, α); a=b:c=1.052:0.88 (trigonal, β); a:b:c=0.995:0.625:0.88 (monoclinic, γ)	Johnson, C M; Sugiharto, A B; Roke, S, Chem. Phys. Lett., 449, 191-95, 2007; Lin, T T; Liu, X Y; He, C, Polymer, 51, 2779-85, 2010.
Polymorphs	-	α, α', β, γ	Kalish, J P; Zeng, X; Yang, X; Hsu, S L, Polymer, in press, 2011.
Lamellae thickness	nm	2.03-28.6	Tsai, C-C; Wu, R-J; Cheng, H-Y; Li, S-C; Siao, Y-Y; Kong, D-C; Jang, G-W, Polym. Deg. Stab., 95, 1292-98, 2010.
Avrami constants, k/n	-	n=1.8-2.3	Tsai, C-C; Wu, R-J; Cheng, H-Y; Li, S-C; Siao, Y-Y; Kong, D-C; Jang, G-W, Polym. Deg. Stab., 95, 1292-98, 2010.
COMMERCIAL POLYMERS			
Some manufacturers	-	Cargill; Durect	
Trade names	-	PLA; Lactel	
PHYSICAL PROPERTIES			
Density at 20°C	g cm^{-3}	1.21-1.29	
Refractive index, 20°C	-	1.35-1.45	
Transmittance	%	2.2	
Melting temperature, DSC	°C	164-178; 180-184 (L-PLA)	Bastioli, C, Handbook of Biodegradable Polymers, Rapra, 2005.
Decomposition temperature	°C	>200	
Glass transition temperature	°C	55-75	Bastioli, C, Handbook of Biodegradable Polymers, Rapra, 2005.
Specific heat capacity	J K^{-1} kg^{-1}	540-600	
Heat of fusion	kJ mol^{-1}	146	
Vicat temperature VST/A/50	°C	55-60	
Enthalpy of fusion	J g^{-1}	21.9-43.8	
Hansen solubility parameters, dD, dP, dH	$(J\ cm^{-3})^{0.5}$	18.50, 9.70, 6.0	Agrawal, A; Saran, A D; Rath, S S; Khanna, A, Polymer, 45, 8603-12, 2004.
Radius of interaction	$(J\ cm^{-3})^{0.5}$	13.53	Agrawal, A; Saran, A D; Rath, S S; Khanna, A, Polymer, 45, 8603-12, 2004.
Hildebrand solubility parameter	MPa0.5	calc.=19.2-20.3; exp.=19.0-21.0	Auras, R; Harte, B; Selke, S, Antec, 2862-6, 2003.
Surface resistivity	ohm	1.9E11	Khoddami, A; Avinc, O; Ghahremanzadeh, F; Prog. Org. Coat., in press, 2011.
Permeability to nitrogen, 25°C	cm^3 cm^{-3} $cmHg^{-1}$ x 10^4	2.2	Bao, L; Dorgan, J R; Knauss, D; Hait, S; Oliveira, N S; Maruccho, I M, J. Membrane Sci., 166-172, 2006.

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Permeability to oxygen, 25°C	$cm^3\ cm^{-3}\ cmHg^{-1} \times 10^4$	2.2-4.9	Bao, L; Dorgan, J R; Knauss, D; Hait, S; Oliveira, N S; Maruccho, I M, J. Membrane Sci., 166-172, 2006.
Permeability to water vapor, 25°C	$cm^3\ m^{-2}\ 24h^{-1}$	110	Zenkiewicz, M; Richert, J; Rytlewski, P; Moraczewski, K; Stepczynska, M; Karasiewicz, T, Polym. Test., 28, 412-18, 2009.
Diffusion coefficient of nitrogen	$cm^2\ s^{-1} \times 10^8$	2.4	Bao, L; Dorgan, J R; Knauss, D; Hait, S; Oliveira, N S; Maruccho, I M, J. Membrane Sci., 166-172, 2006.
Diffusion coefficient of oxygen	$cm^2\ s^{-1} \times 10^8$	5.6-7.6	Bao, L; Dorgan, J R; Knauss, D; Hait, S; Oliveira, N S; Maruccho, I M, J. Membrane Sci., 166-172, 2006.
MECHANICAL & RHEOLOGICAL PROPERTIES			
Tensile strength	MPa	52-72; 27-41 (DL); 55-82 (L)	
Tensile modulus	MPa	2700-16000	
Tensile stress at yield	MPa	65.6-77	Carrasco, F; Pages, P; Gamez-Perez, J; Santana, O O; Maspoch, M L, Polym. Deg. Stab., 95, 116-25, 2010.
Tensile creep modulus, 1000 h, elongation 0.5 max	MPa	48-70	
Elongation	%	4-6; 3-10 (DL); 5-10 (L)	
Tensile yield strain	%	2.4-10	
Flexural strength	MPa	83	
Flexural modulus	MPa	1,000-3,800	
Young's modulus	MPa	3,700-4,100	
Izod impact strength, notched, 23°C	$J\ m^{-1}$	13-24.6	
Tenacity (fiber)	$cN\ tex^{-1}$	32-36	
Intrinsic viscosity, 25°C	$dl\ g^{-1}$	0.15-1.2	
Melt index, 230°C/3.8 kg	g/10 min	3-30	
Water absorption, equilibrium in water at 23°C	%	0.5	
CHEMICAL RESISTANCE			
Alcohols	-	poor	
Aromatic hydrocarbons	-	poor	
Esters	-	poor	
Greases & oils	-	good	
Halogenated hydrocarbons	-	poor	
Ketones	-	poor	
Good solvent	-	acetone, benzene, chloroform, m-cresol, dichloromethane, dioxane, DMF, ethyl acetate, isoamyl alcohol, toluene, xylene	
FLAMMABILITY			
Limiting oxygen index	$\%\ O_2$	19; 23-26 (with flame retardant)	
Heat release	$kW\ m^{-2}$	427	Wei, L-L; Wang, D-Y; Chen, H-B; Chen, L; Wang, X-L; Wang, Y-Z, Polym. Deg. Stab., in press, 2011.

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NBS smoke chamber	m2 kg^{-1}	63	
Char at 500°C	%	0-1.4; 1.4-3.2 (with flame retardant)	Wei, L-L; Wang, D-Y; Chen, H-B; Chen, L; Wang, X-L; Wang, Y-Z, Polym. Deg. Stab., in press, 2011.
Heat of combustion	J g^{-1}	19,000	Perepelkin, K E, Fibre Chem., 34, 2, 2002.
UL 94 rating	-	V-0 (FR)	
WEATHER STABILITY			
Depth of UV penetration	μm	bulk erosion	
Important initiators and accelerators	-	nano-titanium dioxide	
Products of degradation	-	double bonds, chain cleavage	
Stabilizers	-	Phenolic antioxidant: pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate); HAS: decanedioic acid, bis(2,2,6,6-tetramethyl-1-(octyloxy)-4-piperidinyl) ester, reaction products with 1,1-dimethylethylhydroperoxide and octane; Phosphite: bis(2-ethylhexyl)phosphite	
BIODEGRADATION			
Typical biodegradants	-	composting: complete fragmentation in 15 days; degradation complete in 4.8 years at 25°C; lipases from *Cryptococcus sp*. and proteases from *Bacillus* strains	Hartmann, M; Whiteman, N, Antec, 4-8, 2001; Kawai, F; Nakadai, KK; Nishioka, E; Nakajima, H; Ohara, H; Masaki, Iefuji, H, Polym. Deg. Stab., 96, 1343-48, 2011.
TOXICITY			
NFPA: Health, Flammability, Reactivity rating	-	1/1/0	
Carcinogenic effect	-	not listed by ACGIH, NIOSH, NTP	
Oral rat, LD_{50}	mg kg^{-1}	>5,000	
Skin rabbit, LD_{50}	mg kg^{-1}	>2,000	
ENVIRONMENTAL IMPACT			
Aquatic toxicity, *Daphnia magna*, LC_{50}, 48 h	mg l^{-1}	1,000	
Power consumption for production	MJ kg^{-1}	92 (fiber)	Perepelkin, K E, Fibre Chem., 34, 2, 2002.
CO2 liberation	kg kg^{-1}	4.1-6.5	Perepelkin, K E, Fibre Chem., 34, 2, 2002.
PROCESSING			
Typical processing methods	-	extrusion, extrusion coating, injection molding, microcellular foaming, spinning	
Preprocess drying: temperature/ time/residual moisture	°C/h/%	80 (vac)/8/	
Processing temperature	°C	220-255 (extrusion); 280-300 (fibers)	
Processing pressure	MPa	82 (injection)	
Process time	min		

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Additives used in final products	-	Plasticizers: polyethylene glycol, polypropylene glycol, partial fatty ester, glucose monoester, citrate, adipate and azelate esters, epoxidized soybean oil, acetylated coconut oil, linseed oil, acetyl tributyl citrate, glycerol triacetate, glycerol tripropionate; Antistatics: ethoxylated fatty amines, polyethylene glycol ester, quaternary ammonium salt; Antiblocking: diatomaceous earth, talc; Slip: erucamide	
Applications	-	clip, envelope with window, fabrics, fibers, film, sheet, shopping bag, synthetic paper, trash bag	
Outstanding properties	-	sustainable, biodegradable	
BLENDS			
Suitable polymers	-	chitosan, PC, PCL, PEG, PET, PR, PVP, starch	
ANALYSIS			
FTIR (wavenumber-assignment)	cm^{-1}/-	C=O – 1748; reference – 1451	Rudnik, E; Briassoulis, D, Ind. Crops Prod., 33, 648-58, 2011.
Raman (wavenumber-assignment)	cm^{-1}/-	C-O – 1128; C-C – 1044	Yang, X; Kang, S; Yang, Y; Aou, K; Hsu, S L, Polymer, 45, 4241-48, 2004.
NMR (chemical shifts)	ppm	C NMR: C=O – 170.8; -CH – 70.5; $-CH_3$ – 18.1	Zhang, X; Espiritu, M; Bilyk, A; Kurniawan, L, Polym. Deg. Stab., 93, 1964-70, 2008.