SMM5773 - ***Estrutura e propriedades dos materiais poliméricos***

Horário das aulas: as quintas-feiras das 10h20 a 12h20 e segundo dia a definir– Googel Meet

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Objetivos do Curso:

Dois são os objetivos desse curso:

- Prover os participantes de erudição no tema do curso (Ciência dos Polímeros). Isso implica uma visão geral, abrangente e integrada dos principais tópicos sobre a ciência e tecnologia de polímeros,

- Aprofundar em conhecimentos específicos sobre polímeros que são considerados fundamentais.

Bibliografia

J.M.G. Cowie, V. Arrighi, Polymer Chemistry and Physics of Modern Materials, CRC Press, 3ª ed.
L. Akcelrud, Fundamentos da Ciência dos Polímeros, Manole,
F.W. Billmeyer Jr., Textbook of Polymer Science, Wiley-Interscience, 3ª ed.
S.V. Canevarolo Jr., Ciência dos Polímeros, Artliber, 2ª ed.
A. Rudin, The Elements of Polymer Science and Eng., Academic Press, 1982.
J.R. Fried, Polymer Science and Technology, PHI Learning, 2ª ed.
Osswald/Menges, Materials Science of Polymers for Engineers, Hanser.

Avaliação: Duas provas, sendo uma na metade e a outra combinada com um seminário ao final do curso. Além disso, será solicitado uma monografia versando sobre todo o conteúdo organizada na forma de resumo onde deverão ser dados destaques aos pontos fundamentais(definições, equações etc.) (25 a 50 páginas), que terá peso 30% em relação a nota final onde cada uma das provas terá peso de 35% cada.

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Temas principais que compõem o curso (entre parênteses os capítulos correspondentes do Cowie):

1. Histórico, classificação, nomenclatura, materiais poliméricos, massa molar, forma e tamanho, (termoplásticos, termorrígidos, elastômeros, fibras sintéticas, adesivos, aditivos), aplicações. (cap 1)
2. Polimerização em etapas (policondensação). (cap. 2)
3. Polimerização por radicais livres (polimerização de adição ou em cadeia). (cap. 3)
4. Polimerização iônica e polimerização via ATRP. (cap. 4 e 5.10.1)
5. Copolímeros, polímeros enxertados, dendrímeros (cap. 5)
6. Conformação/configuração, estereoquímica, dimensões de cadeia. (cap. 6 e 10.1 - 10.4)
7. Polímeros em solução (cap. 8) e dimensões e rigidez das cadeias moleculares (cap. 10)
8. Determinação da massa molecular (cap. 9)
9. Cristalinidade. (cap. 11)
10. O estado vítreo, propriedades térmicas, temperaturas de transição. (cap. 12)
11. Reologia, propriedades mecânicas, viscoelasticidade e elastômeros. (cap. 13)
12. Relação estrutura-propriedades. (cap. 15)
13. Técnicas de caracterização de polímeros. (cap. 10)

Aula 01: Introdução Geral

Definição:

Os **polímeros** pertencem à classe das **macromoléculas**. No caso dos polímeros especificamente é possível obsevar uma estrutura (**unidades monoméricas**) que se repetem.

Plásticos: Comumente empregado como sinônimo de polímeros. Deveriam ficar restritos aos termoplásticos.

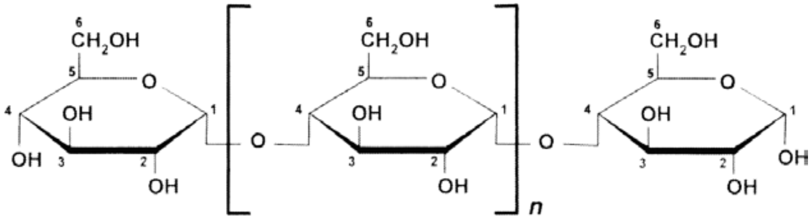
História: Origens do uso de materiais poliméricos

- Polímeros naturais:
  - Madeira
  - Algodão
  - Couro
  - Proteínas
  - Borracha
  - Seda
  - Lã
  - Celulose

- Primeiras aplicações mais conhecidas:
  - Bolas de borracha usadas pelos Incas
  - Betume

Polímeros ou Macromoléculas: O material de construção da natureza

Estrutural


6
CH_2OH
5
O
1
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OH
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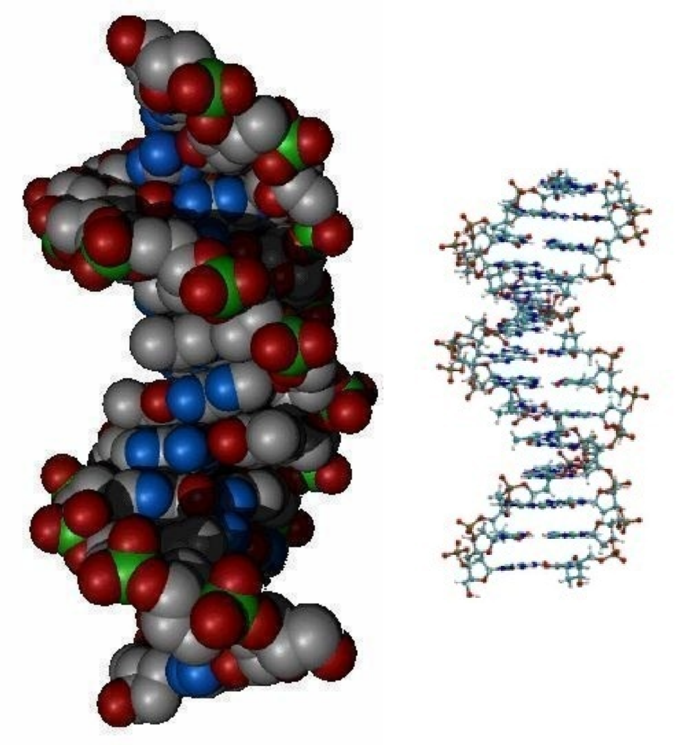
n

Reserva de energia

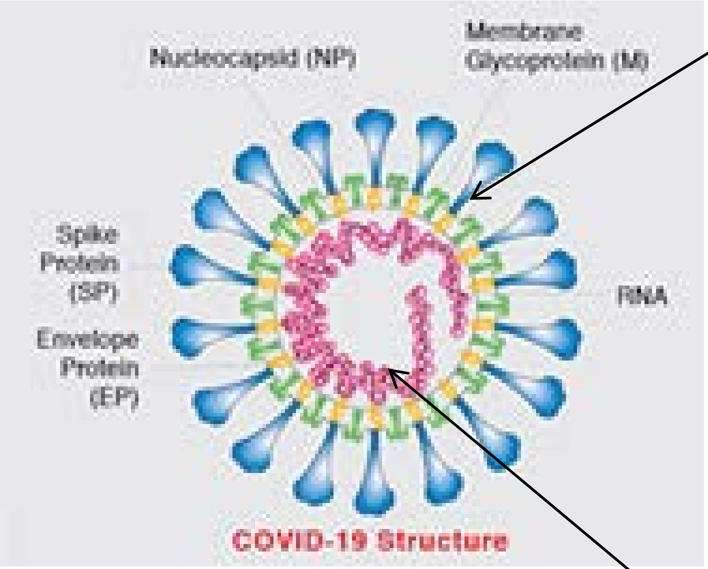


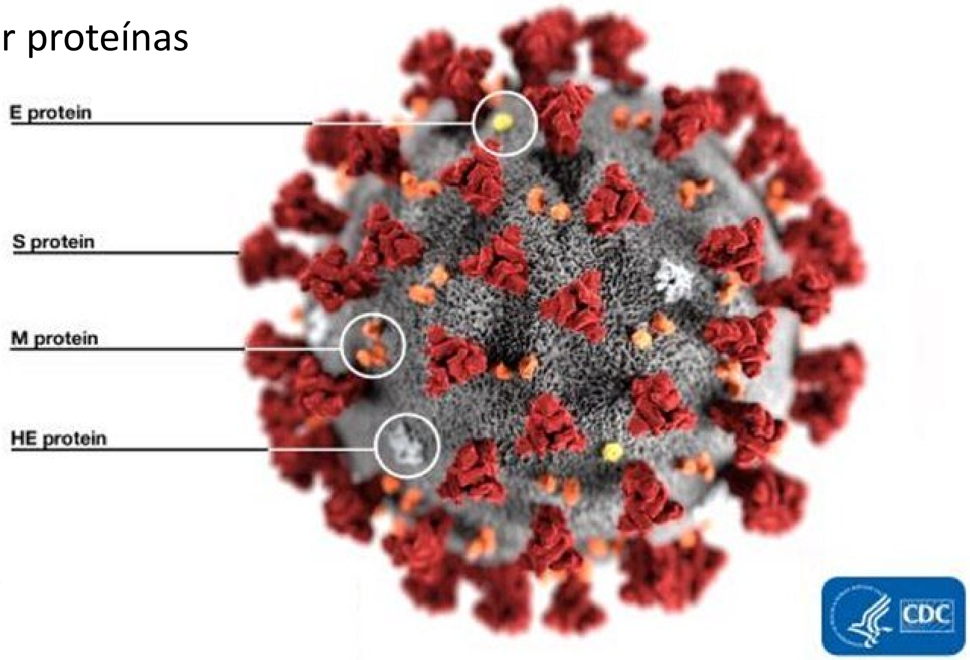
Codificação

Uma curiosidade atual: Os vírus são basicamente constituídos de macromoléculas

Por exemplo, o COVID-19

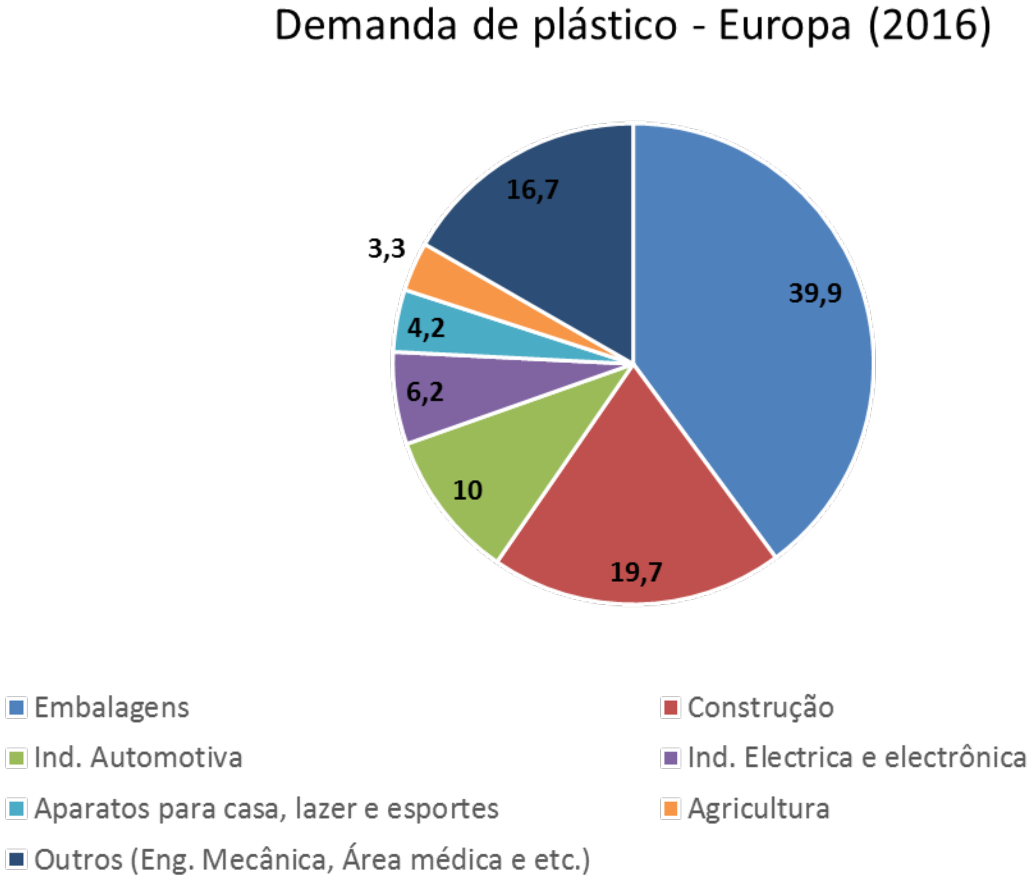
Toda estrutura de encapsulamento do viro é formada por proteínas


Nucleocapsid (NP)
Membrane Glycoprotein (M)
Spike Protein (SP)
RNA
Envelope Protein (EP)
COVID-19 Structure


E protein
S protein
M protein
HE protein
CDC

Macromolécula de RNA

Principais aplicações dos Plásticos



Fonte: Plastics Europe -
https://www.plasticseurope.org/application/files/5715/1717/4180/Plastics_the_facts_2017_FINAL_for_website_one_page.pdf

A descoberta dos Polímeros precede a compreensão acerca de sua estrutura

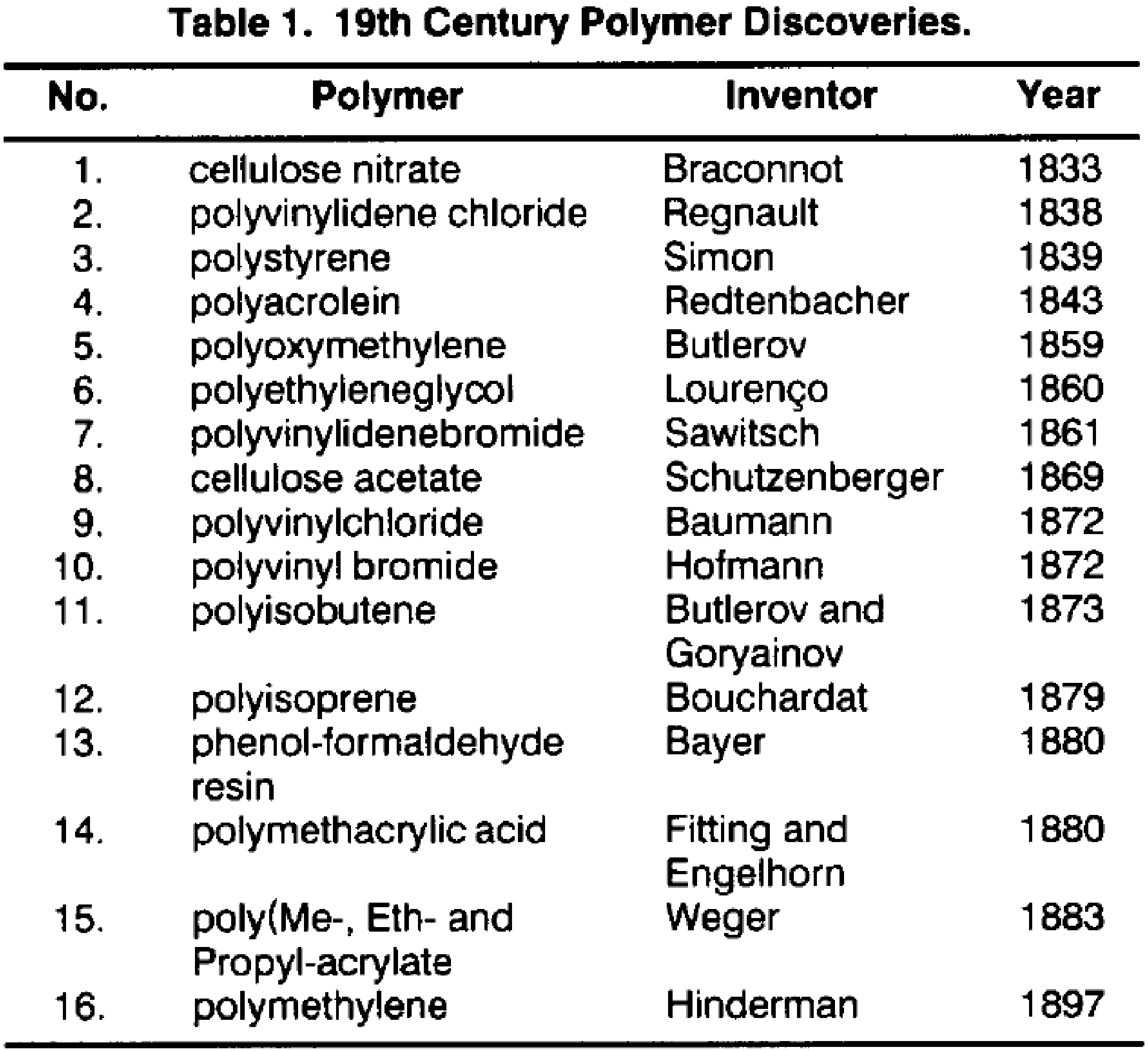
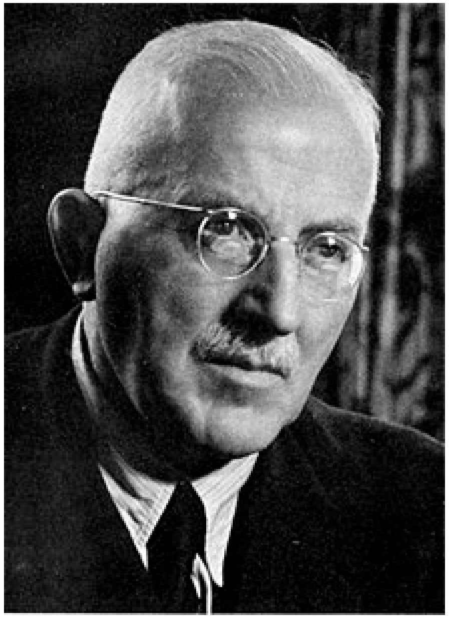


Table 1. 19th Century Polymer Discoveries.

No.	Polymer	Inventor	Year
1.	cellulose nitrate	Braconnot	1833
2.	polyvinylidene chloride	Regnault	1838
3.	polystyrene	Simon	1839
4.	polyacrolein	Redtenbacher	1843
5.	polyoxymethylene	Butlerov	1859
6.	polyethyleneglycol	Lourenço	1860
7.	polyvinylidenebromide	Sawitsch	1861
8.	cellulose acetate	Schutzenberger	1869
9.	polyvinylchloride	Baumann	1872
10.	polyvinyl bromide	Hofmann	1872
11.	polyisobutene	Butlerov and Goryainov	1873
12.	polyisoprene	Bouchardat	1879
13.	phenol-formaldehyde resin	Bayer	1880
14.	polymethacrylic acid	Fitting and Engelhorn	1880
15.	poly(Me-, Eth- and Propyl-acrylate	Weger	1883
16.	polymethylene	Hinderman	1897

A descoberta dos Polímeros precede a compreensão acerca de sua estrutura

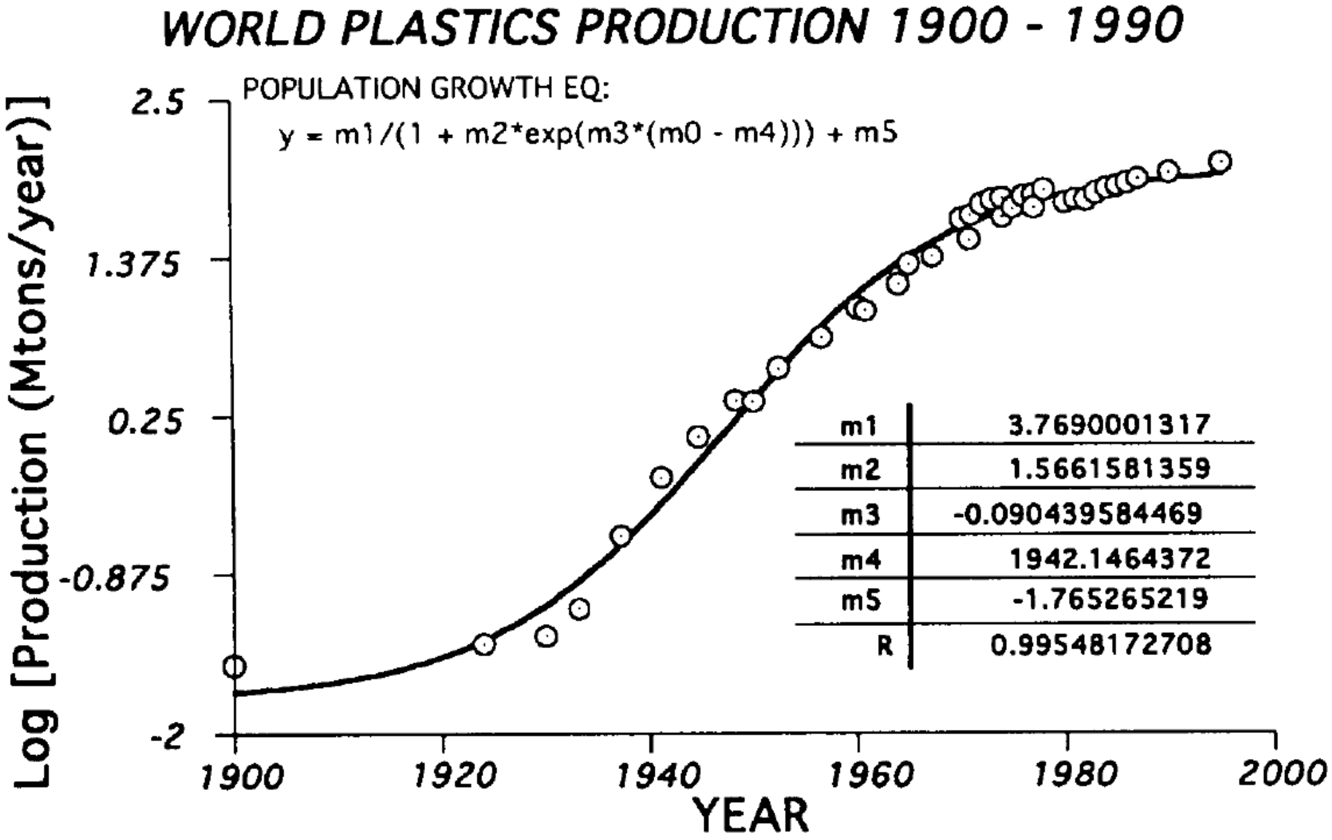


H. Staudinger 1881 - 1965

Em 1924 Herman Staudinger (cientista alemão) propôs um modelo que descrevia os polímeros como sendo formados por cadeias lineares.

A ideia de Staudinger de que os polímeros eram moléculas gigantes foi na época ridicularizada por seus pares que acreditavam que a borracha natural, por exemplo, era formada por agregados denominados de coloides.

Em 1953 Staudinger recebeu o Premio Nobel por sua contribuição pioneira na ciência dos polímeros.



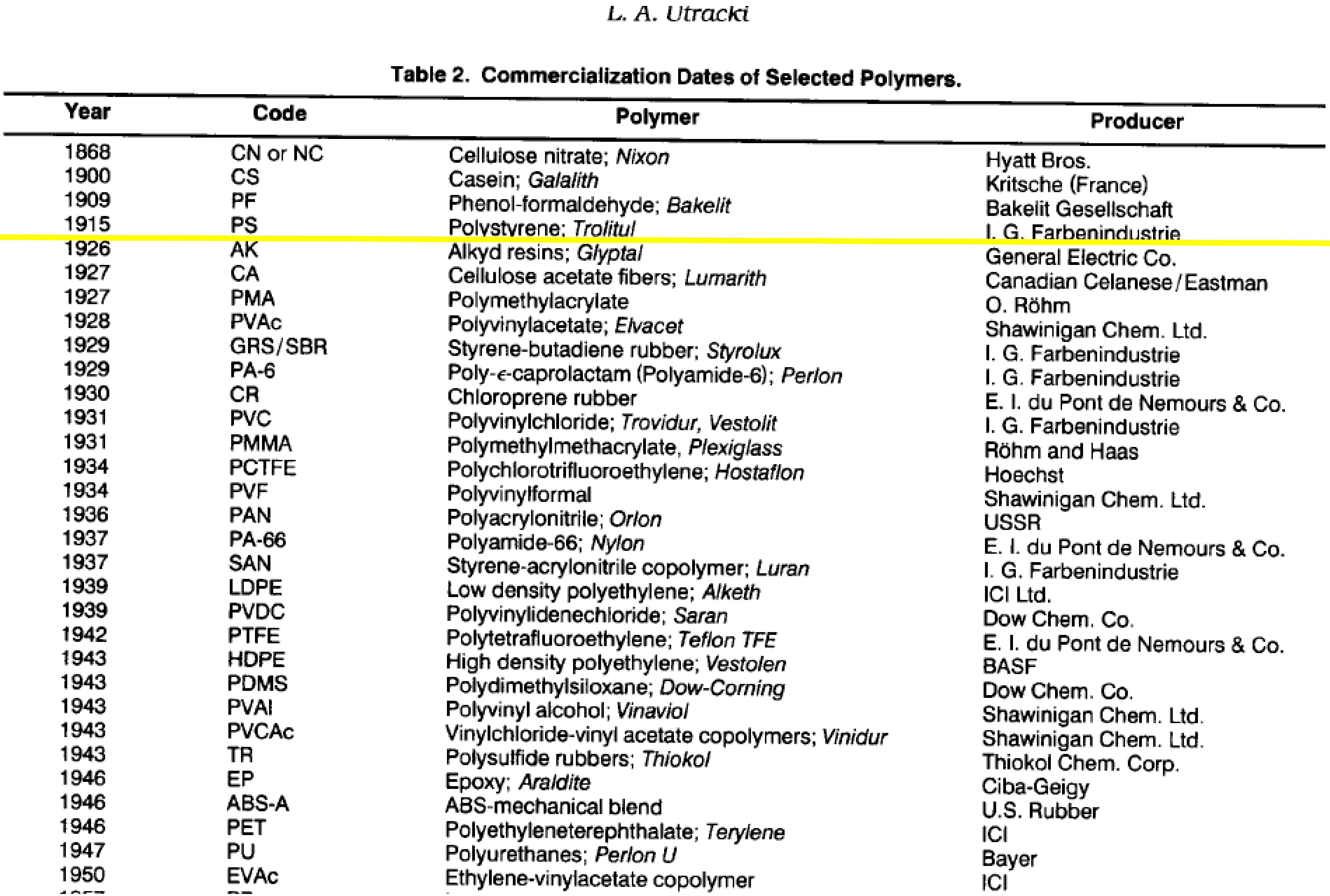
POPULATION GROWTH EQ:

y = m1/(1 + m2*exp(m3*(m0 - m4))) + m5

m1	3.7690001317
m2	1.5661581359
m3	-0.090439584469
m4	1942.1464372
m5	-1.765265219
R	0.99548172708

Fig. 1. World plastics production during the years 1900 to 1990 (in million metric tons per years).

Data a partir da qual os polímeros começaram a ser comercializados



L. A. Utracki

Table 2. Commercialization Dates of Selected Polymers.

Year	Code	Polymer	Producer
1868	CN or NC	Cellulose nitrate; *Nixon*	Hyatt Bros.
1900	CS	Casein; *Galalith*	Kritsche (France)
1909	PF	Phenol-formaldehyde; *Bakelit*	Bakelit Gesellschaft
1915	PS	Polystyrene; *Trolitul*	I. G. Farbenindustrie
1926	AK	Alkyd resins; *Glyptal*	General Electric Co.
1927	CA	Cellulose acetate fibers; *Lumarith*	Canadian Celanese/Eastman
1927	PMA	Polymethylacrylate	O. Röhm
1928	PVAc	Polyvinylacetate; *Elvacet*	Shawinigan Chem. Ltd.
1929	GRS/SBR	Styrene-butadiene rubber; *Styrolux*	I. G. Farbenindustrie
1929	PA-6	Poly-ϵ-caprolactam (Polyamide-6); *Perlon*	I. G. Farbenindustrie
1930	CR	Chloroprene rubber	E. I. du Pont de Nemours & Co.
1931	PVC	Polyvinylchloride; *Trovidur, Vestolit*	I. G. Farbenindustrie
1931	PMMA	Polymethylmethacrylate, *Plexiglass*	Röhm and Haas
1934	PCTFE	Polychlorotrifluoroethylene; *Hostaflon*	Hoechst
1934	PVF	Polyvinylformal	Shawinigan Chem. Ltd.
1936	PAN	Polyacrylonitrile; *Orlon*	USSR
1937	PA-66	Polyamide-66; *Nylon*	E. I. du Pont de Nemours & Co.
1937	SAN	Styrene-acrylonitrile copolymer; *Luran*	I. G. Farbenindustrie
1939	LDPE	Low density polyethylene; *Alketh*	ICI Ltd.
1939	PVDC	Polyvinylidenechloride; *Saran*	Dow Chem. Co.
1942	PTFE	Polytetrafluoroethylene; *Teflon TFE*	E. I. du Pont de Nemours & Co.
1943	HDPE	High density polyethylene; *Vestolen*	BASF
1943	PDMS	Polydimethylsiloxane; *Dow-Corning*	Dow Chem. Co.
1943	PVAl	Polyvinyl alcohol; *Vinaviol*	Shawinigan Chem. Ltd.
1943	PVCAc	Vinylchloride-vinyl acetate copolymers; *Vinidur*	Shawinigan Chem. Ltd.
1943	TR	Polysulfide rubbers; *Thiokol*	Thiokol Chem. Corp.
1946	EP	Epoxy; *Araldite*	Ciba-Geigy
1946	ABS-A	ABS-mechanical blend	U.S. Rubber
1946	PET	Polyethyleneterephthalate; *Terylene*	ICI
1947	PU	Polyurethanes; *Perlon U*	Bayer
1950	EVAc	Ethylene-vinylacetate copolymer	ICI

1957	PP	Isotactic polypropylene: *Pro-Fax*	Montecatini/Hercules/Hoechst
1958	PC	Polycarbonate of bisphenol-A; *Makrolon*	Bayer AG
1959	CPE	Chlorinated polyethylene; *Hostapren*	Hoechst
1959	POM	Polyoxymethylene (Acetal); *Delrin*	E. I. du Pont de Nemours & Co.
1960	EPR	Ethylene-propylene elastomer; *Vistalon*	Exxon
1960	LLDPE	Linear low density polyethylene; *Sclair*	DuPont-Canada
1961	Aramid	Poly(m-phenyleneisophthalamide); *Nomex*	E. I. du Pont de Nemours & Co.
1961	TPU	Thermoplastic polyurethane; *Estane*	B. F. Goodrich
1962	PVDF	Polyvinylidenefluoride; *Kynar*	Pennwalt Chem. Co.
1962	Phenoxy	Polyhydroxyether of bisphenol-A; *Phenoxy*	Union Carbide
1962	PI	Polyimides; *Kapton*	E. I. du Pont de Nemours & Co.
1963	EPDM	Ethylene-propylene-diene; *Nordel*	E. I. du Pont de Nemours & Co.
1963	SMA	Styrene-maleic anhydride; *Cadon, Dylark*	Sinclair Petrochemicals Co.
1964	Ionomers	Ethylene copolymer ionomers; *Surlyn*	E. I. du Pont de Nemours & Co.
1964	PPE	Polyphenylene ether; *PPO*	General Electric Co.
1965	PAI	Polyamide-imide; *Torlon*	Amoco Chem. Corp.
1965	PSF	Polysulfone of bisphenol-A; *Udel*	Union Carbide Corp./Amoco
1965	SBS	Poly(styrene-b-butadiene); *Kraton D*	Shell Chem. Co.
1966	PPE blend	Polyphenylene ether; *Noryl*	General Electric Co.
1969	PMP	Poly-4-methyl pentene-1; *XT*	ICI/Mitsui Petrochem.
1969	PBT	Polybutyleneterephthalate; *Celanex*	Celanese
1972	Aramid	Poly(p-phenyleneisophthalamide); *Kevlar*	E. I. du Pont de Nemours & Co.
1972	LCP	Liquid crystal polymers; *Ekkcel I-2000*	Carborundum
1972	PES	Polyethersulfone; *Victrex*	ICI Ltd.
1972	SEBS	Hydrogenated SBS; *Kraton G*	Shell Chem. Co.
1973	PPS	Polyphenylene sulfide; *Rayton R*	Phillips Petroleum Co.
1974	PAr	Polyarylates: *U-polymer*	Unitika
1978	PEEK	Polyetheretherketone; *Victrex*	ICI Ltd.
1980	APEC	Aromatic polyestercarbonate; *Apec*	Chem. Werke Albert; Bayer
1981	PEBA	Polyether-block-amide; *Pebax*	Atochem
1982	PEI	Polyetherimide; *Ultem*	General Electric Co.
1983	PAS	Polyarylsulfone; *Radel*	Amoco
1985	PAE	Polyarylether; *Parylen*	Union Carbide
1986	PISF	Polyimidesulfone	Celanese
1987	PTES	Polythioethersulfone; *Amoroon*	Dainippon Ink & Chemicals
1987	PA-46	Polyamide-4,6; *Stanyl*	DMS
1989	sPS	Syndiotactic polystyrene	Idemitsu/Dow
1991	PPA	Polyphthalamide; *Amodel*	Amoco
1992	sPP	Syndiotactic polypropylene	Sumitomo Chemical

O desenvolvimento dos métodos de moldagem dos polímeros: Processamento e transformação dos polímeros

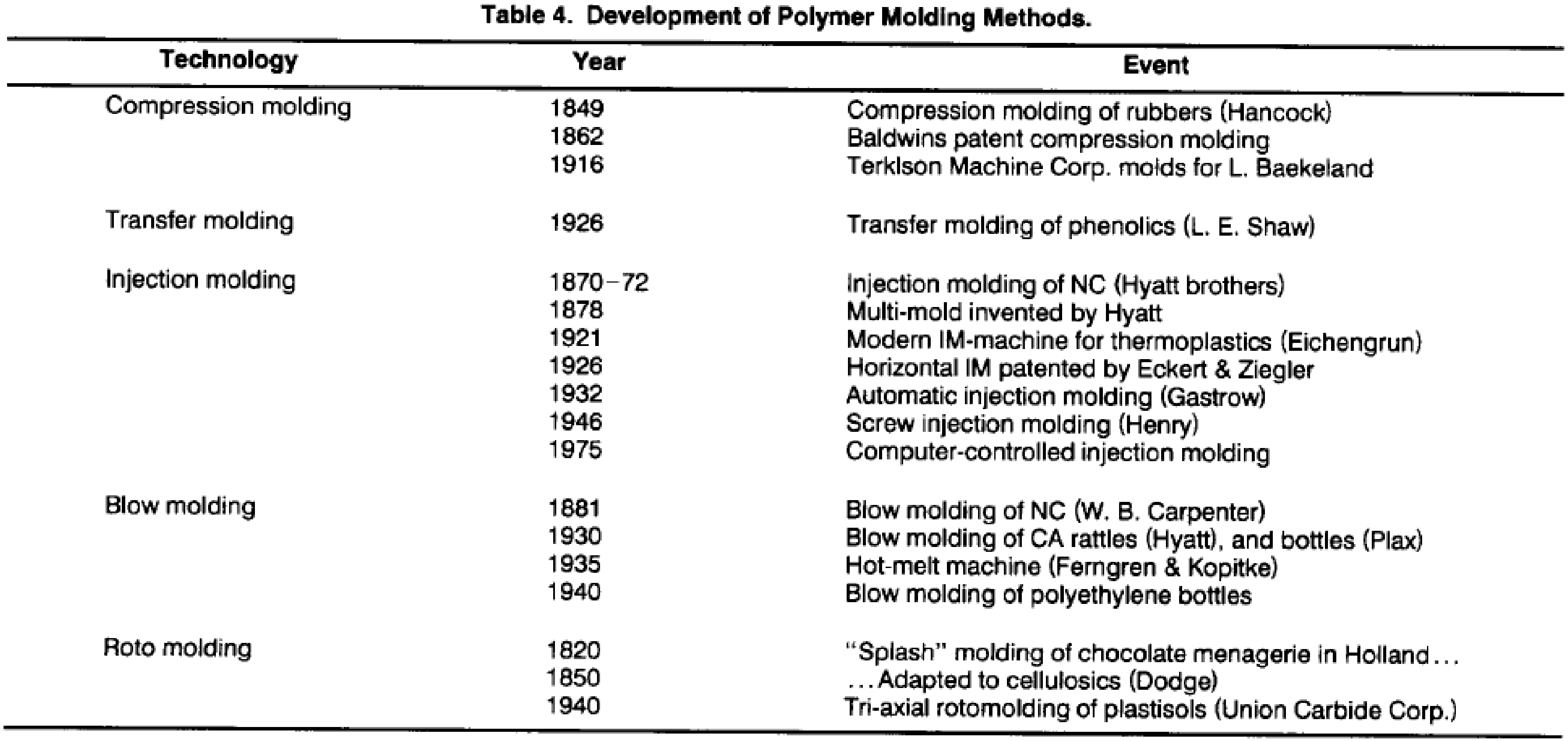


Table 4. Development of Polymer Molding Methods.

Technology	Year	Event
Compression molding	1849	Compression molding of rubbers (Hancock)
	1862	Baldwins patent compression molding
	1916	Terklson Machine Corp. molds for L. Baekeland
Transfer molding	1926	Transfer molding of phenolics (L. E. Shaw)
Injection molding	1870–72	Injection molding of NC (Hyatt brothers)
	1878	Multi-mold invented by Hyatt
	1921	Modern IM-machine for thermoplastics (Eichengrun)
	1926	Horizontal IM patented by Eckert & Ziegler
	1932	Automatic injection molding (Gastrow)
	1946	Screw injection molding (Henry)
	1975	Computer-controlled injection molding
Blow molding	1881	Blow molding of NC (W. B. Carpenter)
	1930	Blow molding of CA rattles (Hyatt), and bottles (Plax)
	1935	Hot-melt machine (Ferngren & Kopitke)
	1940	Blow molding of polyethylene bottles
Roto molding	1820	"Splash" molding of chocolate menagerie in Holland...
	1850	...Adapted to cellulosics (Dodge)
	1940	Tri-axial rotomolding of plastisols (Union Carbide Corp.)

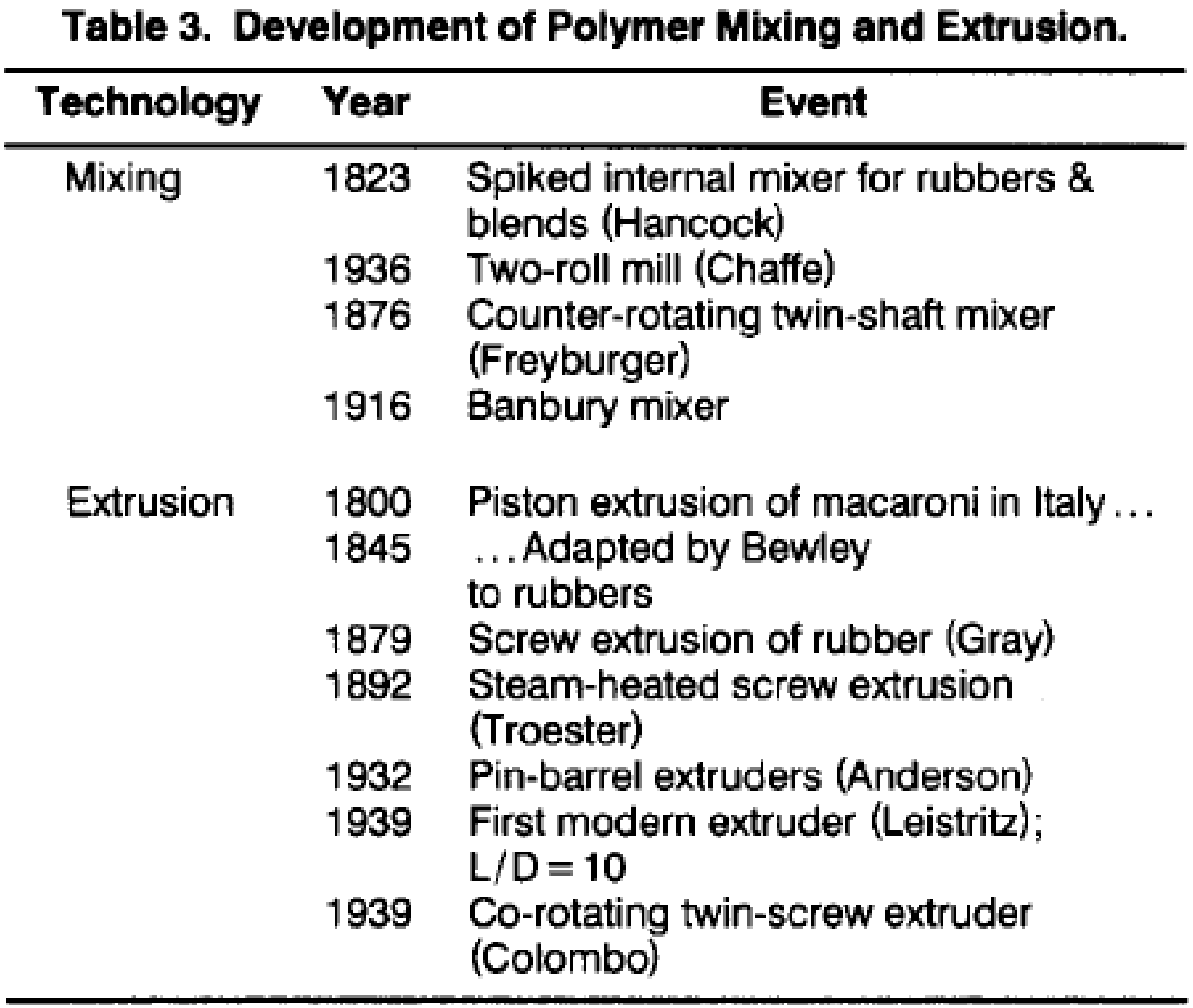


Table 3. Development of Polymer Mixing and Extrusion.

Technology	Year	Event
Mixing	1823	Spiked internal mixer for rubbers & blends (Hancock)
	1936	Two-roll mill (Chaffe)
	1876	Counter-rotating twin-shaft mixer (Freyburger)
	1916	Banbury mixer
Extrusion	1800	Piston extrusion of macaroni in Italy…
	1845	…Adapted by Bewley to rubbers
	1879	Screw extrusion of rubber (Gray)
	1892	Steam-heated screw extrusion (Troester)
	1932	Pin-barrel extruders (Anderson)
	1939	First modern extruder (Leistritz); L/D = 10
	1939	Co-rotating twin-screw extruder (Colombo)

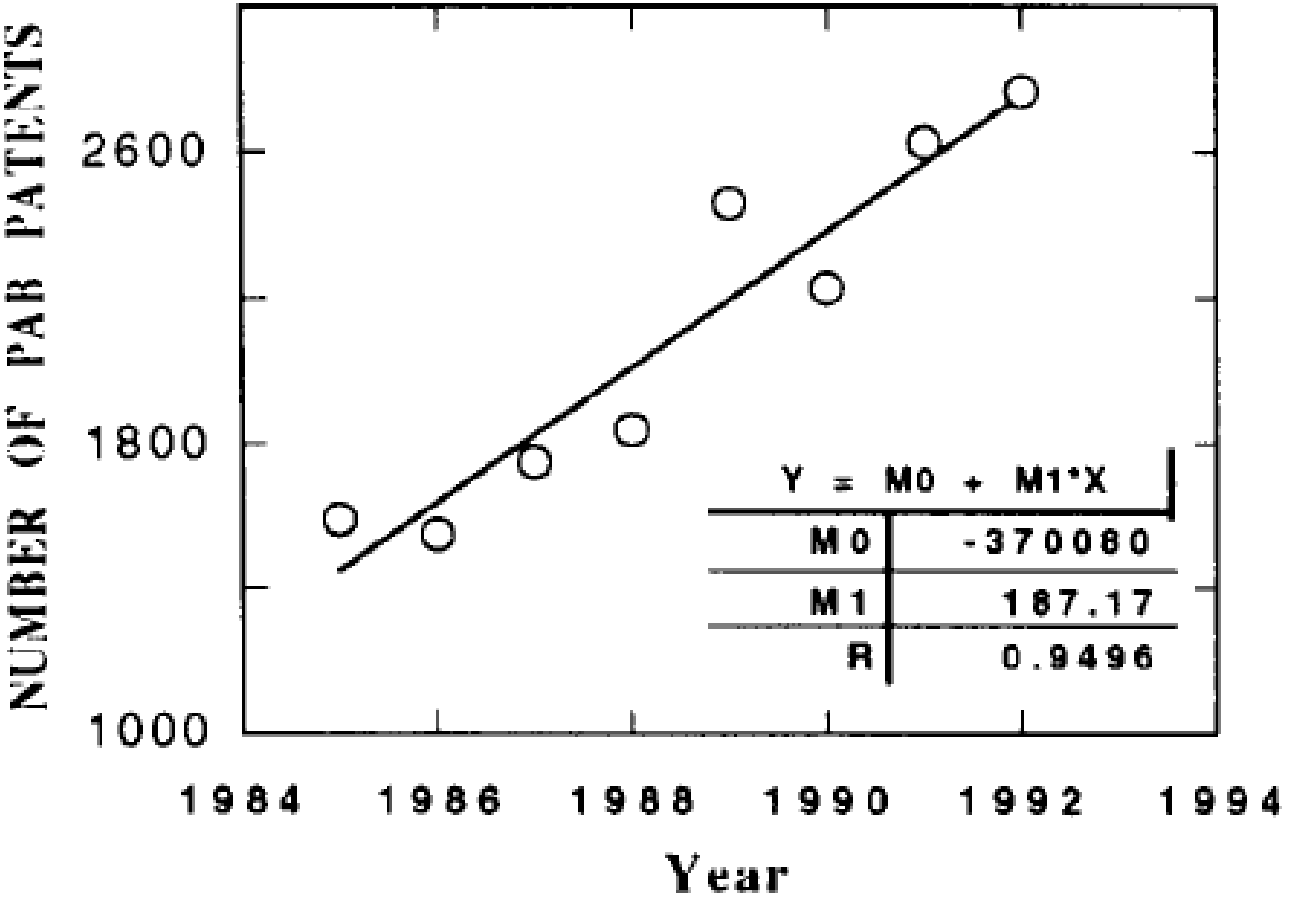
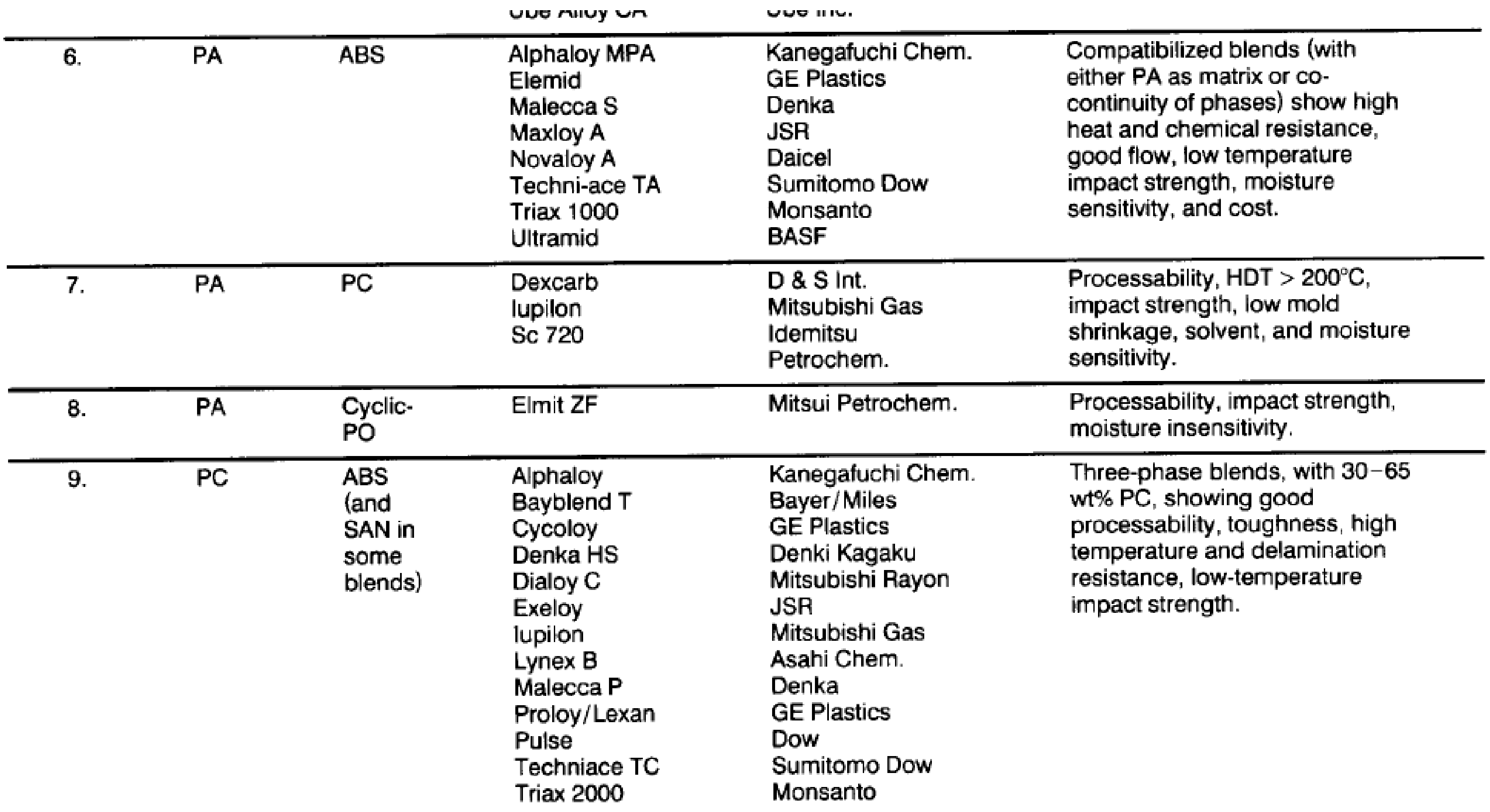


Fig. 2. The annual output of polymer blend patents published during the years 1985 to 1992.

Table 5. Examples of Commercial Alloys and Blends.

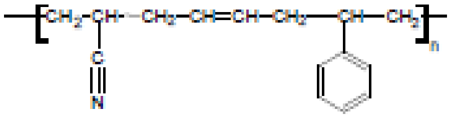
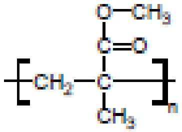
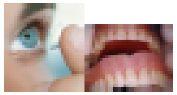
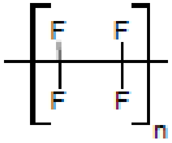
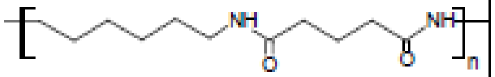
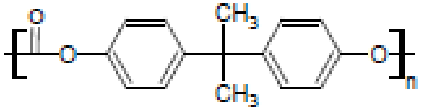
No.	Polymer A	Polymer B	Name	Supplier	Comments
1.	PP	EPR or EPDM	Milastormer Santoprene Sarlink Sumitomo TPE Dynaflex	Mitsui Petrochem. Monsanto Novacor Sumitomo Chem. JSR	Dynamically vulcanized, tough, composition-dependent (≤ 30 wt% EPR) low-temperature modulus and impact-strength.
2.	PVC	PMMA	Acrylivin Haibulen Kane-ace Kydene Metabulen Polycast Sunloid KD	Gen. Tire & Rub. Nippon Zeon Kanegafuchi Chem Rohm & Haas Mitsubishi Rayon Royalite Tsusunaka	Thermoformable, flexible sheets with high impact strength, excellent outdoor performance, good flame, chemicals, and solvent resistance.
3.	PVC	NBR	Geon/Hycar Denka LCS JSR NV Krynac Nipol Paracril OZO Vynite	BF Goodrich Showa Denka Jap. Synt. Rub. Polysar Nippon Zeon Uniroyal Alpha Chem.	Good processability, fast calendering and extrusion, impact and tear strength, oil, fuel, chemical, abrasion, weathering, and ozone resistance, antistatic, flame and moisture resistance.
4.	PVC	ABS, ASA, ABS, or SMA	Cycovin Geloy Kaneka Enplex	GE Plastics GE Plastics Kanegafuchi (and all other ABS manufacturers in Japan)	Good processability and impact strength, flame retardancy, cost/performance ratio (blends with ASA show superior weatherability; with SMA—high HDT).
5.	PA	PP	Akuloy RM Dexpro, Dexlon Flexloy Novamid AC Orgalloy Poliblend NH Systemer	DSM Dexter Corp. Sumitomo Chem. Mitsubishi Chem. Atochem Poliresins SA Showa Denko K. K.	Good processability, low water absorption, dimenensional stability, low density (i.e., low cost per volume), low liquid and vapor permeability, moderate impact strength, good resistance to alcohols and glycols.

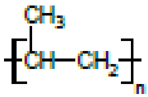
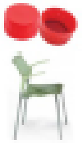
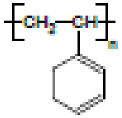
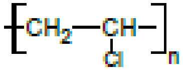
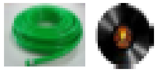
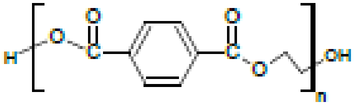
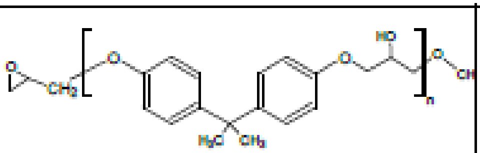


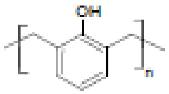
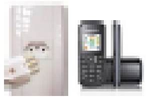
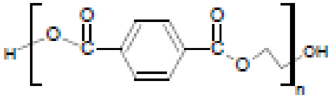
			Ube Alloy CA	Ube Inc.	
6.	PA	ABS	Alphaloy MPA	Kanegafuchi Chem.	Compatibilized blends (with either PA as matrix or co-continuity of phases) show high heat and chemical resistance, good flow, low temperature impact strength, moisture sensitivity, and cost.
			Elemid	GE Plastics	
			Malecca S	Denka	
			Maxloy A	JSR	
			Novaloy A	Daicel	
			Techni-ace TA	Sumitomo Dow	
			Triax 1000	Monsanto	
			Ultramid	BASF	
7.	PA	PC	Dexcarb	D & S Int.	Processability, HDT > 200°C, impact strength, low mold shrinkage, solvent, and moisture sensitivity.
			Iupilon	Mitsubishi Gas	
			Sc 720	Idemitsu Petrochem.	
8.	PA	Cyclic-PO	Elmit ZF	Mitsui Petrochem.	Processability, impact strength, moisture insensitivity.
9.	PC	ABS (and SAN in some blends)	Alphaloy	Kanegafuchi Chem.	Three-phase blends, with 30–65 wt% PC, showing good processability, toughness, high temperature and delamination resistance, low-temperature impact strength.
			Bayblend T	Bayer/Miles	
			Cycoloy	GE Plastics	
			Denka HS	Denki Kagaku	
			Dialoy C	Mitsubishi Rayon	
			Exeloy	JSR	
			Iupilon	Mitsubishi Gas	
			Lynex B	Asahi Chem.	
			Malecca P	Denka	
			Proloy/Lexan	GE Plastics	
			Pulse	Dow	
			Techniace TC	Sumitomo Dow	
			Triax 2000	Monsanto	

Características e Aplicações para Diversos Materiais Poliméricos

Características e Aplicações para Diversos Materiais Poliméricos

Polímero	Estrutura	Nome Comercial	Principais Características	Aplicações
Polímeros Termoplásticos				
Acrilonitrila-butadieno-estireno (ABS)			Excepcionais resistências mecânicas e tenacidade, resistência a distorção térmica; boas propriedades elétricas; inflamável e solúvel em alguns solventes orgânicos	
Acrílicos [poli(metil metacrilato)]			Excepcional transmissão da luz e resistência às intempéries; propriedades mecânicas apenas regulares	
Fluorcarbonos (PTFE ou TFE)			Quimicamente inertes em quase todos os ambientes, excelentes propriedades elétricas; baixo coeficiente de atrito; podem ser usados até 260 °C; relativamente pouco resistentes e propriedades de escoamento a frio ruins	
Poliamidas (náilons)			Boa resistência mecânica, resistência à abrasão e tenacidade; baixo coeficiente de atrito; absorvem água e alguns outros líquidos	
Policarbonatos			Dimensionalmente estáveis; baixa absorção de água; transparentes; muito boas resistências ao impacto e ductilidade; a resistência química não é excepcional	

Polietileno	$\left[CH_2-CH_2- \right]_n$		Quimicamente resistente e isolante elétrico; tenaz e com coeficiente de atrito relativamente baixo; baixa resistência e resistência ruim às intempéries	
Polipropileno	 $\left[CH(CH_3)-CH_2 \right]_n$		Resistente à distorção térmica; excelentes propriedades elétricas e resistência à fadiga: quimicamente inerte; relativamente barato; resistência ruim á luz UV	
Poliestireno			Excelentes propriedades elétricas e clareza óptica; boa estabilidade térmica e dimensional; relativamente barato	
PVC (Vinil)	 $\left[CH_2-CH(Cl)- \right]_n$		Bons materiais de baixo custo poara uso geral; normalmente rígidos, mais podem ser tornados flexíveis com plastificantes; frequentemente copolimerizados; suscetíveis à distorção térmica	
Poliéster (PET ou PETE)			Um dos filmes plásticos mais tenazes; excelentes resistências à fadiga e ao rasgamento, e resistência à umidade, ácidos, graxas, óleos e solventes	
Polímeros Termofixos				
Epóxis			Excelente combinação de propriedades mecânicas e de resistência a corrosão; dimensionalmente estáveis; boa adesão; relativamente baratos; boas propriedades elétricas	

Fenólicos			Excelente estabilidade térmica ate acima de 150 °C; podem ser combinados com um grande numero de resinas, cargas etc; baratos	
Poliésteres			Excelentes propriedades elétricas e baixo custo; podem ser formulados para uso à temperatura ambiente ou em temperaturas elevadas; geralmente são reforçados com fibras	

A constituição dos Polímeros e sua diversidade

A maioria das macromoléculas naturais e polímeros sintéticos é formada pelos elementos C, H, O, N.

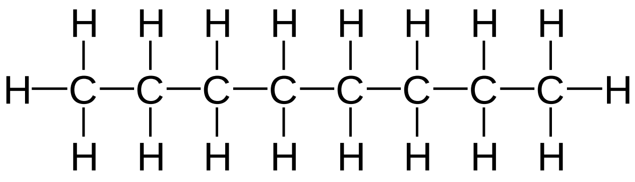
Também são encontrados em menor proporção o S, P e Si.

A constituição dos Polímeros e sua diversidade - Isomeria

- Dois compostos com a mesma fórmula química podem apresentar estruturas muito distintas

Ex: C_8H_{18}

- n-octano

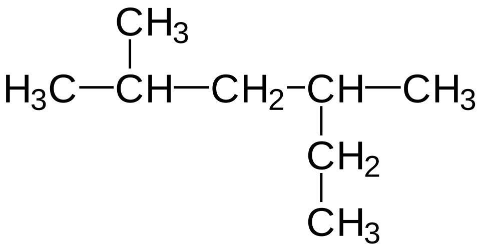


$$\begin{array}{ccccccccccccccccc} & & H & & H & & H & & H & & H & & H & & H & & H \\ & & | & & | & & | & & | & & | & & | & & | & & | \\ H & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - H \\ & & | & & | & & | & & | & & | & & | & & | & & | \\ & & H & & H & & H & & H & & H & & H & & H & & H \end{array} = H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

$\Downarrow$

$H_3C-(CH_2)_6-CH_3$

- 2-metil-4-etil pentano (isooctano)

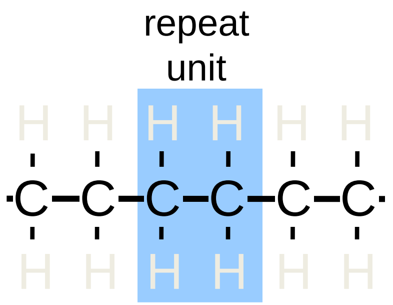


$$\begin{array}{lllllllll} & & CH_3 & & & & & & \\ & & | & & & & & & \\ H_3C & - & CH & - & CH_2 & - & CH & - & CH_3 \\ & & & & & & | & & \\ & & & & & & CH_2 & & \\ & & & & & & | & & \\ & & & & & & CH_3 & & \end{array}$$

Polímeros: Definições

O que é um polímero?

Poli	mer
Muitos	unidades repetitivas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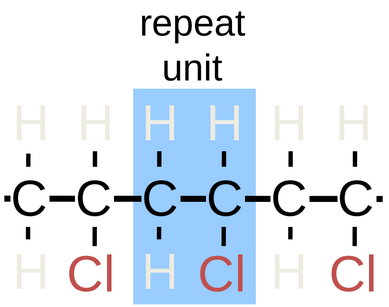
Polietileno (PE)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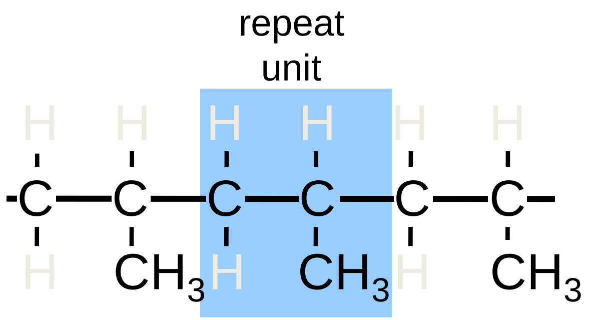
Cloreto de polivinila (PVC)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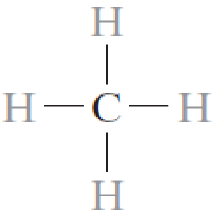
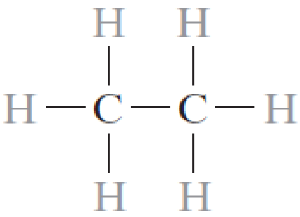
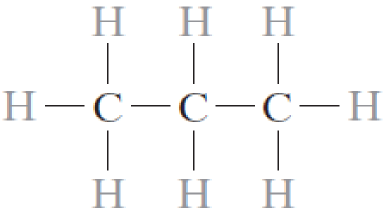
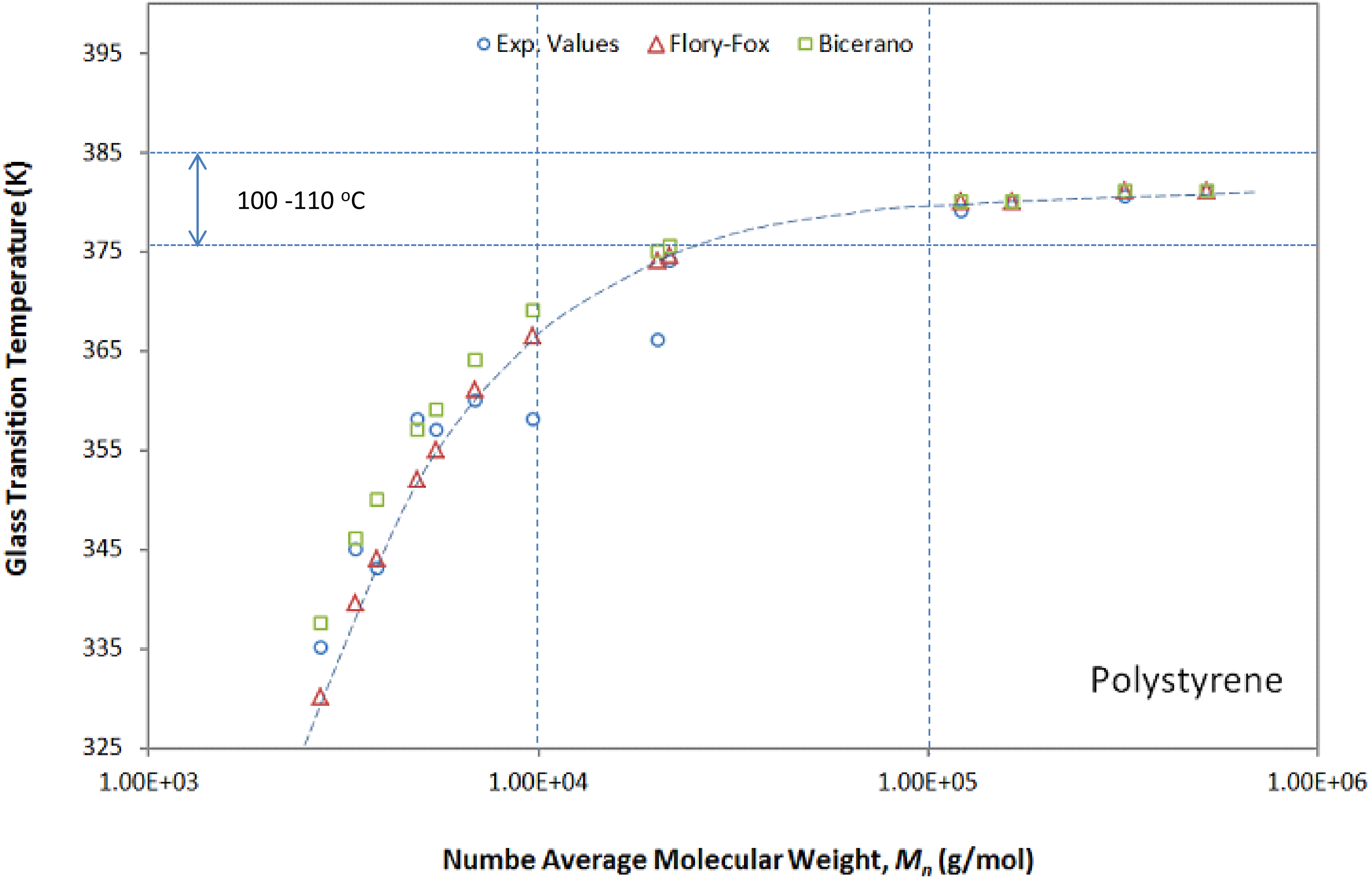
Polipropileno (PP)

A natureza macromolecular dos polímeros: Uma série homóloga – Parafinas lineares com fórmula química C_nH_{2n+2}

Table 14.1 **Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}**

Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4	 $\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}$	−164
Ethane	C_2H_6	 $\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}$	−88.6
Propane	C_3H_8	 $\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}$	−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

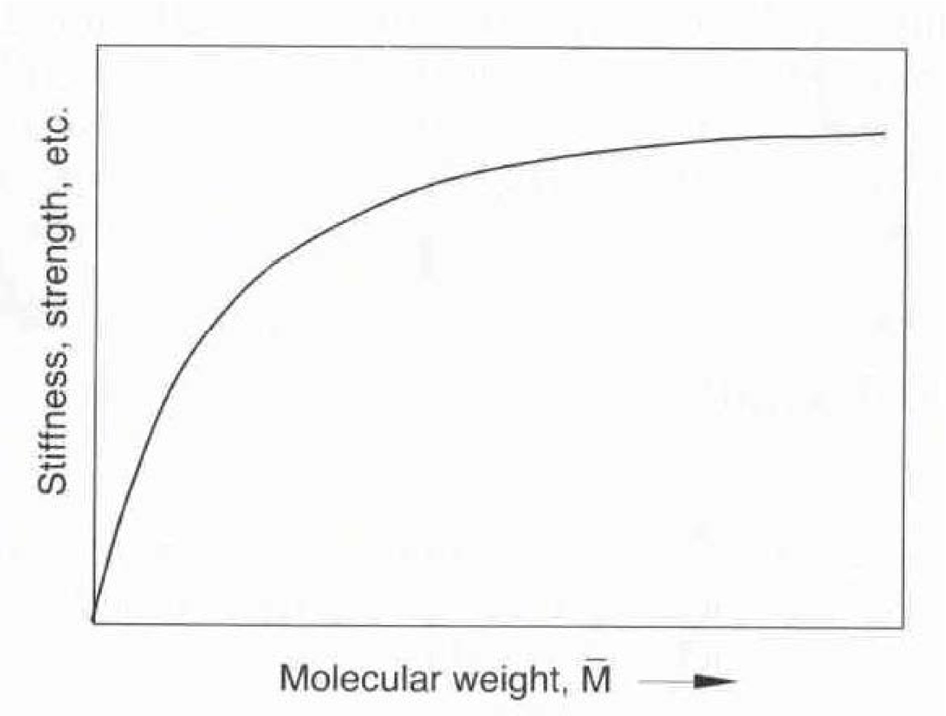
Influência da massa molar nas propriedades dos polímeros



Fonte: *Polymer Properties Database*

Influência da massa molar nas propriedades dos polímeros

A rigidez aumenta com a massa molar, chegando a um valor assintótico após um certo valor de massa molar.



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Por favor estudem o Capítulo 1