

EMAC 276

Lecture 17: Continuation of Elastomers

Part 1: SBR (Cont'd)

Part 2: Polyisobutylene

Part 3: Polydimethylsiloxane

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March 3, 2025

Domain Formation by Block Copolymers

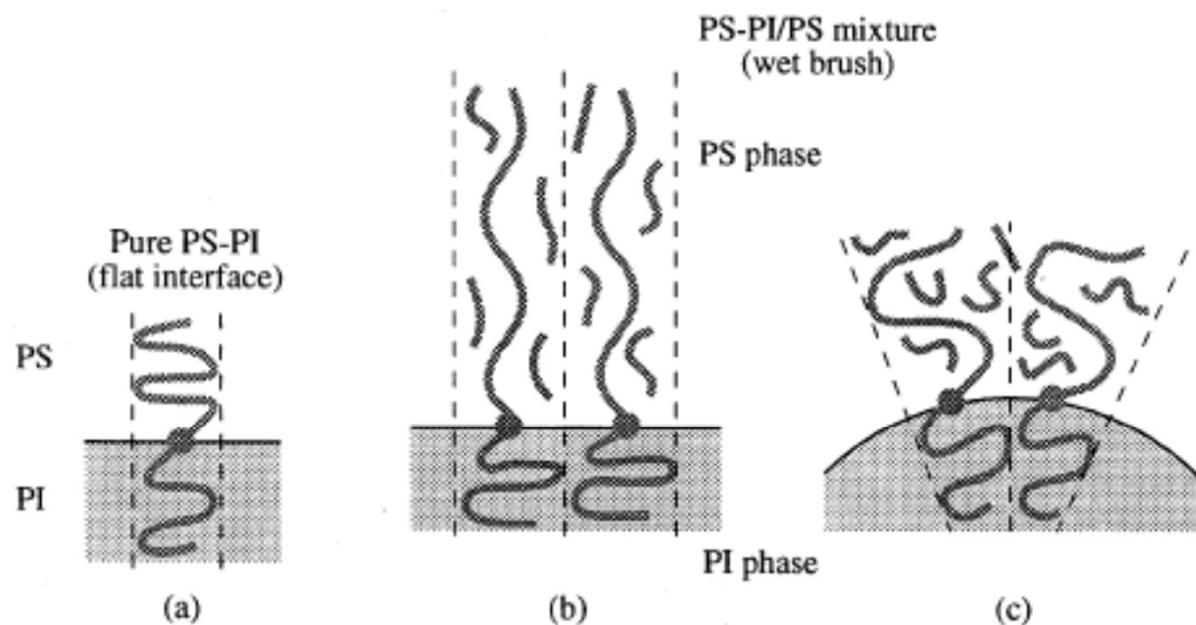
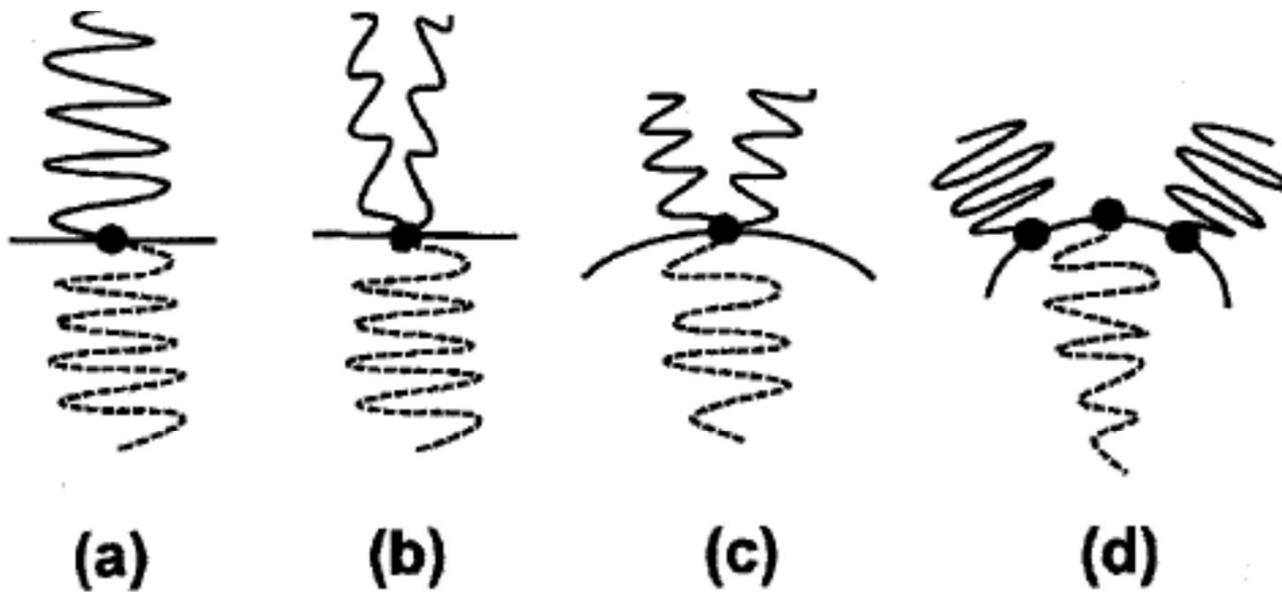


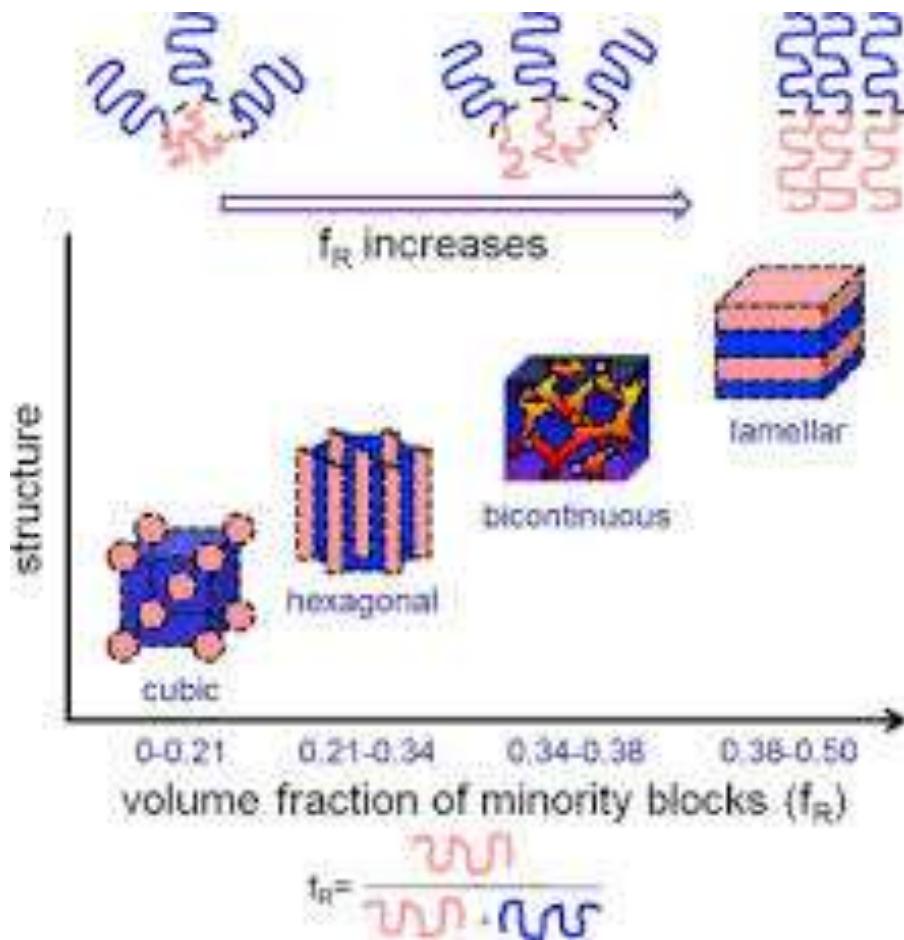
Figure 2.11: Schematic illustration of chain packing: a) pure SI diblock copolymer chain with symmetrical volume fraction forming a flat interface, b) swelling of PS lamellae by uniform solubilization of hPS molecules causes stretching of PS-block chains and/or compression of PI-block chains resulting in a decrease in conformational entropy, c) alternatively a curved interface is formed to gain entropy [76].

Domain Formation by Block Copolymers

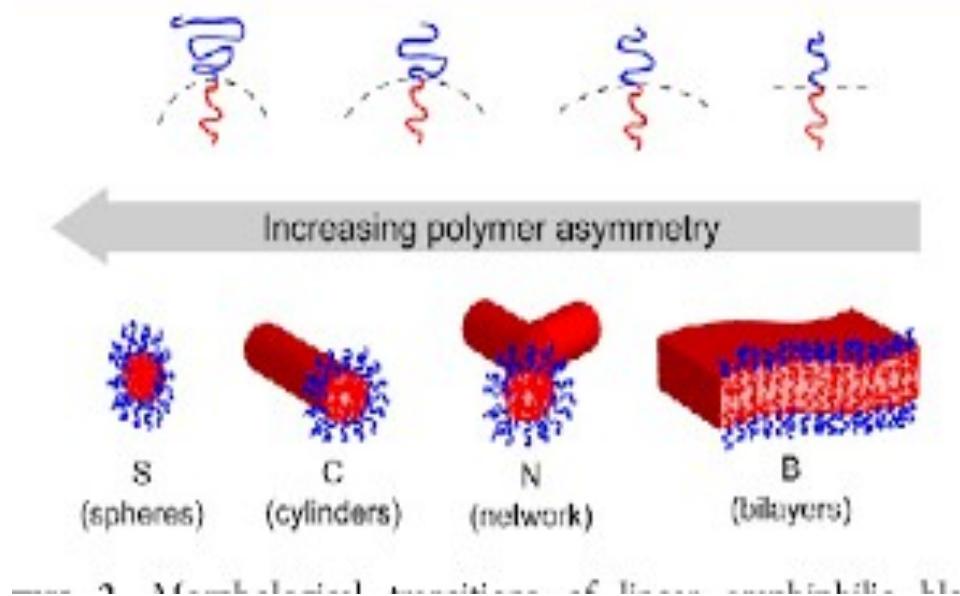


2.6: Schematic of A-B junction points on an interface for a) (2A)B linear diblock copolymers, b) A₂B block copolymers with a trifunctional branch point at a flat interface, c) A₂B single graft block copolymer with a trifunctional branch point at a curved interface and d) A₂B block copolymers with approximation of equal spacing between the grafted A blocks. The curvature of the interface represents the shifts of the OOT lines towards higher B volume fractions on the morphology diagrams [30,32].

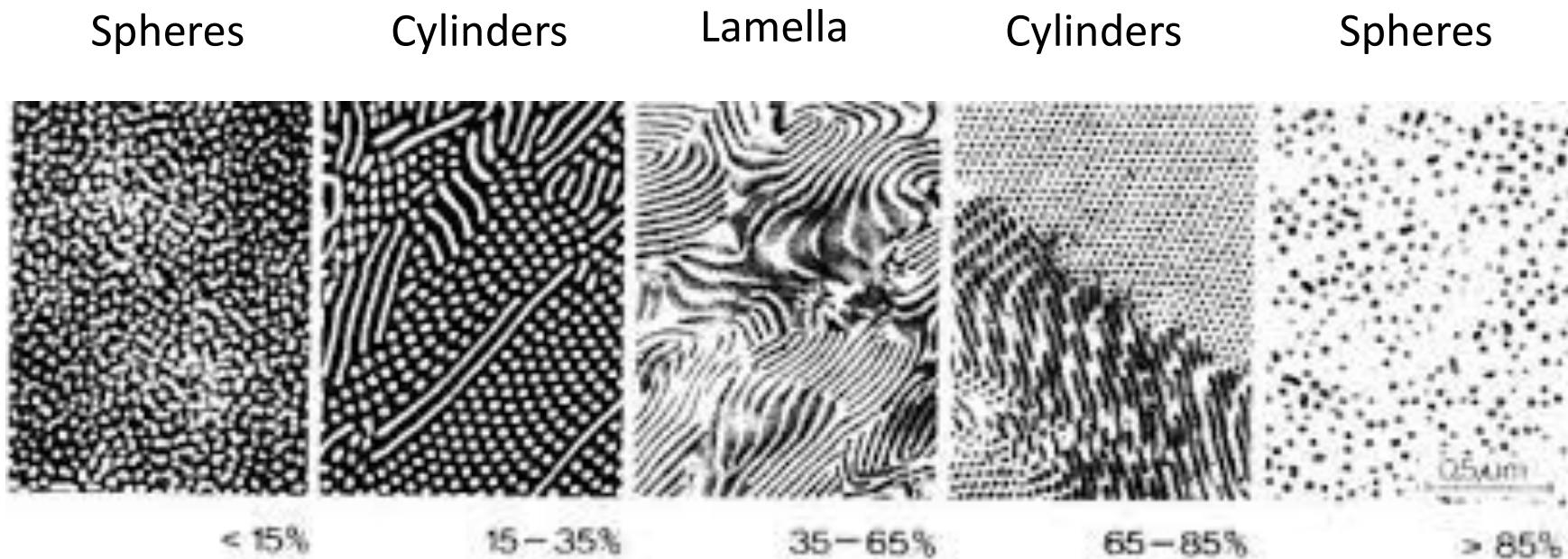
Domain Formation by Block Copolymers



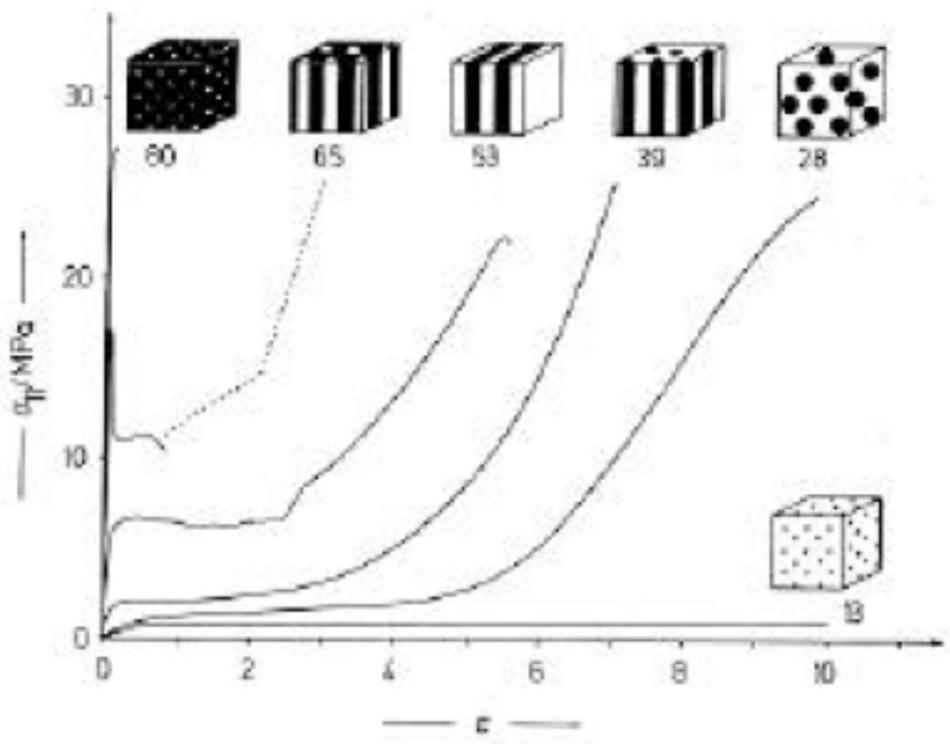
Curvature of the interface is based upon the ratio between the styrene and the butadiene segments and is critical in determining the morphology of the domains.



Domain Morphology of Block Copolymers



Phase Dependent Mechanical Properties

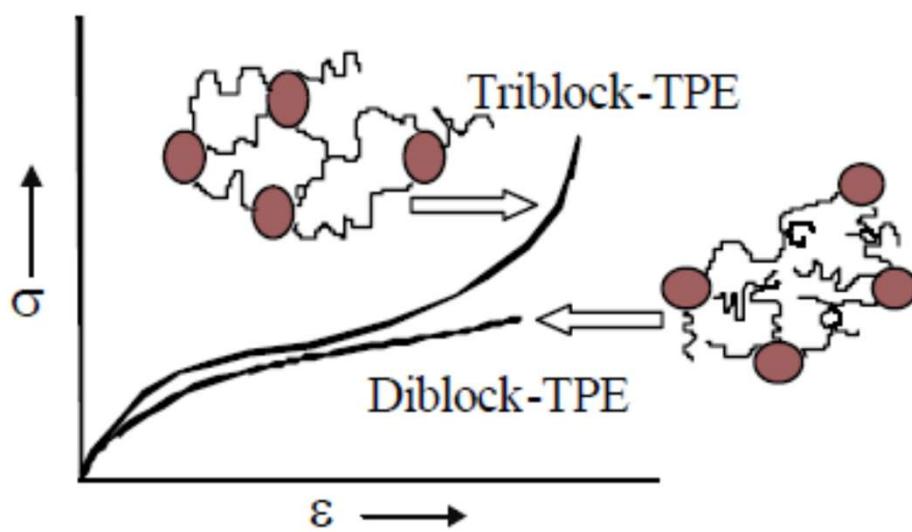


Phase Dependent Mechanical Properties

Styrene – Black Domain – Hard Phase

Butadiene – White Domain – Soft (Rubber) Phase

Elastomers are Derived from a Tri-block Copolymer



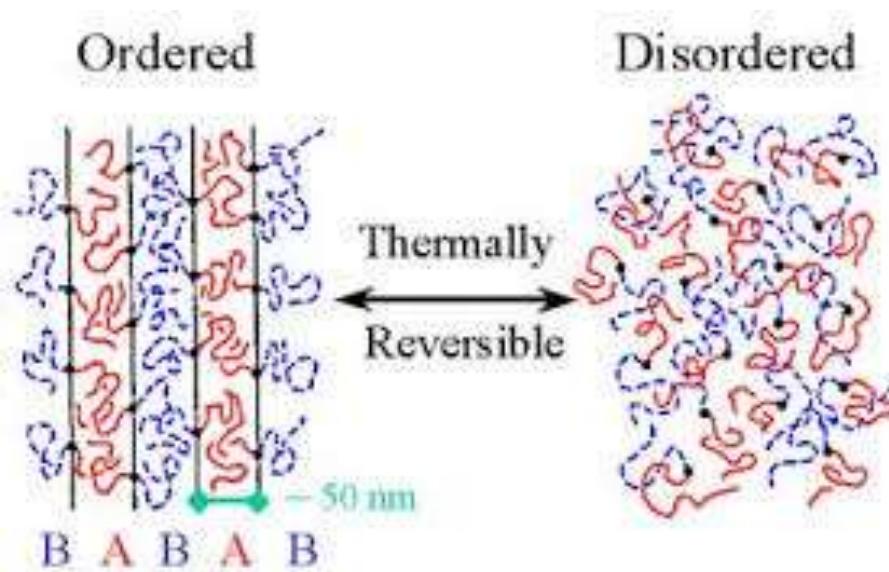
A styrene-butadiene-styrene copolymer defines the morphology of a thermoplastic elastomer.

The styrene segments are the minor component of the S-B-S copolymer and the butadiene segments are the major components.

The styrene components form the rigid spherical domains acting like crosslinks.

The butadiene segments form the elastomeric network.

What defines a Thermoplastic Elastomer?

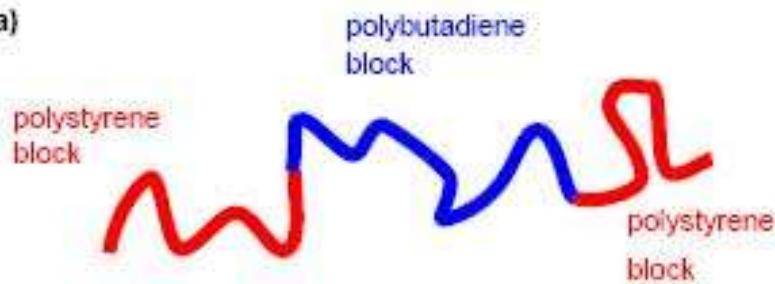


When the temperature is raised above the glass transition temperature of styrene (i.e., 100C) the styrene domains melt allowing the material to Become disordered and flow.

Once this melt is formed into the final form or geometry the material is cooled and the styrene domains are formed imparting the elastomeric properties.

Formation of a TPE by SBS Polymers

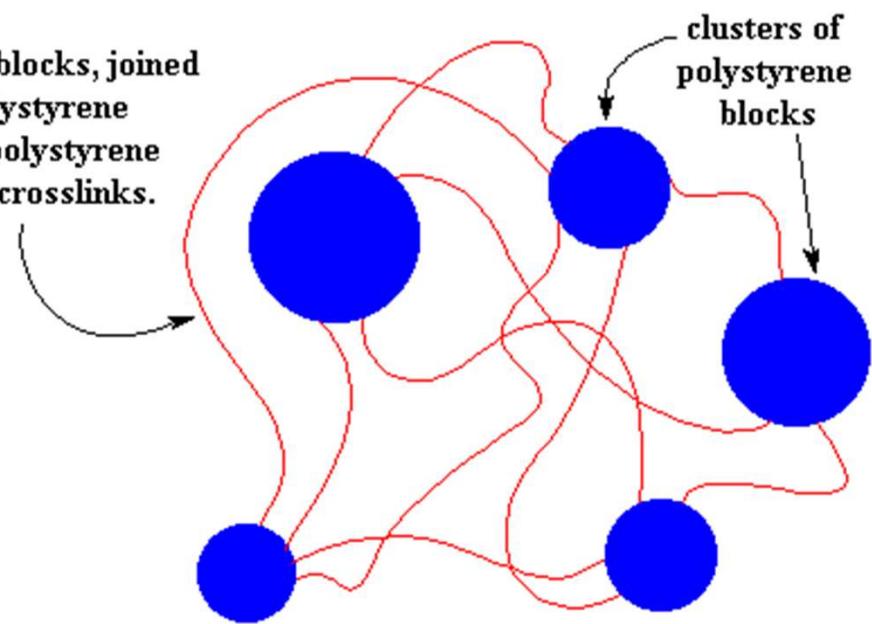
(a)



(b)



Polybutadiene blocks, joined together by polystyrene clusters. The polystyrene clusters act as crosslinks.



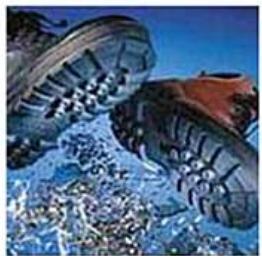
Polystyrene domain morphology is amorphous and glassy.

Comparative Mechanical Properties of Elastomers

	Durometer hardness range	Tensile strength at room temp, psi	Elongation at room temp, %	Temp. range of service °C	Weather resistance
Natural rubber	20–100	1,000–4,000	100–700	–55–80	Fair
Styrene-butadiene rubber (SBR)	40–100	1,000–3,500	100–700	–55–110	Fair
Polybutadiene	30–100	1,000–3,000	100–700	–60–100	Fair
Polyisoprene	20–100	1,000–4,000	100–750	–55–80	Fair
Polychloroprene	20–90	1,000–4,000	100–700	–55–100	Very good
Polyurethane	62–95 A 40–80 D	1,000–8,000	100–700	–70–120	Excellent
Polyisobutylene	30–100	1,000–3,000	100–700	–55–100	Very good

Table 1 Selected properties of some elastomers.

Examples of S-B-S Thermoplastic Elastomer Products



From: Science, Volume 96, Number 2490, Page 10, September 18, 1942

BUTYL RUBBER TIRES

BUTYL rubber tires in actual tests on New Jersey highways have shown a life of 20,000 miles if kept below a maximum of 40 miles an hour, was reported by J. P. Haworth and F. P. Baldwin, of the Esso Laboratories, before the Buffalo meeting of the American Chemical Society.

Possibilities of "tailor-made" rubber for the different parts of a tire were pointed out. In the average light car tire, weighing about 12 pounds, only about four pounds is in the conspicuous part, the tread. Requirements for tread are different from those of side wall, and these in turn differ from those of carcass and inner tube. Synthetic rubbers can be given properties to suit the uses to which they will be put, which is not possible with natural rubber.

Comparative Properties of Elastomers

BUTADIENE BASED RUBBERS

SBR (STYRENE BUTADIENE RUBBER) RUBBER AND POLYBUTADIENE

ADVANTAGES:

SBR provides good abrasion, wear, and tensile qualities. SBR can be readily substituted for NATURAL RUBBER in many applications with significant cost savings. Resilience is about the same as NATURAL RUBBER.

DISADVANTAGES:

Like its natural counterpart, SBR offers little resistance to oils and chemicals. SBR must be specially compounded to provide resistance to ozone, sunlight, and heat.

TYPICAL APPLICATIONS:

Washers, gaskets, grommets.

Comparative Properties of Elastomers

ISOPRENE BASED RUBBERS NATURAL (ISOPRENE) RUBBER AND POLYISOPRENE

ADVANTAGES:

NATURAL RUBBER exhibits high resilience, good tensile strength, and tear resistance. In addition to excellent wear resistance, NATURAL RUBBER also offers low permanent set characteristics plus good flexing qualities at low temperatures.

DISADVANTAGES:

NATURAL RUBBER does not perform well when exposed to chemicals and petroleum derivatives, including petrochemicals. It is not recommended for outdoor applications where maximum resistance to sunlight, ozone, oxygen or heat aging is major factors.

TYPICAL APPLICATIONS: Boots, belts, bumpers, tubing.

Comparative Properties of Elastomers

NEOPRENE® (POLYCHLOROPRENE) RUBBER

ADVANTAGES:

NEOPRENE® is resistant to ozone, sunlight, oxidation and many petroleum derivatives. Added advantages include good resistance to water, many chemicals, good resilience characteristics and high tensile strength properties.

DISADVANTAGES:

NEOPRENE® has few practical limitations. While NEOPRENE® is slightly higher in price than general purpose synthetic rubbers, its resistance to ozone, oil and chemicals make it cost effective in many applications. It is generally attacked by strong oxidizing acids, esters, ketones, chlorinated, aromatic and nitro hydrocarbons.

TYPICAL APPLICATIONS:

Plumbing fixtures; gaskets; hose; mechanical seals; mechanical belts; solid rocket propellant; garden hose; inner tubes; laboratory tubing.

Polyisobutylene

What does this elastomer have to do with baseball, Wrigley Field, or Chicago?



Polyisobutylene

What does it have to do with motor oil?



Polyisobutylene

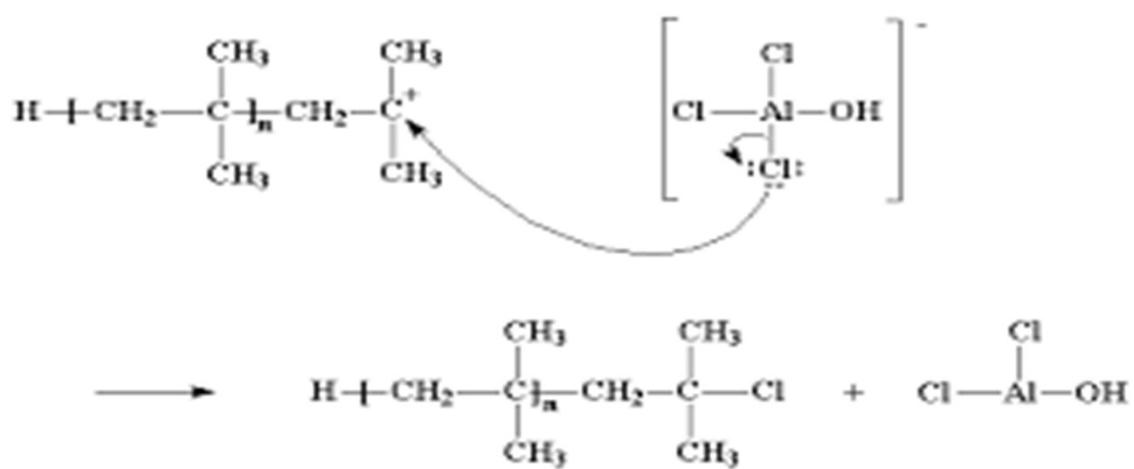
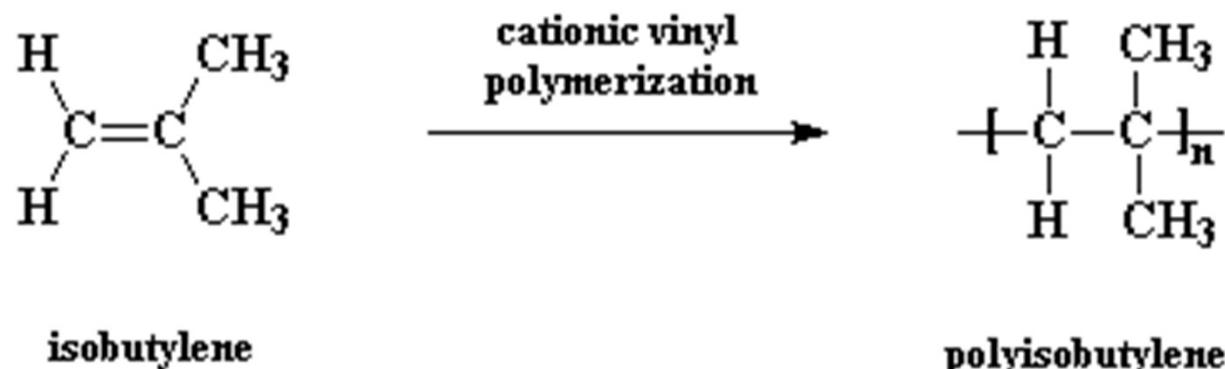
Polyisobutylene is a major component of chewing gum.

The Wrigley Company is a major purchaser of this elastomer.

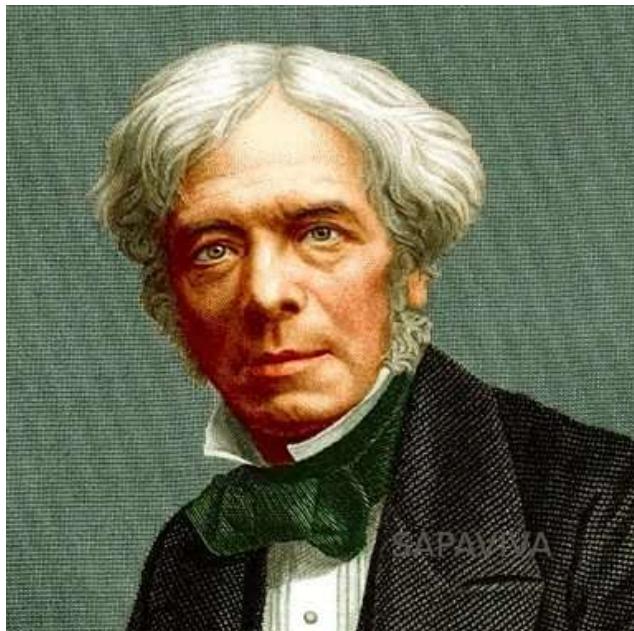


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Polyisobutylene (PIB)



Polyisobutylene



Isobutylene was discovered by Michael Faraday in 1825.

Polyisobutylene (PIB) was first developed by the BASF unit of IG Farben in 1931 using a boron trifluoride catalyst at low temperatures.

PIB remains a core business for BASF to this day.

PIB homopolymers of high molecular weight (100,000–400,000) are polyolefin elastomers: tough extensible rubber-like materials over a wide temperature range; with low density (0.913–0.920), low permeability and excellent electrical properties.

Polyisobutylene and Butyl Rubber

Polyisobutylene is 100% isobutylene monomer.

Butyl Rubber is 98% isobutylene and 2% isoprene.

PIB was developed into butyl rubber in 1937, by researchers William J. Sparks and Robert M. Thomas, at Standard Oil of New Jersey's Linden, N.J., laboratory. Today, the majority of the global supply of butyl rubber is produced by two companies, ExxonMobil (one of the descendants of Standard Oil) and Polymer Corporation, a Canadian federal crown corporation established in 1942.

Properties and Applications

Butyl rubber (IIR) is the copolymer of isobutylene and a small amount of isoprene. First commercialized in 1943, the primary attributes of butyl rubber are excellent impermeability/air retention and good flex properties, resulting from low levels of unsaturation between long polyisobutylene segments. Tire innertubes were the first major use of butyl rubber, and this continues to be a significant market today.

Polyisobutylene/Butyl Rubber

Butyl rubber is impermeable to air and used in many applications requiring an airtight rubber.

The first major application of butyl rubber was tire inner tubes.

This remains an important segment of its market even today in addition to other similar applications.



Polyisobutylene and Butyl Rubber Uses

- the manufacture of adhesives,
- agricultural chemicals,
- fiber optic compounds,
- ball bladders (i.e., basketball, football, soccer, etc.) ,
- O-rings,
- caulk and sealants,
- cling film,
- electrical fluids,
- lubricants (2 stroke engine oil) paper and pulp,
- personal care products,
- pigment concentrates,
- for rubber and polymer modification,
- for protecting and sealing certain equipment for use in areas where chemical contamination is present,
- as a gasoline/diesel fuel additive.

And, also in chewing gum!



Polyisobutylene in Chewing Gum

Composition of Chewing Gum

	<u>Weight Percent</u>
Isobutylene-Isoprene L polymer	8.82%
Polyisobutylene	20.15%
Hydrogenated Vegetable Oil	36.83%
Hydroxylated Lecithin	3.60%
Calcium Carbonate	10.20%
Polyvinyl Acetate	16.20%
Glyceryl Monostearate	1.70%
Glyceryl Ester of Partially Hydrogenated Wood Rosin	2.50%

Polyisobutylene in Chewing Gum

Most modern chewing gum uses food-grade butyl rubber as the central gum base, which contributes not only the gum's elasticity but an obstinate, sticky quality which has led some municipalities to propose taxation to cover costs of its removal.

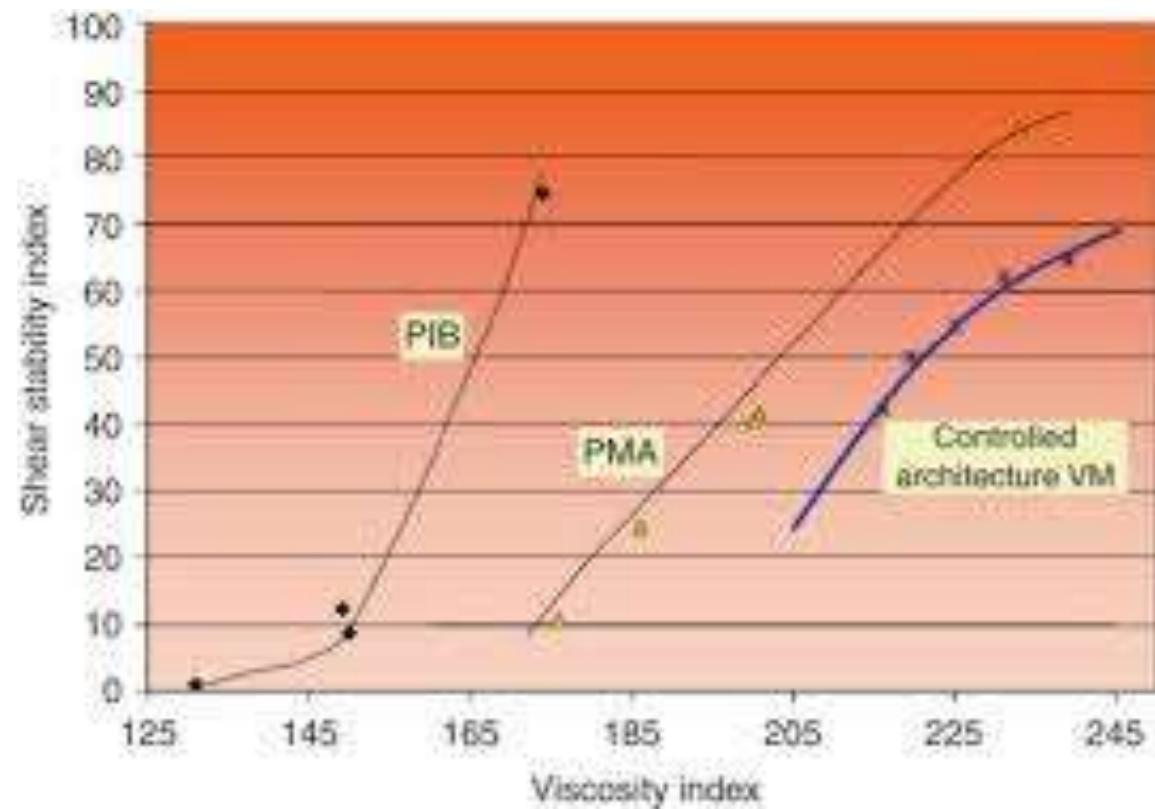
Recycled chewing gum has also been used as a source of recovered polyisobutylene. Amongst other products, this base rubber has been manufactured into coffee cups and 'Gumdrop' gum-collecting bins. When filled, the collecting bins and their contents are shredded together and recycled again.



Gumdrop bin made from polyisobutylene for recycling polyisobutylene.

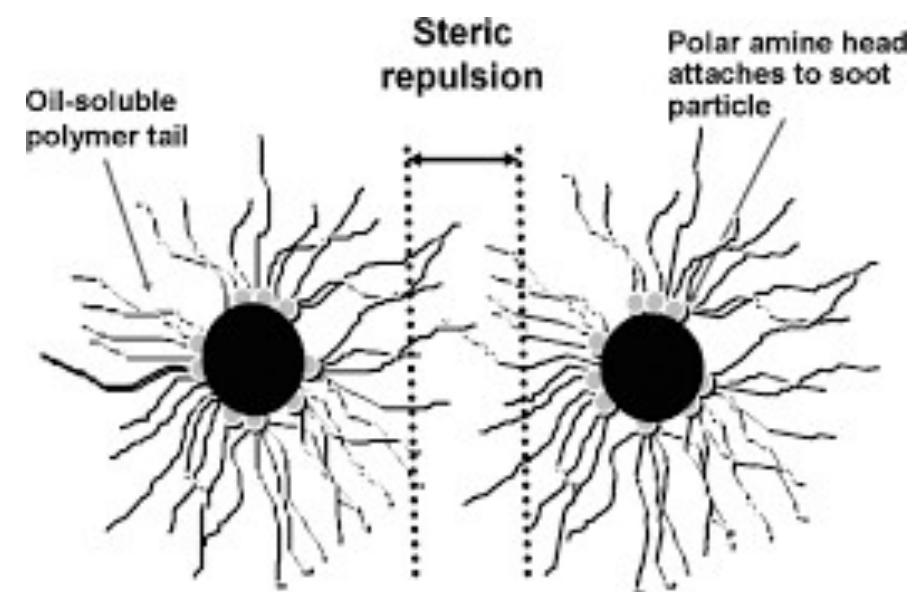
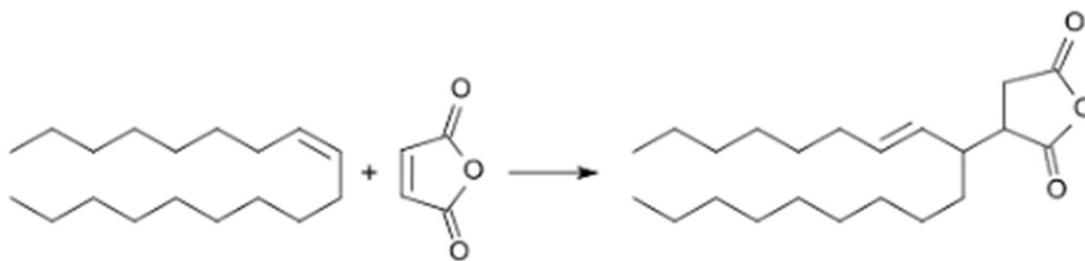
Polyisobutylene is a Major Component in Engine Oils as a Viscosity Modifier

base-oil-containing lubricant	
highly-reactive polyisobutene (1200-1600 mm ² /s [100°C], Mn 2000 to 2500 g/mol, GPC)	15-30 wt%
ester	7-13 wt%
additive component	2-6 wt%
base oil	45-60 wt%
antioxidant	0.5-2 wt%



Polyisobutylene(Succinic Anhydride) - PIBSA

Alkenyl succinic anhydrides (ASA) are modified five-membered succinic anhydrides bearing a branched iso-alkenyl chain (C_{14} to C_{22}):



Carbon polymer tails maintain separation between particles

Polyisobutylene Succinic Anhydride - PIBSA

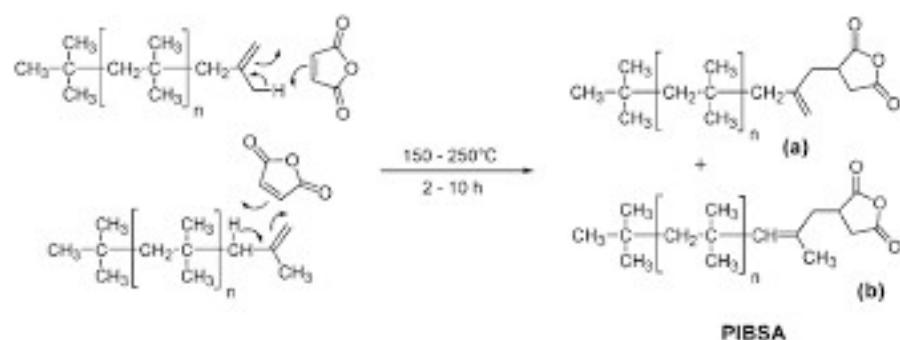
Polyisobutylene succinimides (PIBSA) are used to make dispersants that are used in tailor-made formulations to meet the challenging demands of engine oils.

Polyisobutylene succinimides are critical engine oil additives that keep engines clean by dispersing harmful debris generated during operation that can thicken the oil, and cause wear.

They reduce the formation of deposits on metal surfaces and inhibit soot agglomeration via stable micelle formation.

Their dispersant action helps keep small particles suspended so that they can be removed by the oil filter and not build up in the engine.

Lubrizol (Wickliffe, OH) is a leading manufacturer of PIBSA in the world.



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Table 1 Selected properties of some elastomers.

Polydimethylsiloxane

What does a B-29: Superfortress have to do with this polymer?



First Flight: December 30, 1942

Production of First Operational
Planes: April 15, 1944

Produced: 1945 – 1955(?)

Number Build: <4,000

Speed: 220 – 365 mph

Range: 5800 miles

Altitude: >32,000 feet

Load: 20,000 lbs

Polydimethylsiloxane

What does a B-29: Superfortress have to do with this polymer?

Answer: A lot!



First Flight: December 30, 1942

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Produced: 1945 – 1955(?)

Number Build: <4,000

Speed: 220 – 365 mph

Range: 5800 miles

Altitude: >32,000 feet

Load: 20,000 lbs

NOTE: The IX Center in Cleveland, OH was one of the initial manufacturing facilities for the B-29.

Polydimethylsiloxane

The B-29 Superfortress was a “state-of-the-art” airplane having a pressurized cabin for high altitude flight and the first ever rudimentary (computer) controlled fire control system.

The load capacity of the B-29 over two-times that of the B-17 requiring high performance state-of-the-art radial piston engines.

The period between December 1942 and April 1944 was a period of developmental problems and the need for necessary resolutions to these problems.

One major problem identified during this period was the limitations of the hydrocarbon-based oils, lubricants and gaskets in the high horsepower, high altitude engines.

These problems required a new material.

Polydimethylsiloxane



Polymer Chemistry



Silicone Chemistry



Silicone Based Oils and Polymers

The Dow Corning Corporation was formally established in 1943 as a joint venture between the American conglomerates The Dow Chemical Company and The Corning Glass Company to explore the potential of silicone based lubricants and polymers.

The Dow Corning Corporation was a manufacturer of products for use by the U.S. military in World War II. The company began operating its first plant, in Midland, MI, in 1945.

Polydimethylsiloxane

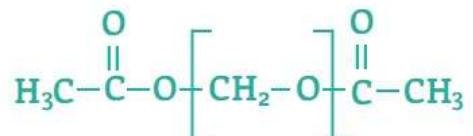
Why silicone based materials – Similarity to carbon in the periodic table – But Heavier.

elements

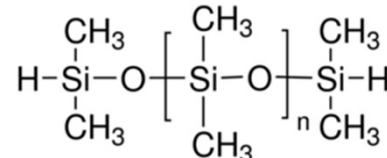
13	14	15	16	17	18	
5 B boron 10.81 [10.805, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999 [15.999, 16.000]	9 F fluorine 18.998 [18.998]	2 He helium 4.0026	
12	13 Al aluminium 26.982 [26.981, 26.983]	14 Si silicon 28.085 [28.084, 28.086]	15 P phosphorus 30.974 [30.959, 32.076]	16 S sulfur 32.06 [32.059, 32.076]	17 Cl chlorine 35.45 [35.446, 35.457]	18 Ar argon 39.95 [39.952, 39.953]
30 Zn zinc 65.38(2) [65.38, 65.39]	31 Ga gallium 69.723 [69.72, 69.725]	32 Ge germanium 72.630(8) [72.63, 72.631]	33 As arsenic 74.922 [74.92, 74.923]	34 Se selenium 78.971(8) [78.97, 78.972]	35 Br bromine 79.904 [79.901, 79.907]	36 Kr krypton 83.798(2) [83.798, 83.799]
48 Cd cadmium 112.41 [112.41, 112.42]	49 In indium 114.82 [114.82, 114.83]	50 Sn tin 118.71 [118.71, 118.72]	51 Sb antimony 121.76 [121.76, 121.77]	52 Te tellurium 127.60(3) [127.6, 127.61]	53 I iodine 126.90 [126.9, 126.91]	54 Xe xenon 131.29 [131.29, 131.30]
80 Hg	81 Tl	82 Dy	83 Ri	84 Pa	85 At	86 Rn

Carbon and silicon share many characteristics. Each has a so-called valence of four--meaning that individual atoms make four bonds with other elements in forming chemical compounds. Each element bonds to oxygen. Each forms long chains, called polymers, in which it alternates with oxygen. **Silicon yields polymeric silicones, which we use to waterproof cloth or lubricate metal and plastic parts.**

Polydimethylsiloxane

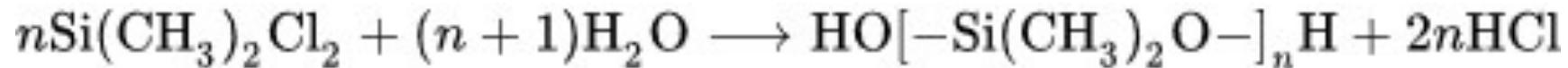


Polyoxymethylene

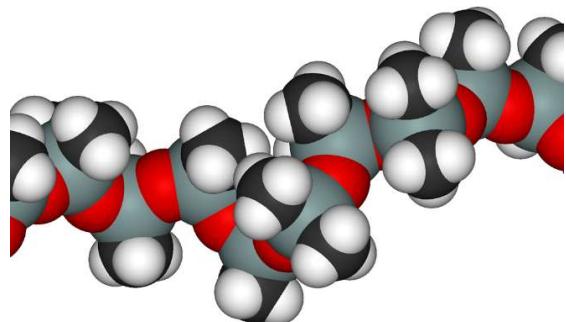


Polydimethylsiloxane

Industrial synthesis can begin from dimethyldichlorosilane and water by the following net reaction:



The polymerization reaction evolves [hydrochloric acid](#).



Reasons why Silicon is not used as the base of life are:

- Reactions of Silicon are much slower than reactions of Carbon.
- Bonds between Si and Si or between Si and H are not as stable as the bond between C and H.
- Molecules based on Si and H are not very stable in presence of water.

Comparison of Silicone Oil with Other Base Oils

	MINERAL OIL	PHOSPHATE ESTER	POLYGLYCOL	POLYESTER	DIESTER	PERFLUOROPOLYETHER	SILICONE	POLYALPHOLEFIN
Cost	L	VH	M	M	M	VH	H	M
Seal compatibility	AA	BA	A	BA	BA	AA	AA	AA
Compatible with mineral oil	-	BA	BA	A	A	BA	BA	E
Corrosion stability	E	AA	A	BA	BA	BA	A	E
Oxidation stability	BA	AA	AA	AA	A	E	E	AA
Viscosity range	AA	BA	A	BA	BA	A	A	A
Flash point	M	E	A	AA	A	E	E	AA
Pour point	A	AA	M	L	L	L	VL	L
Temperature range	BA	A	A	AA	A	E	E	AA

KEY	
E	EXCEPTIONAL
AA	ABOVE AVERAGE OR VERY GOOD
A	AVERAGE OR GOOD
BA	BELOW AVERAGE OR LESS THAN IDEAL
VL	VERY LOW
L	LOW
M	MEDIUM
H	HIGH
VH	VERY HIGH
NA	NOT AVAILABLE

Patent Competition Regarding PDMS 1947 (1951?)

Patented Dec. 2, 1947

2,431,878

UNITED STATES PATENT OFFICE

2,431,878

TREATING DIMETHYL SILICONE POLYMER WITH BORIC OXIDE

Rob Roy McGregor, Verona, and Earl Leathen Warrick, Pittsburgh, Pa., assignors to Corning Glass Works, Corning, N. Y., a corporation of New York

Treating Dimethyl Silicone with Boric Oxide

Rob Roy McGregor and
Earl Leathen Warrick



Patented Feb. 13, 1951

2,541,851

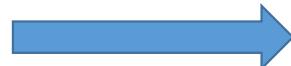
UNITED STATES PATENT OFFICE

2,541,851

PROCESS FOR MAKING PUTTYLIKE ELASTIC PLASTIC, SILOXANE DERIVATIVE COMPO- SITION CONTAINING ZINC HYDROXIDE

James G. E. Wright, Schenectady, N. Y., assignor
to General Electric Company, a corporation of
New York

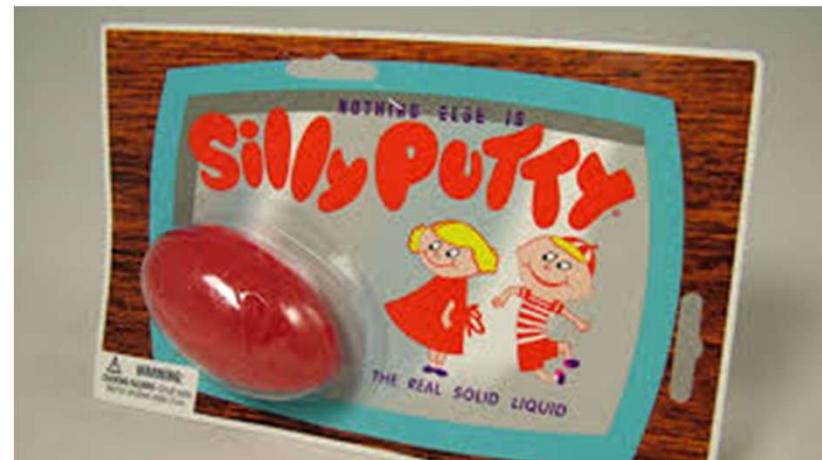
James G. E. Wright



Process for Making Putty-Like Plastic, Siloxane Derivative
Composition Containing Zinc Hydroxide

Silly Putty is Made from PDMS

Composition	Weight percentage
PDMS	65%
Silica	17%
Thixotrol	9%
Boric acid	4%
Glycerine	1%
Titanium dioxide	1%
Dimethyl cyclosiloxane	1%



Among a lot of other things, Silly Putty makes a great fire starter as it burns fairly easily and slowly, as well as gets white hot.

Hodgson developed and marketed Silly Putty. By the time of his death in 1976, Hodgson's net worth was around \$140 million.

Interestingly, Silly Putty dissolves in alcohol. Because of this, alcohol-based hand sanitizer is often the best way to get the putty out of hair or clothing.



Cross-linking of Polydimethylsiloxane to form an Elastomer

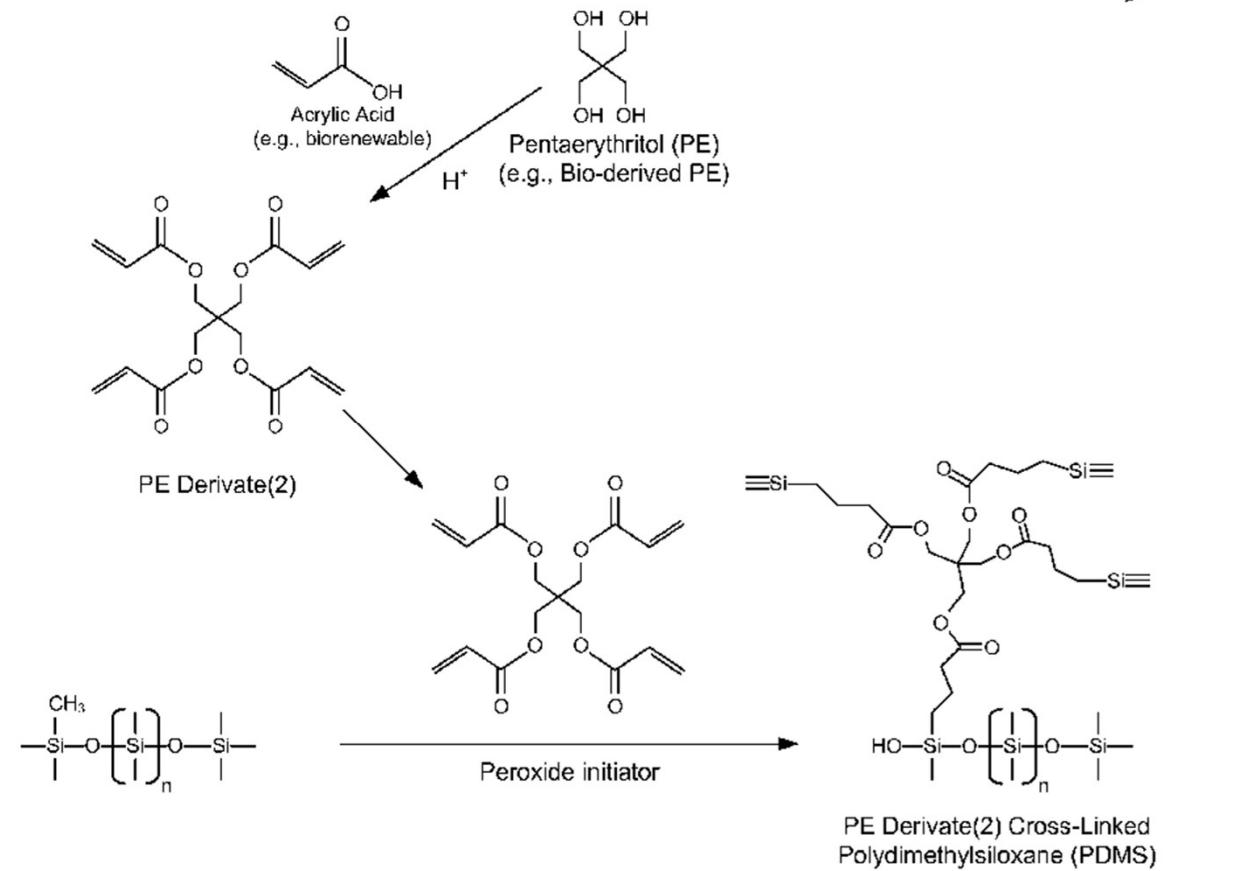
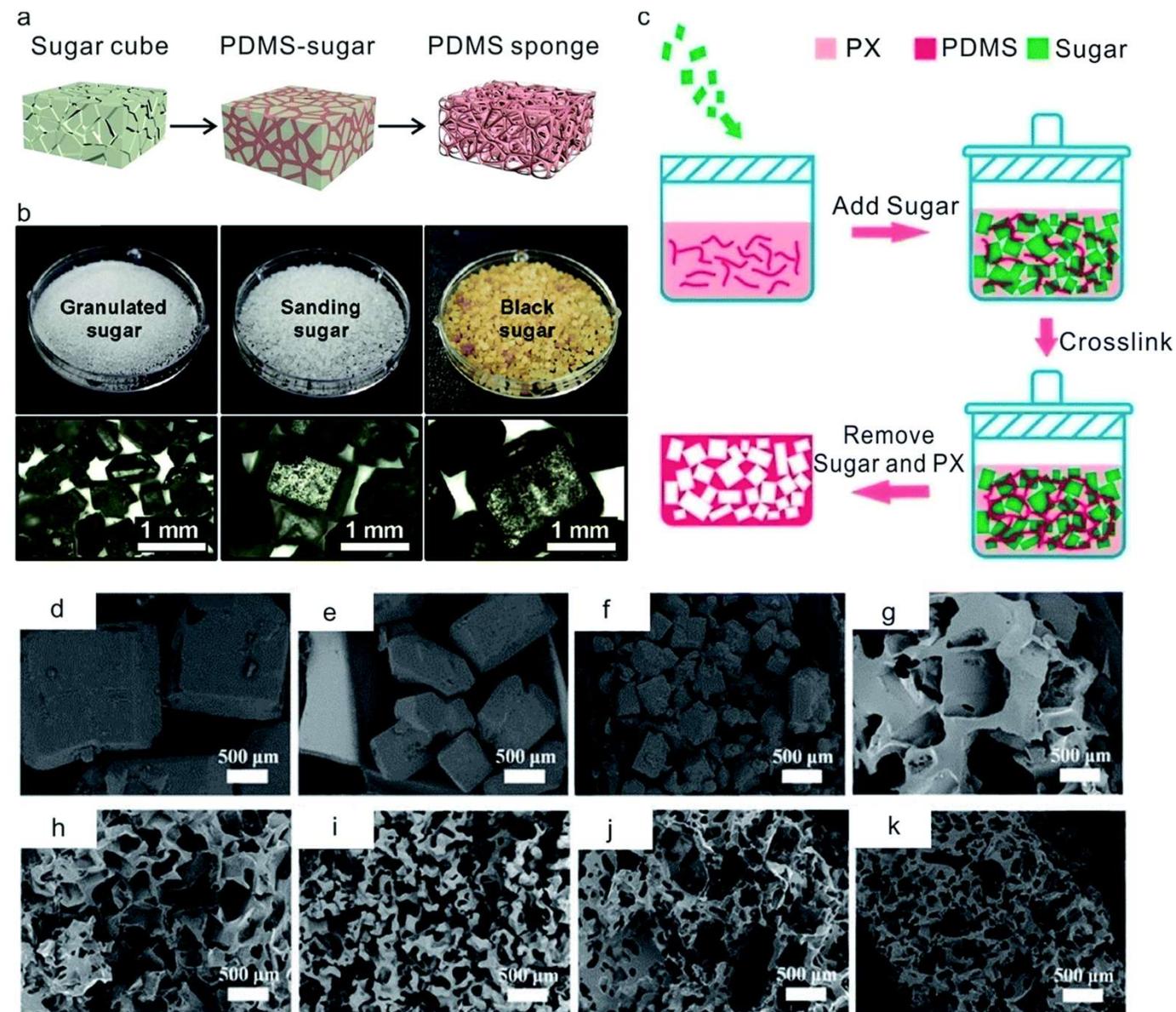
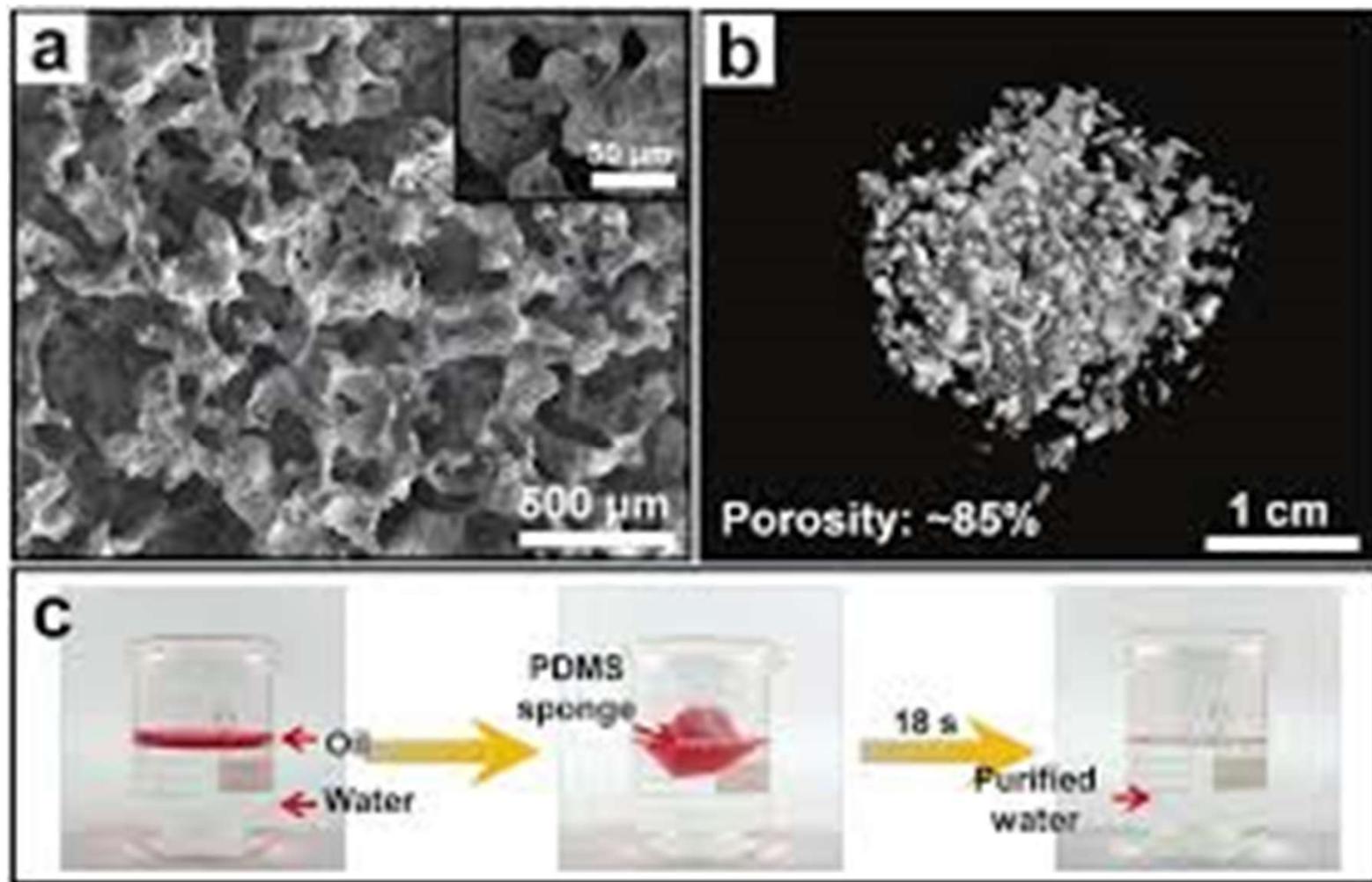


FIG. 4

Production of a PDMS Foam by using a Sugar Cube Template



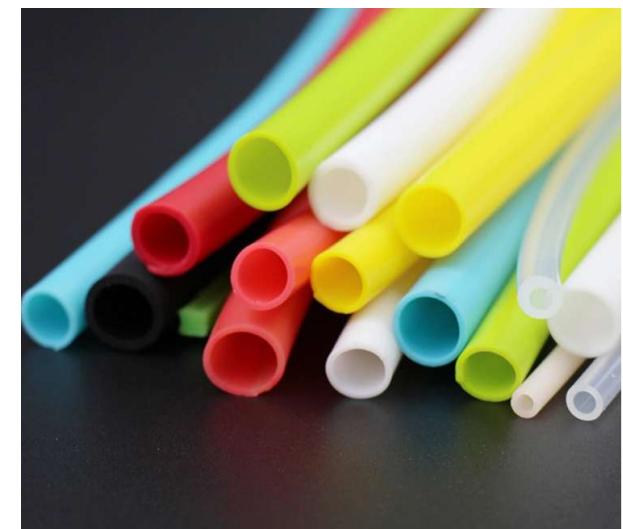
Oil Adsorption by a Crosslinked PDMS Sponge



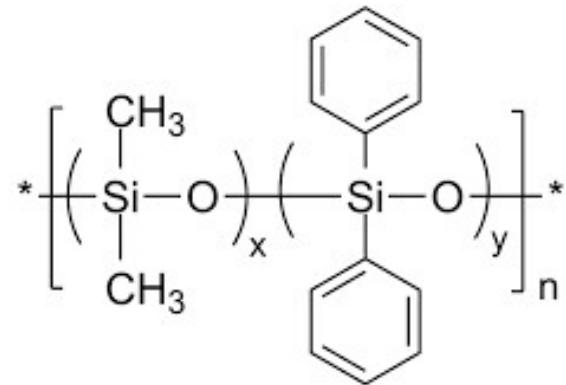
Properties of Silicone Rubber

40 Duro Red Silicone Rubber	Physical Properties
Color	Red
Durometer Hardness Shore A (± 5)	40 ($+/- 5$)
Service Temperature Limits (°F)	-80°F to 450°F
Tensile Strength - ASTM D412 (psi)	600 psi
Ultimate Elongation - ASTM D412 (%)	400%
Specific Gravity - ASTM D297 (g/cc)	1.25 g/cc
Available Widths (inches)	36" & 48"
Available Thicknesses (inches)	1/16" to 1"

Uses of Polydimethylsiloxane – Silicone Rubber



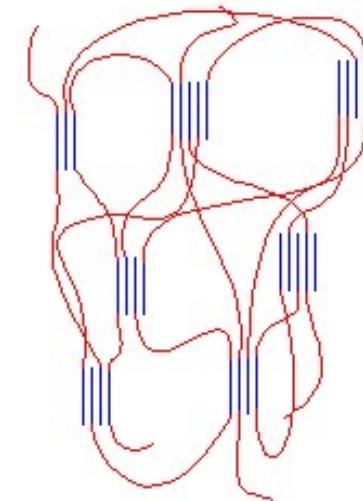
Tri Block Copolymer of Poly(diphenyl-co-dimethyl-co-diphenyl) Siloxane



Polydimethylsiloxane is an amorphous rubbery material.

Polydiphenylsiloxane is a semicrystalline polymer.

When polymerized the morphology of these tri-block copolymers will be similar to the domain morphology exhibited by styrene-butadiene-styrene tri-block copolymers.



Polydiphenylsiloxane domain morphology is semicrystalline.

Lecture 17: Continuation of Elastomers

Part 1: SBR (Cont'd)

Part 2: Polyisobutylene

Part 3: Polydimethylsiloxane

Questions?



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"I just asked myself if I was crazy and we all said 'No'"

<https://www.bbc.com/future/article/20210308-rubber-the-wonder-material-we-are-running-out-of>