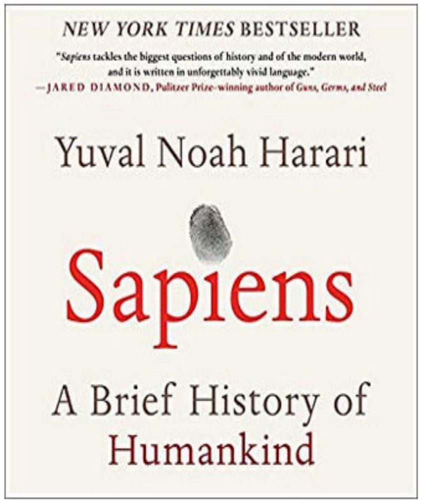
2. The History of Polymers

A Brief History

The Evolution of Humankind

Human beings:	2.4 million years
Homo Sapiens:	150,000 years.
The Cognitive Revolution:	70,000 years ago
The Agricultural Revolution:	11,000 years ago
The Scientific Revolution:	500 years ago
The Industrial Revolution:	250 years ago
The Information Revolution:	50 years ago
The Biotechnological Revolution:	



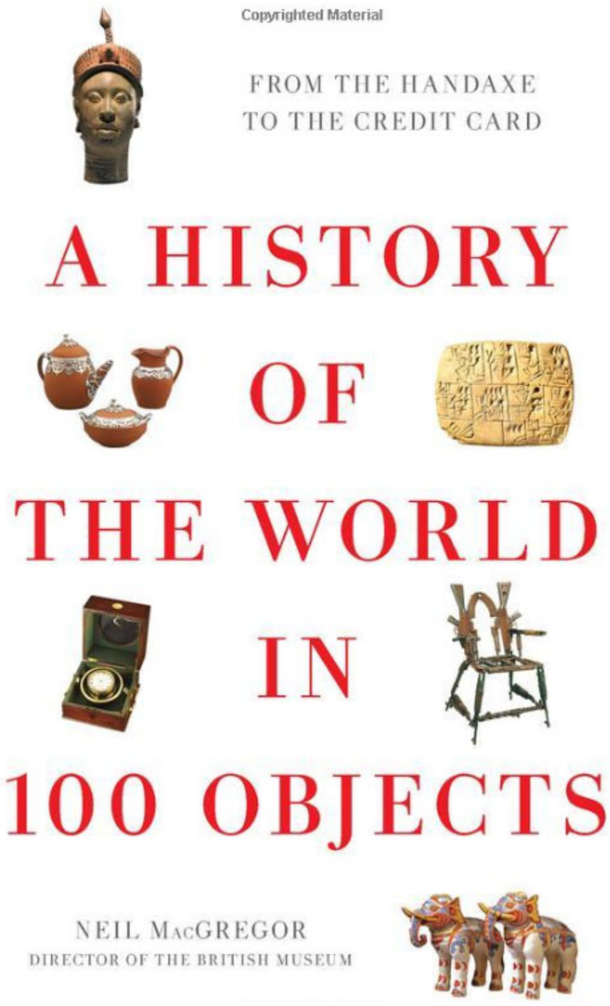
NEW YORK TIMES BESTSELLER

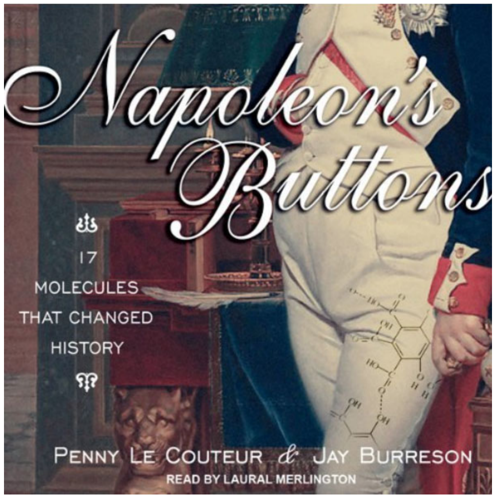
"*Sapiens* tackles the biggest questions of history and of the modern world, and it is written in unforgettably vivid language."
—JARED DIAMOND, Pulitzer Prize-winning author of *Guns, Germs, and Steel*

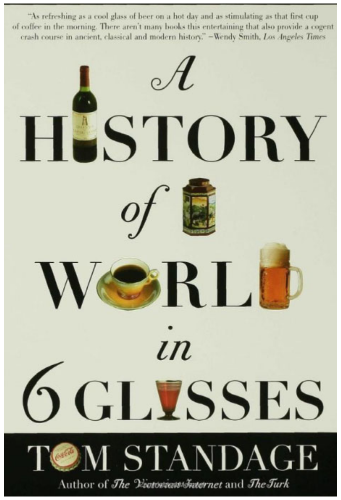
Yuval Noah Harari

Sapiens

A Brief History of Humankind



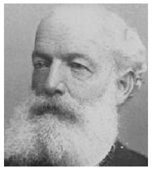




A Timeline of Polymer History

1858. Karl Nageli uses the term molecule. Karl Nageli was a Swiss botanist who claimed starches were made of 'molecules'. This term had not yet been popularized so there was confusion as to what it meant in the science community. Scientists like Cannizzaro and Avogadro had different definitions.

1860. Karlsruhe Conference defines molecule; Negali retracts. At the Karlsruhe Conference, scientists establish a meaning to the term molecule after being persuaded by the research of Avogadro and Cannizzaro. This definition is essentially the same today. Negali's usage did not correspond to the new usage so he changed his term to micelle (an association of molecules that formed a crystalline array).

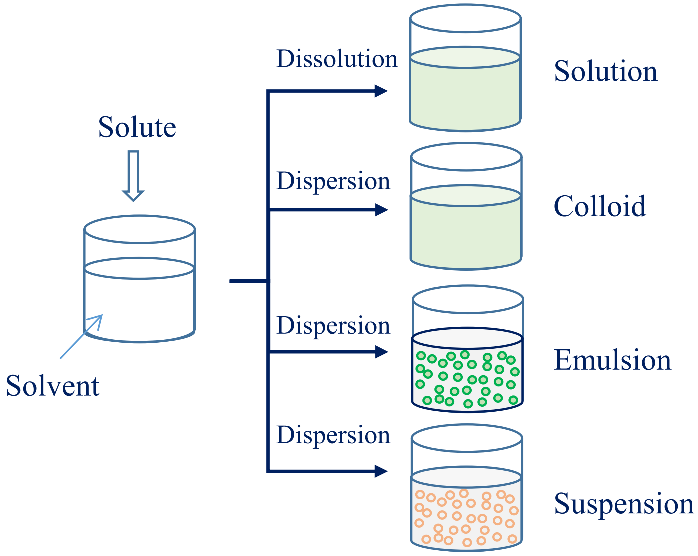


1877. Kekule proposes fairly accurate model. Kekule proposes that molecules are like 'net or sponge-like masses formed by the union of many univalent molecules with polyvalent atoms acting as centers of attachment". He did not introduce the idea of chains of atoms, but it did explain molecular masses. This concept was not accepted and micellar theory was used to explain colloid conditions by proposing that the molecules had associations and formed ring-like structures.

1882. New methods for determining molecular weight. In 1882, Raoult's Law was introduced as a method of obtaining molecular weights by freezing and in 1886, van't Hoff introduced a method of obtaining molecular weights by osmotic pressure. Both methods produced variable answers and it was deemed that these equations didn't work for colloidal solutions. The error of the methods for macromolecules produced errors greater than the measurement

https://www.timetoast.com/timelines/history-of-polymers

Solution, Colloid, Emulsion, & Suspension



Solution

The solute is dissolved in the solvent for complete miscibility at a given temperature.
A clear homogeneous mixture and the solute particles are no longer visible.
The particles of solute are of molecular size dimensions and do not scatter a light beam.

Colloid

A dispersion of particles (liquid or solid) of 1~1,000 nm in the liquid solvent.
A homogeneous mixture and the solute does not settle out on standing.
Colloids exhibit light scattering. Milk consists of fat particles evenly distributed in water.

Emulsion

A dispersion of two or more immiscible liquids (e.g., oil and water) when mixed and shaken.
Emulsions generally appear cloudy. Stabilized by surfactants or particles (Pickering emulsion)
Some emulsions tend to form a film over another phase in the solution.

Suspension

A dispersion of insoluble solid particles in a liquid medium.
On shaking the solute particles can be evenly dispersed in the medium.
The solute particles ranging from 0.5 to 5 µm tend to settle down.

https://lab-training.com/understanding-differences-solutions-emulsions-colloids-dispersions/
Deepak 2017, Understanding differences between solutions, emulsions, colloids and dispersions.

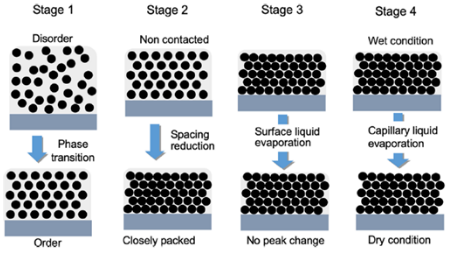


Figure 10. Schematic of the colloidal crystal film formation mechanism after the EPD process and during the drying process.

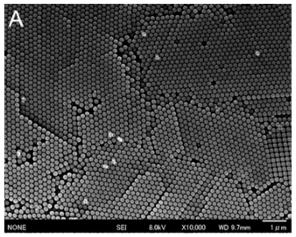


Figure 2. SEM images of the colloidal crystal film
Tran 2020, Rapid growth of colloidal crystal films from the concentrated aqueous ethanol suspension

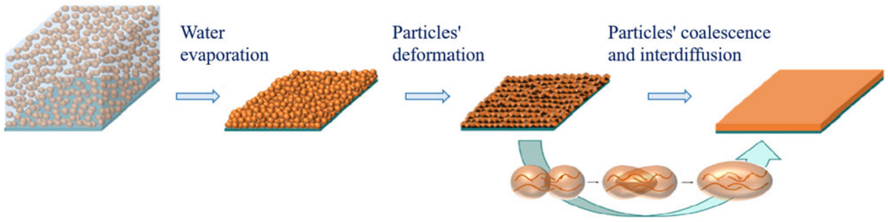
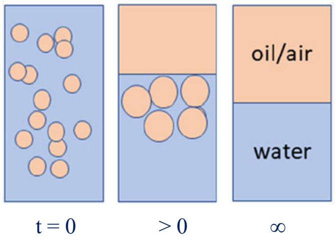


Figure 4. Film formation process.
Aguirre 2023, Polymer colloids- Current challenges, emerging applications, and new developments

Emulsion/Foam time destabilisation



Langevin 2023, Recent advances on emulsion and foam stability

Film Formation of Colloidal Polymers

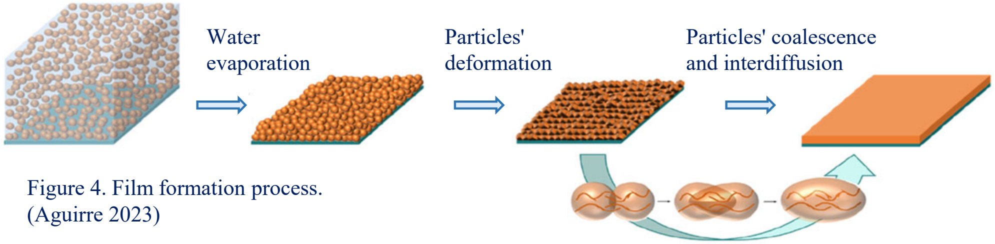


Figure 4. Film formation process. (Aguirre 2023)

2.3. Understanding and Improving Latex-to-Film Transition.

One particular issue that affects numerous applications of colloidal polymers is the transition between the colloidal state from which the latex is applied and the final dried polymer film. This process is central to the widespread use of polymer colloids as binders in paint formulations. The film formation process of colloidal polymers is constituted by three main steps that are water evaporation, particle deformation, and finally coalescence and interdiffusion of polymer chains between neighboring particles (see Figure 4). As these last steps require the polymer to be in a relatively soft state, i.e., above its glass transition temperature (T_g), the minimum temperature at which a film can be formed (minimum film formation temperature, MFFT) is closely related to the T_g of the polymer forming the film.

If the polymer film is to be used as an adhesive, the relation between the MFFT of the latex and the T_g of the polymer does not represent a major issue, as the adhesives usually possess a T_g well below the application temperature of the films. However, in many coating applications, it is desirable to use a polymer with a T_g higher than the temperature at which the film is formed in order to enhance mechanical performance. As such, these latexes have MFFTs higher than room temperature, which prevents the particle's coalescence-interdiffusion process (Figure 4) and hinders their application to produce hard and homogeneous films at moderate temperatures. This is a major factor in the difficulty in transitioning away from solvent-based products, where the polymers are inherently plasticized during the drying process. In water-based systems, this issue can be solved by the addition of coalescing aids to the latex before film formation. These coalescing aids, which are generally organic molecules of low molar mass, plasticize the hard polymer phase, reducing the T_g and therefore the MFFT of the latex. Once the film is produced, the coalescing aids evaporate, leaving behind a film with high modulus. However, this approach, even if effective, results in the release of organic coalescing aids to the atmosphere, thus masking the environmental benefits of waterborne coatings. As regulation over volatile organic content becomes increasingly strict, new approaches are required to obtain films with good mechanical properties with low MFFT latexes.

In light of this, several approaches have been proposed to overcome the "film formation dilemma", with the aim of reducing the MFFT, while still obtaining hard coating films. The use of reactive coalescing aids (RCA) is one of the approaches that has appeared in the last years. RCAs act as conventional coalescing aids, lowering the MFFT of the latex, but their release is prevented by reaction with themselves or with the polymer present in the latex such that they are incorporated into the final film. While in some cases the reaction does not require any external trigger, the RCA usually requires the incorporation of additional initiator to the latex or the curing of the latex by UV irradiation. Even if attractive, this approach requires the use of complex organic chemistry to synthesize the RCAs which typically utilize dicyclopenteneyloxy acrylates, oxopentanoate functionalized compounds, or hydroxyethyl sulfones.

Hydroplasticization has also been proposed to reduce the MFFT of latexes, by using water to plasticize hydrophilic groups present in polymer latexes. However, at low relative humidity, the film formation process can be significantly affected due to the higher rate of water evaporation and, therefore, the environmental conditions in which hydroplasticization is a viable strategy are limited. Furthermore, the water sensitivity of the final film can be compromised by the presence of the hydrophilic groups. Recently, the use of oligomers produced in situ by the addition of a chain transfer agent at the end of the main polymerization has been described as a scalable method to reduce the MFFT of hard latexes, without significantly affecting the mechanical properties of the final films. IR-assisted sintering of latexes containing hard latexes may also be a useful approach to produce hard films at lower energy consumptions than conventional ovens.

Another potential way to reduce the MFFT is to use a low T_g film forming polymer in combination with a high T_g polymer phase, either in separate particles (in latex blends) or in multiphase particles. In this sense, Geurts et al. produced high performance coatings with low MFFT using blends of small, hard particles and large, soft particle sizes. For this strategy to be successful, stratification of small and big particles must be avoided in order to obtain homogeneous films. Multiphase particles containing soft and hard phases have also been synthesized. This avoids any potential stratification during film formation but comes with additional complications in the synthesis and the film formation processes. For instance, hard core/soft shell particles have been sought, in order to produce films with low MFFT reinforced by the hard cores. However, the mechanical improvements attained with this morphology are not substantial, due to the lack of connectivity between the hard phases located in the cores of the particles. Better mechanical properties can be obtained when the hard polymer is primarily located at the particle surface. In this case, the optimization of the amount of the hard phase and its morphology can lead to low MFFT latexes with highly improved mechanical properties, due to formation of a more interconnected hard phase.

Alternative approaches have not focused on decreasing of the MFFT of the latex but rather at increasing the modulus of the polymer by cross-linking, either after or during film formation. It has to be pointed out that the cross-linking reactions must occur during or after the film formation process, because if they happen earlier, for instance during the main polymerization process, they may completely hinder the film formation. In other words, diffusion of polymer chains must be faster than cross-linking reactions to obtain hard and homogeneous films.

The primary approach to achieve cross-linked films in commercial systems is through chemical cross-linking. Several cross-linking chemistries have been tried, such as melaminehydroxyl, aziridine-carboxylic acid, carbodiimide-caborxylic acid, oxirane or oxazoline-carboxylic acid, isocyanate-hydroxyl, or acetoacetoxy-amine. Traditionally, the cross-linking agent has been mixed with the functionalized latex before film formation, in order to trigger the cross-linking reaction during film formation. For instance, Koukiotis et al. used adipic acid dihydrazide as a cross-linker in diacetone acrylamide functionalized latexes, and the films obtained after drying at room temperature for 14 days presented higher tensile stresses and lower elongations at break, together with improved solvent resistance than non-cross-linked counterparts. However, this approach presents problems from the application point of view, as the use of many of the most common low molar mass crosslinking agents is under scrutiny due to chemical classification, labeling and packaging (CLP) and registration, evaluation, authorization, and restriction of chemicals (REACH). One way to overcome this problem is to include the reactive moieties in separate polymer particles. For example, Tariq et al. produced acetoacetoxy- and amino-functionalized latexes separately and demonstrated that the film obtained upon mixing was harder and more water resistant than the non-cross-linked latexes. The major issue with this strategy is that unlike the reaction between low molar mass compounds, which can be rapid even at low temperatures, when the reactive functional groups are linked to polymer chains, the rate of cross-linking is significantly reduced due to the limited diffusion of the polymer chains, and therefore, elevated temperatures may be required for curing. Another aspect to be taken into consideration when using chemical cross-linking is the stability of the latexes that contain complementary reactive moieties, which may be limited, resulting in aggregation of particles. This can be solved by improving the colloidal stability of the polymer particles, by the activation of reactive groups by dehydration during film formation or by producing the mixture just before the coating application, like in a two-pack system.

As an alternative to chemical cross-linking, physical interactions, driven by ionic interactions or by H-bonding, have been proposed to improve the mechanical properties of films cast from latex dispersions. For example, positively charged latexes (containing for instance 2-(dimethylamino)ethyl methacrylate) and negatively charged latexes (containing acrylic acid or sodium styrenesulfonate) can be synthesized and mixed prior to film formation. Films prepared with blends of this type display slightly improved mechanical properties compared to the individual latexes, indicating some ionic interactions in the final film. However, one important drawback of these films is their poor water resistance, due to the increased amount of charges present in the final film. Furthermore, Argaiz et al. reported that the interdiffusion of polymer chains between neighboring particles was almost completely hindered by the presence of the ionic interactions on the surface of the particles. H-bonding physical interactions have also been reported as a way to reinforce the final films formed at low temperature. For example, Chen et al. synthesized ureidopyrimidone-functionalized latexes to obtain a quadruple H-bonding between polymer particles, which led to films with improved resistance to solvent.

This nonexhaustive list of approaches to solve the "film formation dilemma" should make it clear that at present there is no silver bullet to solve this problem. While many of the strategies show great promise, and indeed many are already in use commercially, it is clear that further refinements need to be made to the present strategies such that low MFFT, high mechanical strength films can be generated from colloidal polymers. This is particularly important as moving forward regulations are likely to become stricter, and therefore, aqueous polymer dispersions will be required for use in even more demanding applications that have traditionally been dominated by solvent-based products.

A Timeline of Polymer History

1899. Partial Valencies by Johannes Thiele. The aggregate or partial valency hypothesis became popular which said that the molecules did not have to have full valences to form molecules and that these collections of molecules made the large structures.

1905. Aggregate theory was introduced. The concept that the odd behavior of synthetic and natural molecules is attributed to the nature of the molecules forming primary and secondary forces with each other and forming larger structures. Alfred Werner was an advocate for aggregate theory.

1920. Staudinger received the following advice in a letter after the discussion: "Dear Colleague, Leave the concept of large molecules well alone; organic molecules with a molecular weight above 5,000 do not exist. Purify your products, such as rubber, then they will crystallize and prove to be lower molecular substances. Molecules can not be larger than the crystallographic unit cell, so there can be no such thing as a macromolecule."

1920. Staudinger's Heated Discussion. After a lecture in Zurich where he disputed the 'secondary forces of association' and **proposed the concept of macromolecules**, he received much criticism and the debate was very hectic. His final words of the discussion were "Here I stand, I cannot do otherwise" (quote from Luther).

1925. Molecular mass estimates renewed. Svedberg and Adair both estimate hemoglobin molecular weight to be around 66,000. Collaboration begins and the theory of aggregate molecules is to be cast aside for macromolecules. Theodore Svedberg

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A Timeline of Polymer History

1928. Tiselius shows mass to charge is constant. This showed that partial valence theory was not likely as described by Werner and that the end groups must have normal valance structures.

1928. X-ray used to determine molecular structure.
Mark and Meyer use X-rays to determine cellulose and rubber crystalline forms. This refuted the idea that the molecule had to be a small molecules built through association.

1929. Carothers synthesizes polyester/polyamides.
Carothers synthesized polyesters and then polyamides (nylon) and shows wool and silk are also polyamides. **(Application of the concept of macromolecules)**

1948. Tiselius receives Nobel Prize for Chemistry.
For his research on electrophoresis and adsorption analysis, especially for his discoveries concerning the complex nature of the serum proteins

1953. Staudinger receives Nobel Prize for Chemistry.
He won the prize for his work on determining that **macromolecules** exist.

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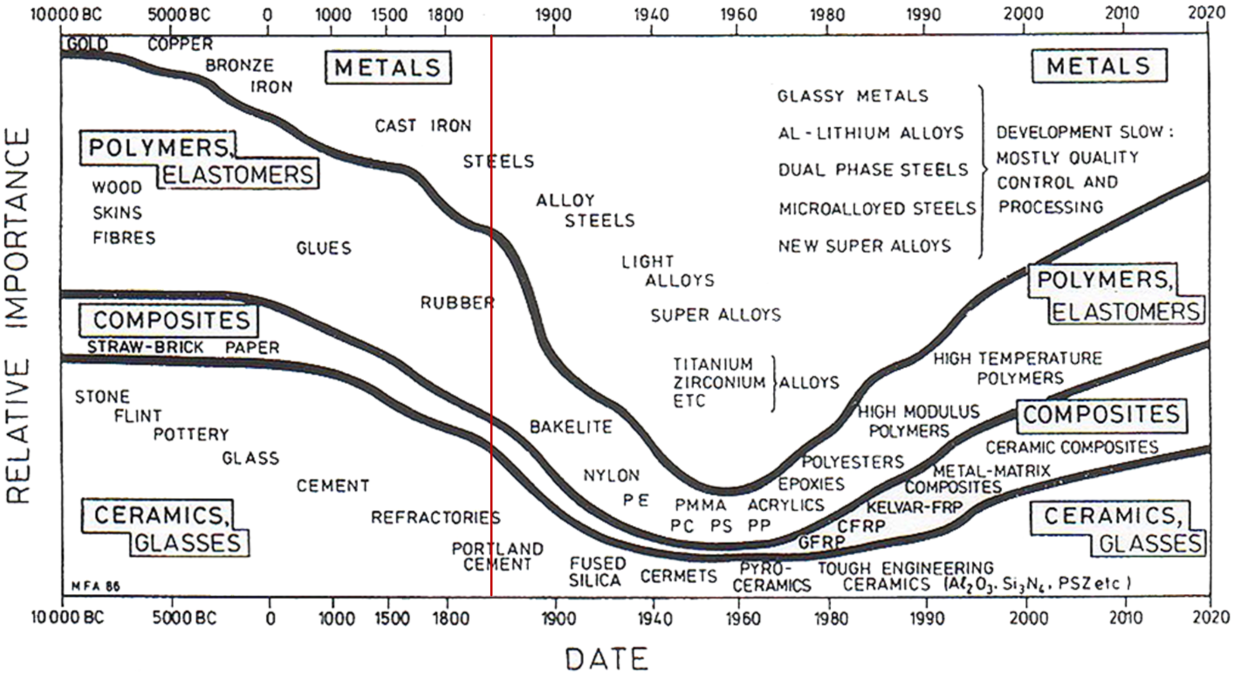
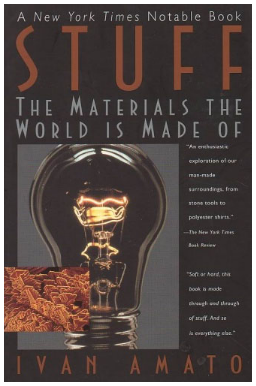
Polymer Stuff

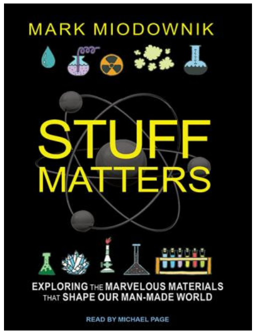


Synthetic: The same chemical structure as the natural.

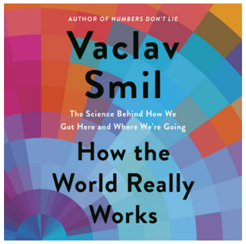
Artificial: The same function but not the structure.

Plastics are a large group of synthetic organic materials whose common quality is that they can be molded into desired shapes—and they are now everywhere. As I type this, the keys of my Dell laptop and a wireless mouse under my right palm are made of acrylonitrile butadiene styrene, I sit on a swivel chair upholstered in a polyester fabric, and its nylon wheels rest on a polycarbonate carpet protection mat that covers a polyester carpet. But plastics are now most indispensable in health care in general and in hospitals in particular. Life now begins (in maternity wards) and ends (in intensive care units) surrounded by plastic items made above all from different kinds of PVC: flexible tubes (for feeding patients, delivering oxygen, and monitoring blood pressure), catheters, intravenous containers, blood bags, sterile packaging, trays and basins, bedpans and bed rails, thermal blankets. (Smil 2022, Essential items in Modern World)





Why is glass see-through? What makes elastic stretchy? Why does a paper clip bend? These are the sorts of questions that Mark Miodownik is constantly asking himself. A globally renowned materials scientist, Miodownik has spent his life exploring objects as ordinary as an envelope and as unexpected as concrete cloth, uncovering the fascinating secrets that hold together our physical world. From the teacup to the jet engine, the silicon chip to the paper clip, the plastic in our appliances to the elastic in our underpants, our lives are overflowing with materials. Full of enthralling tales of the miracles of engineering that permeate our lives, Stuff Matters will make you see stuff in a whole new way. (https://www.amazon.com/Stuff-Matters-Exploring-Marvelous-Materials/dp/B00LOMPF5S)



History of Rubber

HISTORY TEXTILE

Charles Macintosh, a Scottish dye maker, used rubber to create fashionable rain coats. While trying to find a use for naptha, a solvent he derived from coal-tar, Macintosh discovered that a combination of naptha and rubber created a spreadable liquid.

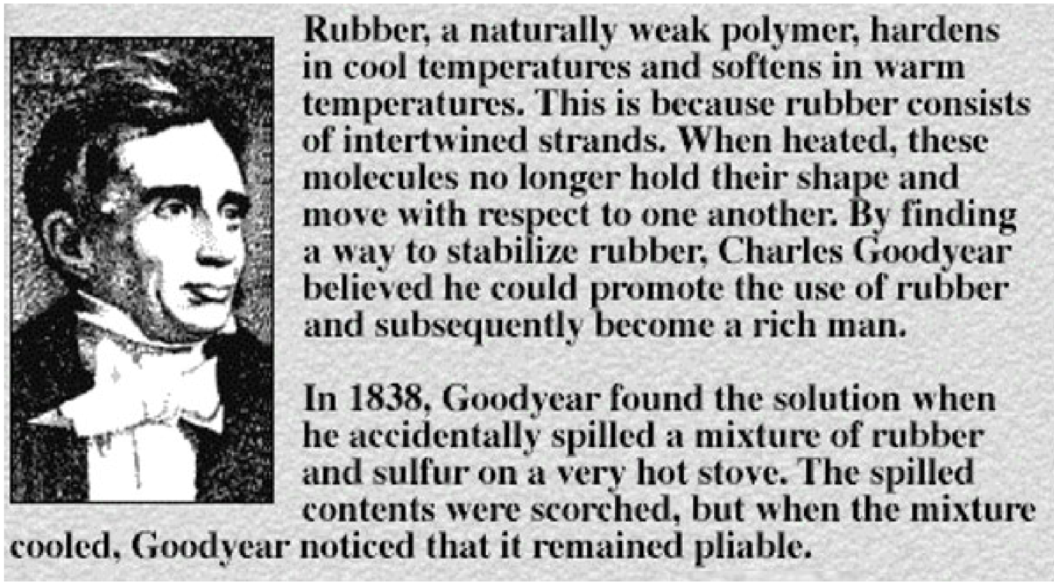
Macintosh brushed the solution on one side of two sheets of cotton canvas. He then pressed the two sheets together - rubber sides adjacent - creating a waterproof fabric. From this cotton-rubber sandwich, he created his waterproof rain gear.

In 1823, Charles Macintosh & Co. began selling "Macks," which soon became very popular. The coat's only problem was that the effectiveness of the waterproofing was inconsistant at very hot and very cold temperatures.

Charles Macintosh used rubber to create fashionable rain coats. He discovered that a combination of **naphtha**, a solvent he derived from coal-tar, and rubber created a spreadable liquid. The effectiveness of the waterproofing was **inconsistent** at very hot and very cold temperatures.

William J. Vinning and Richard S. Stein
Exploring the World of Plastics. V. 1.0
by National Plastics Center and Museum. 1999. Leominster, MA

History of Rubber

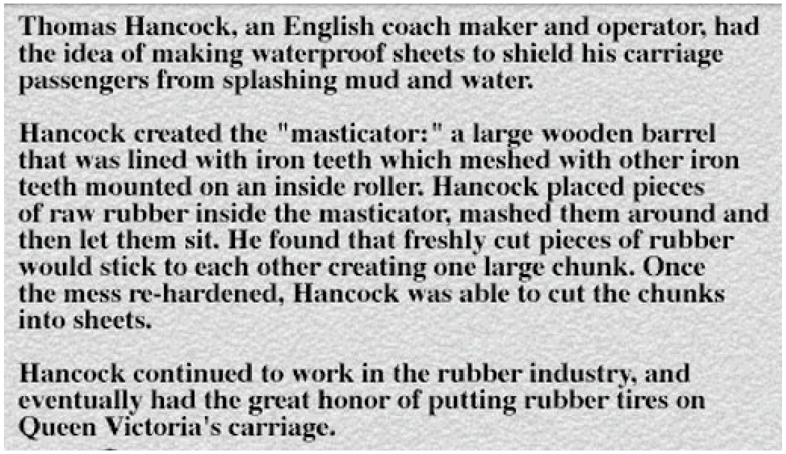


Rubber, a naturally weak polymer, hardens in cool temperatures and softens in warm temperatures. This is because rubber consists of intertwined strands. When heated, these molecules no longer hold their shape and move with respect to one another. By finding a way to stabilize rubber, Charles Goodyear believed he could promote the use of rubber and subsequently become a rich man.

In 1838, Goodyear found the solution when he accidentally spilled a mixture of rubber and sulfur on a very hot stove. The spilled contents were scorched, but when the mixture cooled, Goodyear noticed that it remained pliable.

Goodyear had discovered that heating this combination of rubber and sulfur to high temperatures (>130 °C) created a rubber of greater flexibility. The sulfur molecules bonded between rubber molecules in a "cross-linking" manner, providing a lattice structure. This structure allowed the rubber to maintain its texture and pliability at a wider range of temperatures.

In 1844, Goodyear patented his process in the United States (patent #3633). It wasn't until the British rubber expert Thomas Hancock requested a British patent for this method of adding sulfur to rubber, that this curing process became known as "Vulcanization." Hancock named the process after the Roman armorer and blacksmith to the gods, Vulcan (the god of fire).

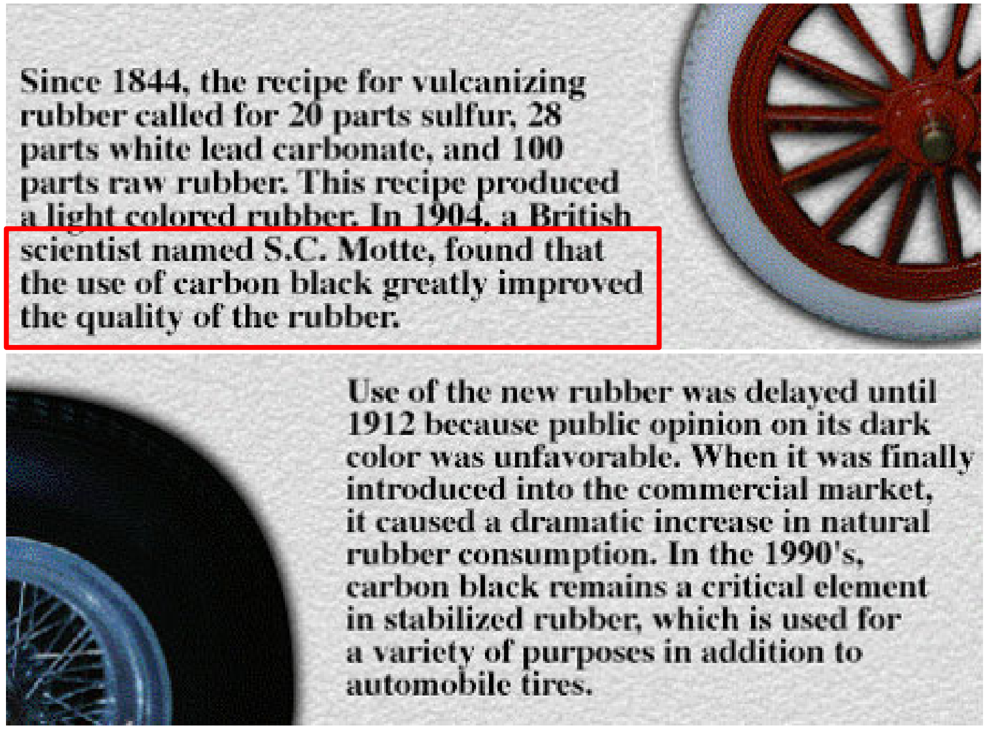


Thomas Hancock, an English coach maker and operator, had the idea of making waterproof sheets to shield his carriage passengers from splashing mud and water.

Hancock created the "masticator:" a large wooden barrel that was lined with iron teeth which meshed with other iron teeth mounted on an inside roller. Hancock placed pieces of raw rubber inside the masticator, mashed them around and then let them sit. He found that freshly cut pieces of rubber would stick to each other creating one large chunk. Once the mess re-hardened, Hancock was able to cut the chunks into sheets.

Hancock continued to work in the rubber industry, and eventually had the great honor of putting rubber tires on Queen Victoria's carriage.

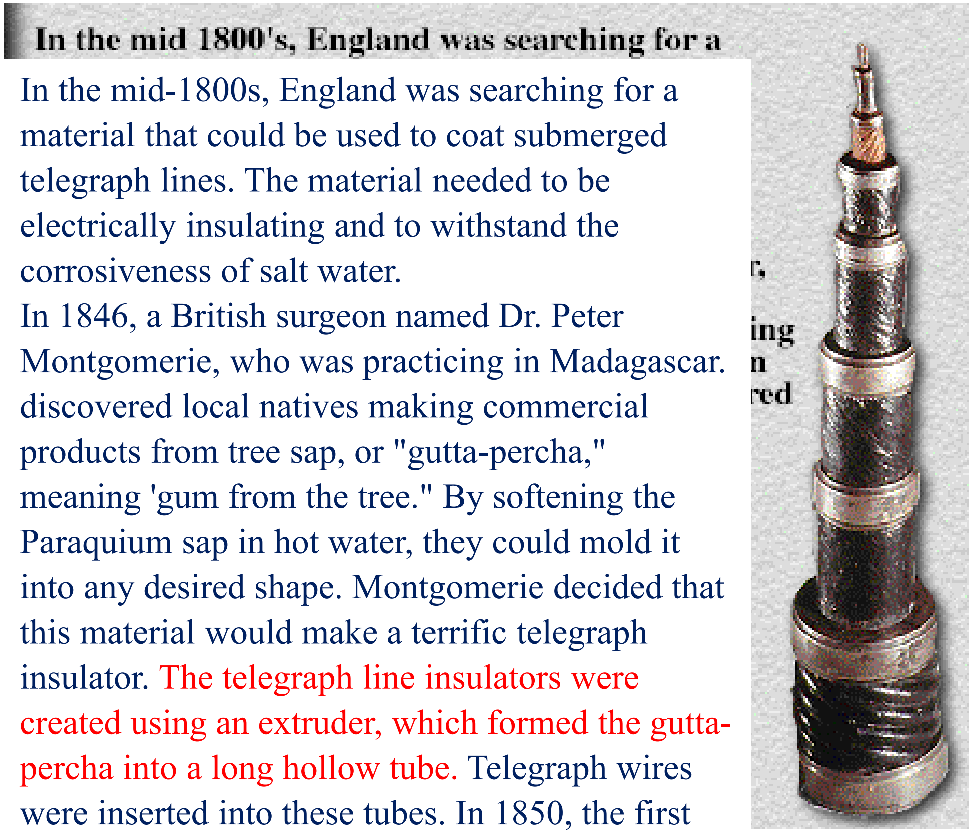
History of Rubber



Since 1844, the recipe for vulcanizing rubber called for 20 parts sulfur, 28 parts white lead carbonate, and 100 parts raw rubber. This recipe produced a light colored rubber. In 1904, a British scientist named S.C. Motte, found that the use of carbon black greatly improved the quality of the rubber.

Use of the new rubber was delayed until 1912 because public opinion on its dark color was unfavorable. When it was finally introduced into the commercial market, it caused a dramatic increase in natural rubber consumption. In the 1990's, carbon black remains a critical element in stabilized rubber, which is used for a variety of purposes in addition to automobile tires.

Since 1844, the recipe for vulcanizing rubber called for 20 parts sulfur, 28 parts white lead carbonate, and 100 parts raw rubber. In 1904, a British scientist named S.C. Motte, found that the use of carbon black greatly improved the quality of the rubber. In the 1990s, carbon black remails a critical element in stabilized rubber, which is used for a variety of purposes in addition to automobile tires.



In the mid 1800's, England was searching for a

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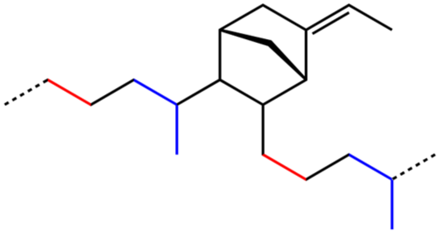
In the mid-1800s, England was searching for a material that could be used to coat submerged telegraph lines. The material needed to be electrically insulating and to withstand the corrosiveness of salt water.

In 1846, a British surgeon named Dr. Peter Montgomerie, who was practicing in Madagascar. discovered local natives making commercial products from tree sap, or "gutta-percha," meaning 'gum from the tree." By softening the Paraquium sap in hot water, they could mold it into any desired shape. Montgomerie decided that this material would make a terrific telegraph insulator. The telegraph line insulators were created using an extruder, which formed the gutta-percha into a long hollow tube. Telegraph wires were inserted into these tubes. In 1850, the first submarine telegraph line, enveloped in gutta-percha, was laid under the English Channel. It ran 25 miles. Gutta-percha was also eventually used for temporary fillings in dentistry.

Rubber-Carbon Black Interactions

EPDM: ethylene propylene diene monomer



Ethylene propylene diene monomer, or EPDM, is a type of synthetic rubber that is commonly used across many industries. Developed in the early 1960s, it is made from ethylene, propylene, and diene monomers and is a very versatile and durable type of rubber with many applications. While natural rubber may deteriorate with exposure to sunlight and ozone and become brittle over time, some synthetic rubbers like EPDM are designed to be able to withstand more extreme conditions and can last much longer.

EPDM has many applications due to its durability, flexibility, ability to withstand a wide range of temperatures, and many other properties. This includes flexible connectors, water gaskets, O-rings, grommets, and a variety of automotive parts, as well as many other outdoor applications. It is also the only rubber that is used for making full roofing systems.

https://lakeerierubber.com/what-is-epdm-rubber-properties-applications-uses/

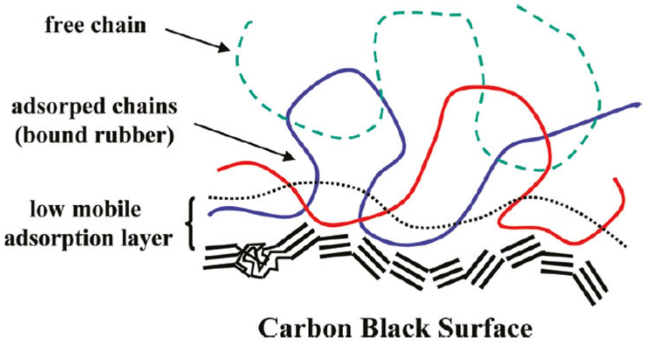


Figure 6. Simplified, graphic representation of EPDM chains at the carbon black surface. Parallel lines show graphite layers of carbon black nanocrystals. Low-mobile chain units adsorbed at the carbon black surface and mobile chain units outside of the rubber-filler interface are distinguished. The low-mobile chain fragments in the interface provide adsorption network junctions for the rubber matrix, explaining the origin of bound rubber. Free rubber chains in the bulk rubber (dashed line) have hardly any contacts with the surface of the carbon black and can be extracted from unvulcanized mixture by extraction with a good solvent.

Litvinov 2011, Rubber-filler interactions and network structure in relation to stress–strain behavior of vulcanized, carbon black filled EPDM

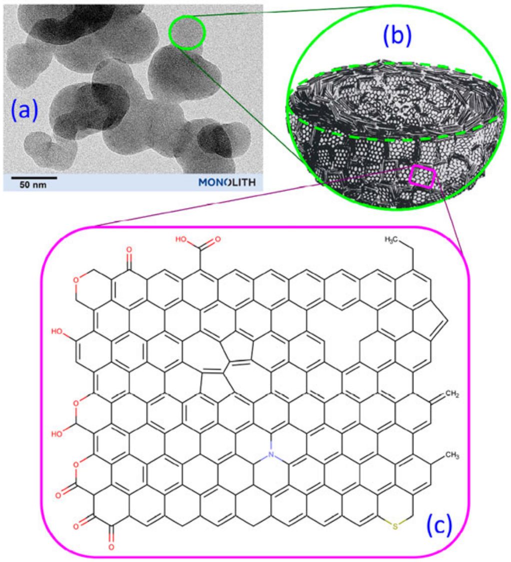
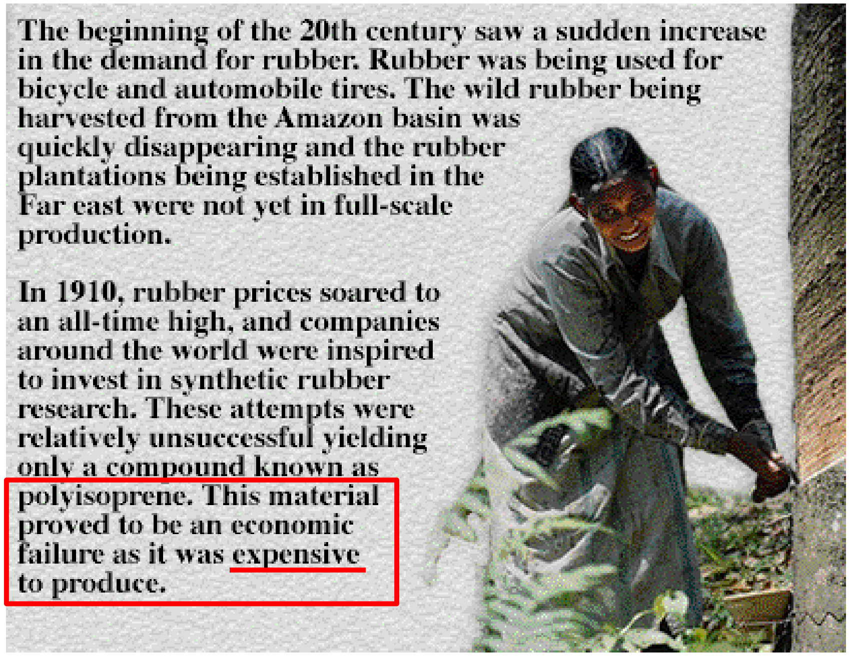


Figure 10. Different levels of structure and chemistry in carbon black: (a) TEM image of N660 carbon black at the indicated magnification; (b) schematic of a primary particle (cut in half to show the internal structure) that is composed of stacks of graphene sheets (adapted from Heidenreich et al. [48]); and (c) depiction of the different chemical groups on a graphene sheet in CB along with possible defects in the sheet. The various functional groups and defects are described in the discussion text.

Robertson 2021, Nature of carbon black reinforcement of rubber

History of Rubber



The beginning of the 20th century saw a sudden increase in the demand for rubber. Rubber was being used for bicycle and automobile tires. The wild rubber being harvested from the Amazon basin was quickly disappearing and the rubber plantations being established in the Far east were not yet in full-scale production.

In 1910, rubber prices soared to an all-time high, and companies around the world were inspired to invest in synthetic rubber research. These attempts were relatively unsuccessful yielding only a compound known as polyisoprene. This material proved to be an economic failure as it was expensive to produce.

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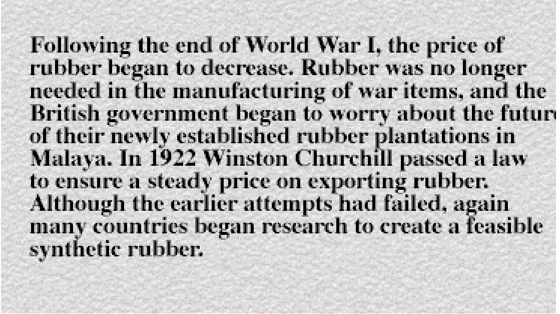
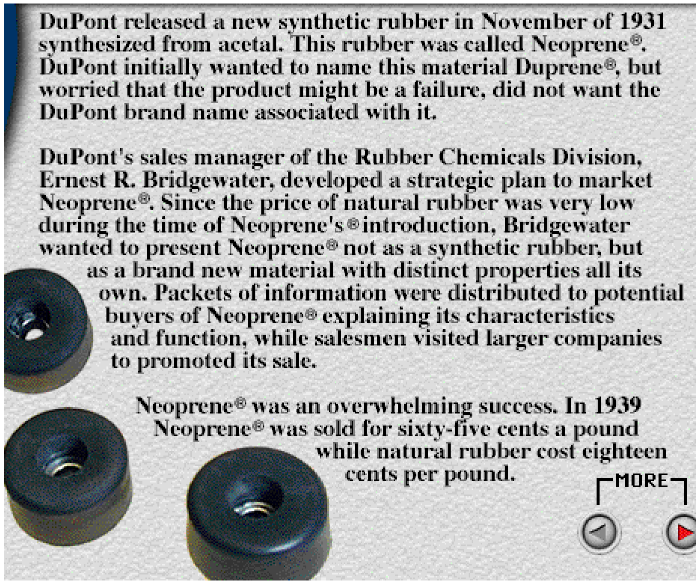


Following the end of World War I, the price of rubber began to decrease. Rubber was no longer needed in the manufacturing of war items, and the British government began to worry about the futur of their newly established rubber plantations in Malaya. In 1922 Winston Churchill passed a law to ensure a steady price on exporting rubber. Although the earlier attempts had failed, again many countries began research to create a feasible synthetic rubber.

Following the end of World War I, the price of rubber began to decrease. Many countries began research to create a feasible synthetic rubber.

DuPont introduced Neoprene, a new synthetic rubber, in November of 1931.

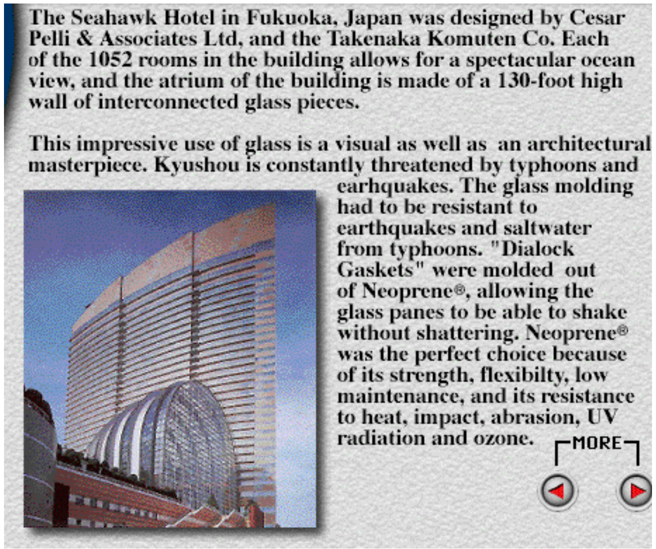


DuPont released a new synthetic rubber in November of 1931 synthesized from acetal. This rubber was called Neoprene®. DuPont initially wanted to name this material Duprene®, but worried that the product might be a failure, did not want the DuPont brand name associated with it.

DuPont's sales manager of the Rubber Chemicals Division, Ernest R. Bridgewater, developed a strategic plan to market Neoprene®. Since the price of natural rubber was very low during the time of Neoprene's® introduction, Bridgewater wanted to present Neoprene® not as a synthetic rubber, but as a brand new material with distinct properties all its own. Packets of information were distributed to potential buyers of Neoprene® explaining its characteristics and function, while salesmen visited larger companies to promoted its sale.

Neoprene® was an overwhelming success. In 1939 Neoprene® was sold for sixty-five cents a pound while natural rubber cost eighteen cents per pound.

History of Rubber



The Seahawk Hotel in Fukuoka, Japan was designed by Cesar Pelli & Associates Ltd, and the Takenaka Komuten Co. Each of the 1052 rooms in the building allows for a spectacular ocean view, and the atrium of the building is made of a 130-foot high wall of interconnected glass pieces.

This impressive use of glass is a visual as well as an architectural masterpiece. Kyushou is constantly threatened by typhoons and earhquakes. The glass molding had to be resistant to earthquakes and saltwater from typhoons. "Dialock Gaskets" were molded out of Neoprene®, allowing the glass panes to be able to shake without shattering. Neoprene® was the perfect choice because of its strength, flexibilty, low maintenance, and its resistance to heat, impact, abrasion, UV radiation and ozone.

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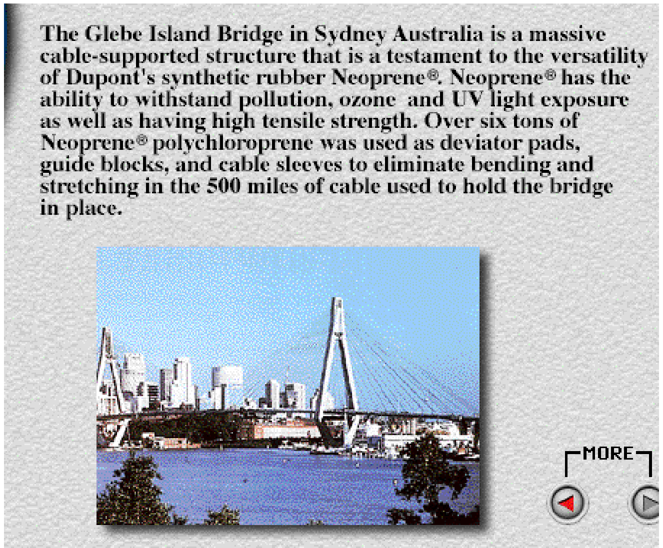
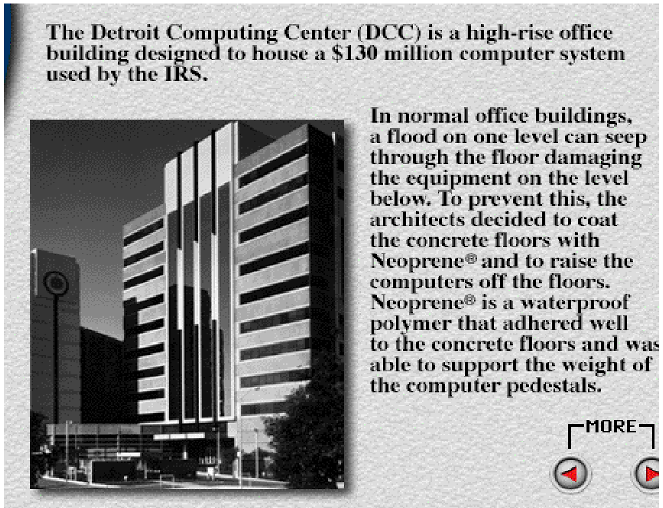


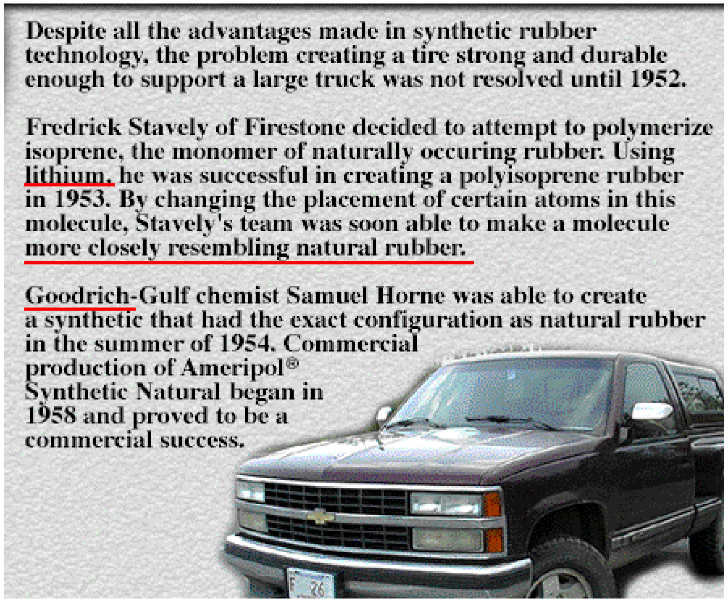
The Glebe Island Bridge in Sydney Australia is a massive cable-supported structure that is a testament to the versatility of Dupont's synthetic rubber Neoprene®. Neoprene® has the ability to withstand pollution, ozone and UV light exposure as well as having high tensile strength. Over six tons of Neoprene® polychloroprene was used as deviator pads, guide blocks, and cable sleeves to eliminate bending and stretching in the 500 miles of cable used to hold the bridge in place.



The Detroit Computing Center (DCC) is a high-rise office building designed to house a $130 million computer system used by the IRS.

In normal office buildings, a flood on one level can seep through the floor damaging the equipment on the level below. To prevent this, the architects decided to coat the concrete floors with Neoprene® and to raise the computers off the floors. Neoprene® is a waterproof polymer that adhered well to the concrete floors and was able to support the weight of the computer pedestals.

Synthetic rubber resembling natural rubber.
Polymerization of isoprene using lithium (1953)



Despite all the advantages made in synthetic rubber technology, the problem creating a tire strong and durable enough to support a large truck was not resolved until 1952.

Fredrick Stavely of Firestone decided to attempt to polymerize isoprene, the monomer of naturally occuring rubber. Using lithium, he was successful in creating a polyisoprene rubber in 1953. By changing the placement of certain atoms in this molecule, Stavely's team was soon able to make a molecule more closely resembling natural rubber.

Goodrich-Gulf chemist Samuel Horne was able to create a synthetic that had the exact configuration as natural rubber in the summer of 1954. Commercial production of Ameripol® Synthetic Natural began in 1958 and proved to be a commercial success.

Future Tires

1 **TREAD**
The patterns in the tyre's rubber tread offer
and traction on the road surface.

2 **BELTS**
Often made from steel cords, the belts sup
and strengthen the tyre's tread.

3 **BODY PLY**
Layers of synthetic materials such as polyes
nylon cord provide the structure of the ove

4 **BEADS**
Typically made from strands of wire, the tyr
beads secure it to the wheel of a car.

5 **INNER LINING**
Typically made from rubber, this maintains
inflation pressure.

6 **SIDEWALL**
Extra-thick rubber protects the internal cor
also features information about the tyre's si
type.

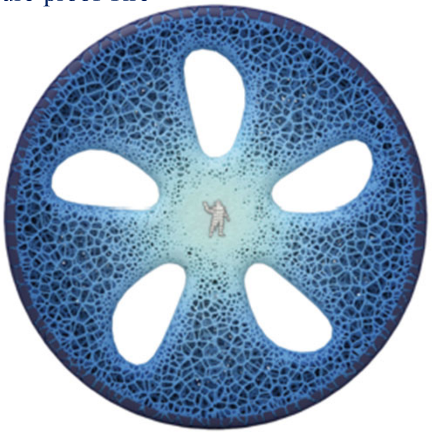
TYRES OF THE FUTURE

Michelin, one of the world's leading tyre manufacturers, is developing a next-generation airless and sustainably sourced tyre called VISION. Unveiled as a concept in 2017, VISION may one day completely change the way tyres are made.

In its proposed designs, Michelin is investigating the use of bio-sourced materials such as butadiene - which is derived from ethanol - airless suspension and alternative production methods such as 3D printing tread to create one of the most sustainable and long-lasting tyres ever made.

On its way to creating VISION, Michelin is set to launch its latest airless tyre, called the Unique Puncture-proof Tire System (UPTIS), to market in 2024. UPTIS is made from glass fibre-reinforced plastic that uses V-shaped 'spokes' to support the weight of the vehicle and replaces air-filled tyres. Michelin hopes to have a completely realised VISION tyre available by 2050. (How It Works, Issue 173)

Puncture-proof Tire



Airless Tire

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express polymer letters

Editorial corner – a personal view

Material circularity in rubber products

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The total rubber production worldwide in 2019 amounted to over 28.8 million tons, of which 13.6 million tons of natural rubber and 15.2 million tons of synthetic rubber (www.statista.com). Rubber products are used for various industrial applications, the most important in terms of volumes being tyres (accounting for about 70% of the total production), followed by other non-tyre automotive applications (such as seals, hoses, belts, anti-vibration mounts for about 13%) industrial applications (8%), footwear (7%) and other applications (2%). In most cases, for a good balance of mechanical strength and wear resistance, rubber products require a vulcanization process with sulfur (most common), peroxide or metal oxides, which ultimately leads to crosslinked polymers. This makes effective recycling and reuse of the scraps generated during the production of parts and rubber products at the end-of-life (EOL) a quite challenging issue (https://doi.org/10.1515/9783110644142). The main current EOL options for tyres are represented by i) stockpiling, ii) landfilling, iii) civil engineering applications (*i.e.* retention walls), iv) energy recovery (incineration), v) retreading, and vi) recycling or reuse.

Despite the fact that in Europe and the USA the recovery rate of scrap tyres is around 90%, around 4 billion EOL tyres are still disposed in landfills and stockpiles worldwide and this amount will increase up to 5 billion by 2030 (https://doi.org/10.1016/j.aiepr.2022.08.006). In addition to the associated loss of valuable resources, stockpiles of waste tyres may also cause environmental problems due to the potential fire hazard and the proliferation of insects caused by water stagnation. Rubber recycling consists of the recovery of materials, converting rubber waste into an economically useful form that is achieved through a shredding process. For tyres, the removal of steel, fibres, and other non-rubber components is also required. Crumb rubber can be used for the production of rubber-modified-asphalt, playground surfaces, artificial turfs, insulating panels, and in small quantities (less than 20 wt%) mixed with virgin rubber for manufacturing of new products.

Reuse is the preferable EOL option since the material is returned to its original application, thus creating a virtual circularity in the materials used. Nevertheless, the reuse of rubber is an obstacle due to the crosslinked nature of rubber products.

Therefore, intense research efforts have been conducted in the last 50 years to find efficient devulcanization methods (https://doi.org/10.1016/j.resconrec.2018.02.016). In an ideal situation, the breakage of the sulfur-carbon or the sulfur-sulfur bonds is induced to obtain a polymer that can be handled and vulcanized similarly to virgin rubber. The principal devulcanization strategies include chemical, ultrasonic, microwave, biological and thermo-mechanical methods (https://doi.org/10.3390/ma13051246). A successful devulcanization allows the use of higher amounts of recovered rubber mixed with virgin rubber (https://doi.org/10.1002/pen.25615) or in brittle thermoplastic matrices to improve their fracture toughness (https://doi.org/10.1007/s10924-020-01717-8). Remarkable progress in the next ten years is expected in both chemical and thermo-mechanical devulcanization methods.

Prof. Alessandro Pegoretti
Member of the International Advisory Board

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Pegoretti 2023, Material circularity in rubber products

Chronological Development of Commercial Polymers

Date	Material (Brand/Trade Name and/or Inventor)	Typical Application
<1800	Cotton, flax, wool and silk fibers; bitumen caulking materials; glass and hydraulic cements, leather,cellulose sheet (paper); balata, shellac. gutta-percha., Hevea braziliensis.	
1839	Vulcanization of rubber (Charles Goodyear)	Tires
1846	Nitration of cellulose (Schönbein)	Coatings
1851	Ebonite (hard rubber; Nelson Goodyear)	Electrical insulation
1860	Molding of shellac and gutta-percha	Electrical insulation
1868	Celluloid (CN: Hyatt)	Combs, mirror, frames
1889	Regenerated cellulosic fibers (Chardonnet)	Fabric
	Cellulose nitrate photographic films (Reichenbach)	Pictures
1890	Cuprammonia rayon fibers (Despeisses) Fabric	
1892	Viscose rayon fibers (Cross, Bevan, and Beadle)	Fabric
1893	Cellulose recognized as a polymer (E. Fischer)	
1907	Phenol-formaldehyde resins (PF: Bakelite; Baekeland)	Electrical
1908	Cellulose acetate photographic films (CA)	
1912	Regenerated cellulose sheet (cellophane)	Sheets, wrappings
1923	Cellulose nitrate automobile lacquers (Duco)	Coatings
1924	Cellulose acetate fibers	
1926	Alkyd polyesters (Kienle)	Electrical insulators
1927	Polyvinyl chloride (PVC; Semon; Koroseal)	Wall covering
1927	Cellulose acetate sheet and rods	Packaging Films
1929	Polysulfide synthetic elastomer (Thiokol; Patrick)	Solvent-resistant rubber
1929	Urea-formaldehyde resins (UF)	Electrical switches and parts
1931	Polymethyl methacrylate plastics (PMMA; Plexiglas; Rohm)	Display signs
1931	Polychloroprenc elastomer (Neoprene; Carothers)	Wire coatings
1933	Polyethylene (LDPE; Fawcett and Gibson)	Cable coating, packaging, squeeze bottles
1935	Ethylcellulose	Moldings
1936	Polyvinyl acetate (PVAc)	Adhesives
1936	Polyvinyl bulyral (PVB)	Safety glass
1937	Polystyrene (PS)	Kitchenware, toys. foam
1937	Styrene- butadiene (Buna-S; SBR), acrylonitrile (Buna-N), copolymer elastomers (NBR)	Tire treads
1938	Nylon 6,6 fibers (Carothers)	Fibers

Date	Material (Brand/Trade Name and/or Inventor)	Typical Application
1938	Fluorocarbon polymers (Teflon; Plunkett)	Gaskets, grease-repellent coatings
1939	Melamine-formaldehyde resins (MF)	Tableware
1938	Copolymers of vinyl chloride & vinylidene chloride (Pliovic)	Films. coatings
1939	Polyvinylidenc chloride (PVDC; Saran)	Films, coatings
1940	Isobutylene-isoprene elastomer (butyl rubber; Thomas & Sparks)	Adhesives, coatings, caulkings
1941	Polyester fibers (PET; Whinfield and Dickson)	Fabric
1942	Unsaturated polyesters (Foster and Ellis)	Boat hulls
1942	Acrylic fibers (Orlon; Acrylan)	Fabric
1943	Silicones (Rochow)	Gaskets, caulkings
1943	Polyurethanes (Baeyer)	Foams, clastomcrs
1944	Styrene-acrylonitrile-maleic anhydride, engineering plastic (Cadon)	Moldings, extrusions
1947	Epoxy resins (Schlack)	Coatings
1948	Copolymers of acrylonitrile butadiene and styrene (ABS)	Luggage, electrical devices
1955	Polyethylene (HOPE: Hogan, Banks, and Ziegler)	Bottles, film
1956	Polyoxymethylenes (acetals)	Moldings
1956	Polypropylene Oxide (Hay; Noryl)	Moldings
1957	Polypropylene (Hogan, Ranks, and Natta)	Moldings, carpet fiber
1957	Polycarbonate (Schnell and Fox)	Appliance parts
1959	cis-Polybutadiene and cis-polyisoprene elastomers	Rubber
1960	Ethylene-propylene copolymer elastomers (EPDM)	Sheets, gaskets
1962	Polyimide resins	High-temperature films & coatings
1965	Polybutene	Films, pipe
1965	Polyarylsulfones	High-temperature thermoplastics
1965	Poly-4-methyl-1-pentene (TPX)	Clear, low-density moldings
1965	Styrene-butadiene block copolymers (Kraton)	Shoe soles
1970	Polybutylene terephthalate (PBT)	Engineering plastic
1970	Ethylene-tetrafluoroethylene copolymers	Wire insulation
1971	Polyphenylene sulfide (Ryton; Hill and Edmonds)	Engineering plastic
1971	Hydrogels, hydroxyacrylates	Contact lenses
1972	Acrylonitrile barrier copolymers (BAREX)	Packaging
1974	Aromatic nylons (Aramids; Kwolek and Morgan)	Tire cord
1980	Polyether ether ketone (PEEK; Rose)	High-temperature service
1982	Polyether imide (Ultem)	High-temperature service

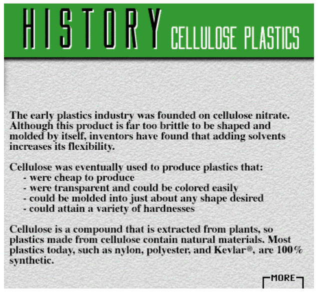
Giant Molecules. Essential Materials for Everyday Living and Problem Solving.
Raymond B. Seymour & Charles E. Carraher. John Wiley & Sons, Inc., 1990, pp. 43-44.

Chronological Development of Commercial Polymers

Date	Material
<1800	Cotton, flax, wool, and silk fibers; bitumen caulking materials; glass and hydraulic cements; leather and cellulose sheet (paper); natural rubber *(Hevea brasiliensis),* gutta percha, balata, and shellac
1823	**Rubber gum** for waterproofing of cotton (Macintosh)
1838	Isolation of cellulose from plant
1839	Vulcanization of rubber (Charles Goodyear)
1846	**Cellulose nitrate** (= Nitrocellulose: Cottom apron + nitric acid + sulfuric acid + heat) (Schönbein)
1846	Collodion (Ménard)
1851	Ebonite (vulcanized hard rubber, Nelson Goodyear)
1862	Parkesine (cellulose nitrate: cellulose + nitric acid + solvent) Precursor of celluloid
1868	Celluloid (camphor-plasticized cellulose nitrate, Hyatt) Artificial billiard ball
1889	Regenerated cellulosic fibers (Chardonnet)
1889	Cellulose nitrate photographic films (Reichenbach)
1890	Cuprammonia rayon fibers (Despeisses)
1891	Rayon: regenerated cellulose (viscose) fibers (Cross, Bevan, and Beadle)

Date	Material
1907	**Phenol-formaldehyde resins** (Bakelite; Baekeland)
1907	Cellulose acetate solutions (dope; Doerfinger)
1908	Cellulose acetate for photographic films and stockings
1912	Regenerated cellulose sheet (cellophane)
1913	Poly(vinyl acetate)
1914	Simultaneous interpenetrating network (SIPN)
1916	Rolls Royce begins to use phenol formaldehyde in its car interiors and boasts about it
1919	First cellulose acetate molding powder (Eichengrun)
1920	Urea-formaldehyde resins
1921	Beginning of rapid growth of phenolic moldings especially for electrical insulation, with addition of phenolic laminates in 1930
1922	Staudinger publishes his work that recognizes that plastics are composed of long chain molecules – leading to Nobel prize in 1953
1923	Cellulose nitrate automobile lacquers
1924	Cellulose acetate fibers
1924	Urea thiourea formaldehyde resins, as the first water white transparent thermosetting molding powder (Rossiter at British Cyanide)

Cellulose Plastics

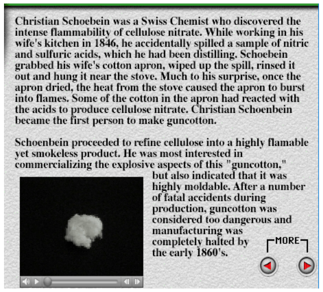


HISTORY CELLULOSE PLASTICS

The early plastics industry was founded on cellulose nitrate. Although this product is far too brittle to be shaped and molded by itself, inventors have found that adding solvents increases its flexibility.

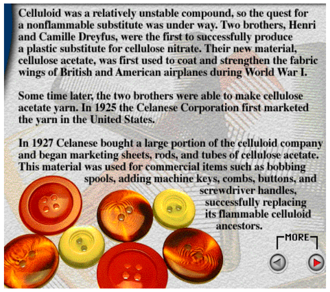
Cellulose was eventually used to produce plastics that:
- were cheap to produce
- were transparent and could be colored easily
- could be molded into just about any shape desired
- could attain a variety of hardnesses

Cellulose is a compound that is extracted from plants, so plastics made from cellulose contain natural materials. Most plastics today, such as nylon, polyester, and Kevlar®, are 100% synthetic.



Christian Schoebein was a Swiss Chemist who discovered the intense flammability of cellulose nitrate. While working in his wife's kitchen in 1846, he accidentally spilled a sample of nitric and sulfuric acids, which he had been distilling. Schoebein grabbed his wife's cotton apron, wiped up the spill, rinsed it out and hung it near the stove. Much to his surprise, once the apron dried, the heat from the stove caused the apron to burst into flames. Some of the cotton in the apron had reacted with the acids to produce cellulose nitrate. Christian Schoenbein became the first person to make guncotton.

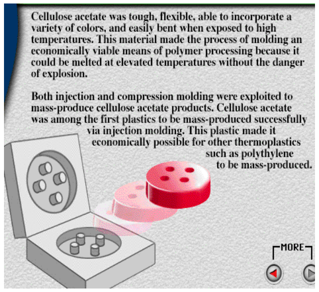
Schoenbein proceeded to refine cellulose into a highly flamable yet smokeless product. He was most interested in commercializing the explosive aspects of this "guncotton," but also indicated that it was highly moldable. After a number of fatal accidents during production, guncotton was considered too dangerous and manufacturing was completely halted by the early 1860's.



Celluloid was a relatively unstable compound, so the quest for a nonflammable substitute was under way. Two brothers, Henri and Camille Dreyfus, were the first to successfully produce a plastic substitute for cellulose nitrate. Their new material, cellulose acetate, was first used to coat and strengthen the fabric wings of British and American airplanes during World War I.

Some time later, the two brothers were able to make cellulose acetate yarn. In 1925 the Celanese Corporation first marketed the yarn in the United States.

In 1927 Celanese bought a large portion of the celluloid company and began marketing sheets, rods, and tubes of cellulose acetate. This material was used for commercial items such as bobbing spools, adding machine keys, combs, buttons, and screwdriver handles, successfully replacing its flammable celluloid ancestors.

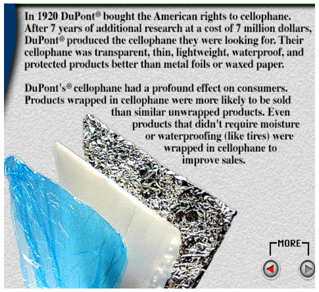


Cellulose acetate was tough, flexible, able to incorporate a variety of colors, and easily bent when exposed to high temperatures. This material made the process of molding an economically viable means of polymer processing because it could be melted at elevated temperatures without the danger of explosion.

Both injection and compression molding were exploited to mass-produce cellulose acetate products. Cellulose acetate was among the first plastics to be mass-produced successfully via injection molding. This plastic made it economically possible for other thermoplastics such as polythylene to be mass-produced.

Cellophane was created by Frenchman Jacque Edwin Brandenberger, whose intent was to make plasticized tablecloths that could resist spills and be cleaned with a damp cloth. Brandenberger, an expert in the chemistry of fabrics, decided that viscose (a solution of cellulose in $CS_2 + NaOH$) would provide the perfect coating for the fabric.

Brandenberger spent two years developing a machine that forced viscose out of tiny horizontal slots into a long thin sheet. He called these viscose sheets "cellophane" ("kellon" = wood or cellulose, and "phaino" = to be seen). Although his attempt to bind the viscose sheets to fabric failed, he eventually marketed his product as a waterproof wrapping.



In 1920 DuPont® bought the American rights to cellophane. After 7 years of additional research at a cost of 7 million dollars, DuPont® produced the cellophane they were looking for. Their cellophane was transparent, thin, lightweight, waterproof, and protected products better than metal foils or waxed paper.

DuPont's® cellophane had a profound effect on consumers. Products wrapped in cellophane were more likely to be sold than similar unwrapped products. Even products that didn't require moisture or waterproofing (like tires) were wrapped in cellophane to improve sales.

The early plastics industry was founded on **cellulose nitrate**. Although this product is far too brittle to be shaped and molded by itself, inventors have found that adding solvents increases its flexibility. Cellulose was eventually used to produce plastics that were cheap to produce, were transparent and could be colored easily, and could be molded into just about any shape desired,. Christian Schoebein was a Swiss Chemist who discovered the intense flammability of cellulose nitrate. While working in his wife's kitchen in 1846, he accidently spilled a sample of nitric and sulfuric acids, which he had been distilling. Schoebein grabbed his wife's cotton apron, wiped up the spill, rinsed it out and hung it near the stove. Once the apron dried, the heat from the stove caused the apron to burst into flames. The cotton in the apron had reacted with the acids to produce cellulose nitrate. After a number of fatal accidents during production, guncotton was considered too dangerous and manufacturing was completely halted by the early 1860s.

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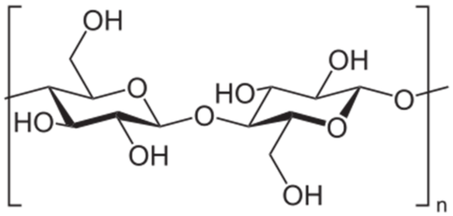
Cellulose and Cellulose Derivatives

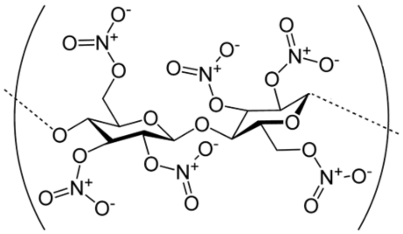
Cellulose (β(1→4) linked D-glucose polymer)



1838

1846

Nitrocellulose = Cellulose nitrate



Flash paper, guncotton

Collodion (a clear gelatinous solution of nitrocellulose in ether and alcohol).

Greek κολλώδης = kollodis (gluey)

- Medical use as a dressing
- Glass photographic plates.

1846

1868

Celluloid: Camphor-plasticized nitrocellulose
Photographic films by Kodak = Nitrate film
Unstable nitrate film is flammable.

1907 Cellulose acetate film (Safety film)

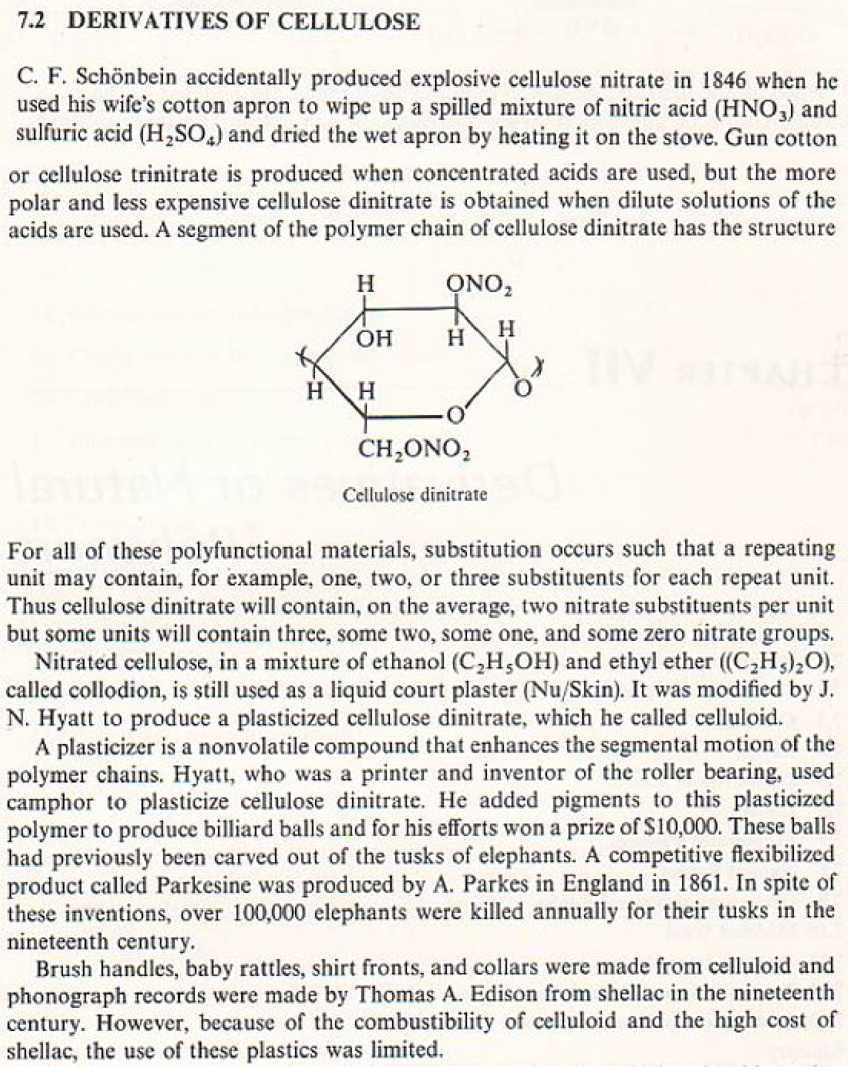
Artificial billiard balls by Hyatt
Collodion + ivory dust + cloth + shellac

1869

Hyatt Pocket Billiard Balls.
The Albany Billiard Ball Company
(1868–1986)

Celluloid™

The first thermoplastic. The first flexible photographic films for still and motion pictures.



7.2 DERIVATIVES OF CELLULOSE

C. F. Schönbein accidentally produced explosive cellulose nitrate in 1846 when he used his wife's cotton apron to wipe up a spilled mixture of nitric acid (HNO_3) and sulfuric acid (H_2SO_4) and dried the wet apron by heating it on the stove. Gun cotton or cellulose trinitrate is produced when concentrated acids are used, but the more polar and less expensive cellulose dinitrate is obtained when dilute solutions of the acids are used. A segment of the polymer chain of cellulose dinitrate has the structure

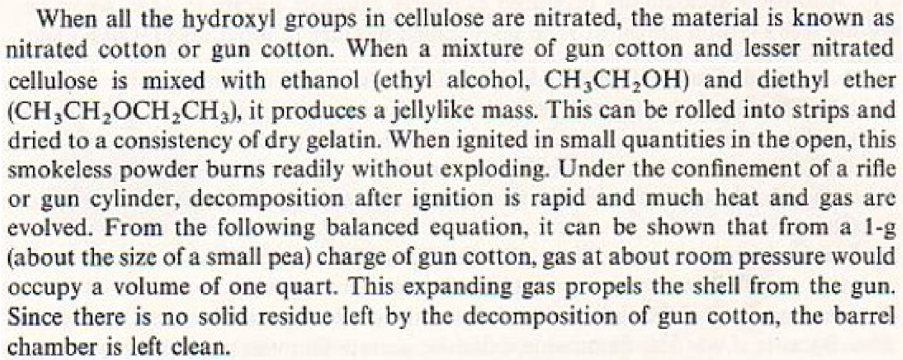
Cellulose dinitrate

For all of these polyfunctional materials, substitution occurs such that a repeating unit may contain, for example, one, two, or three substituents for each repeat unit. Thus cellulose dinitrate will contain, on the average, two nitrate substituents per unit but some units will contain three, some two, some one, and some zero nitrate groups.

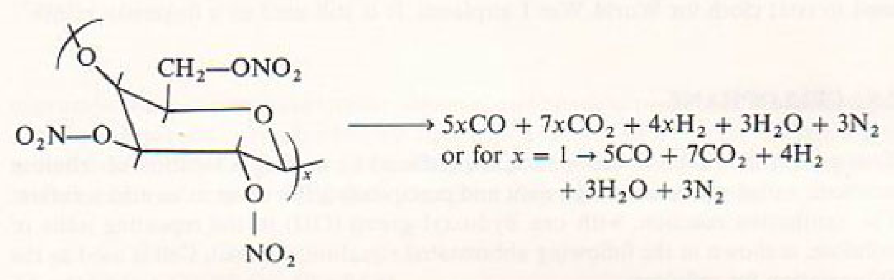
Nitrated cellulose, in a mixture of ethanol (C_2H_5OH) and ethyl ether ($(C_2H_5)_2O$), called collodion, is still used as a liquid court plaster (Nu/Skin). It was modified by J. N. Hyatt to produce a plasticized cellulose dinitrate, which he called celluloid.

A plasticizer is a nonvolatile compound that enhances the segmental motion of the polymer chains. Hyatt, who was a printer and inventor of the roller bearing, used camphor to plasticize cellulose dinitrate. He added pigments to this plasticized polymer to produce billiard balls and for his efforts won a prize of $10,000. These balls had previously been carved out of the tusks of elephants. A competitive flexibilized product called Parkesine was produced by A. Parkes in England in 1861. In spite of these inventions, over 100,000 elephants were killed annually for their tusks in the nineteenth century.

Brush handles, baby rattles, shirt fronts, and collars were made from celluloid and phonograph records were made by Thomas A. Edison from shellac in the nineteenth century. However, because of the combustibility of celluloid and the high cost of shellac, the use of these plastics was limited.

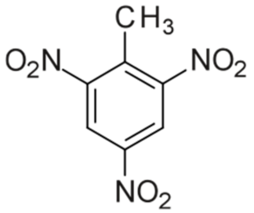


When all the hydroxyl groups in cellulose are nitrated, the material is known as nitrated cotton or gun cotton. When a mixture of gun cotton and lesser nitrated cellulose is mixed with ethanol (ethyl alcohol, CH_3CH_2OH) and diethyl ether ($CH_3CH_2OCH_2CH_3$), it produces a jellylike mass. This can be rolled into strips and dried to a consistency of dry gelatin. When ignited in small quantities in the open, this smokeless powder burns readily without exploding. Under the confinement of a rifle or gun cylinder, decomposition after ignition is rapid and much heat and gas are evolved. From the following balanced equation, it can be shown that from a 1-g (about the size of a small pea) charge of gun cotton, gas at about room pressure would occupy a volume of one quart. This expanding gas propels the shell from the gun. Since there is no solid residue left by the decomposition of gun cotton, the barrel chamber is left clean.

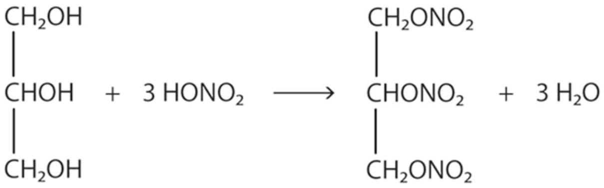


$$\longrightarrow 5xCO + 7xCO_2 + 4xH_2 + 3H_2O + 3N_2$$

$$\text{or for } x = 1 \rightarrow 5CO + 7CO_2 + 4H_2 + 3H_2O + 3N_2$$



Trinitrotoluene (TNT)

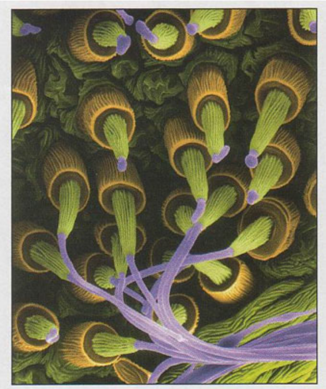


Glyceryl trinitrate (Nitroglycerin)

Giant Molecules. Essential Materials for Everyday Living and Problem Solving. Raymond B. Seymour & Charles E. Carraher. John Wiley & Sons, Inc., 1990, pp.117-119.

Cellulose Fibers and Cellophane

1846	Collodion, resembling silk (or artificial silk)
1855	Nitrocellulose fibers
1890	Cuprammonia rayon fibers (Cuprammonium solution to solubilize cellulose)
1891	Rayon: A textile fiber made from viscose.
1912	Cellophane: Regenerated cellulose sheet (Cellulose + diaphane ("transparent“))



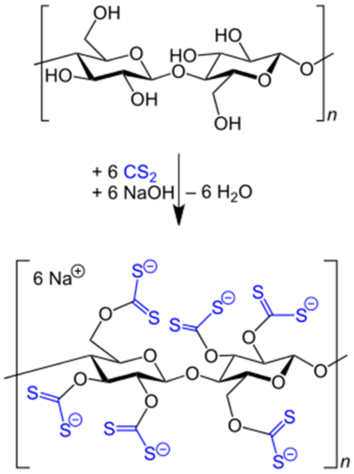
Natural strength. Proteins in strands of silk emerging from a spider's spinnerets combine resilience with extreme toughness.

Study on silkworm by Louis Marie Hilaire Bernigaut, Paris: Silkworm secretes a liquid from a narrow orifice that hardens upon exposure to air (silk).

Idea: Pass a liquid that has similar characteristics to silk before being secreted through a man-made apparatus to form fibers that can spun and feel like silk.

Regenerated Cellulose

Regenerated man-made fibers of cellulose from cuprammonium cellulose, viscose (cellulose xanthate), or cellulose acetate. Wash viscose in a bath of dilute sulfuric acid and sodium sulfate to reconvert into cellulose. (Plasticizer” Glycerin)

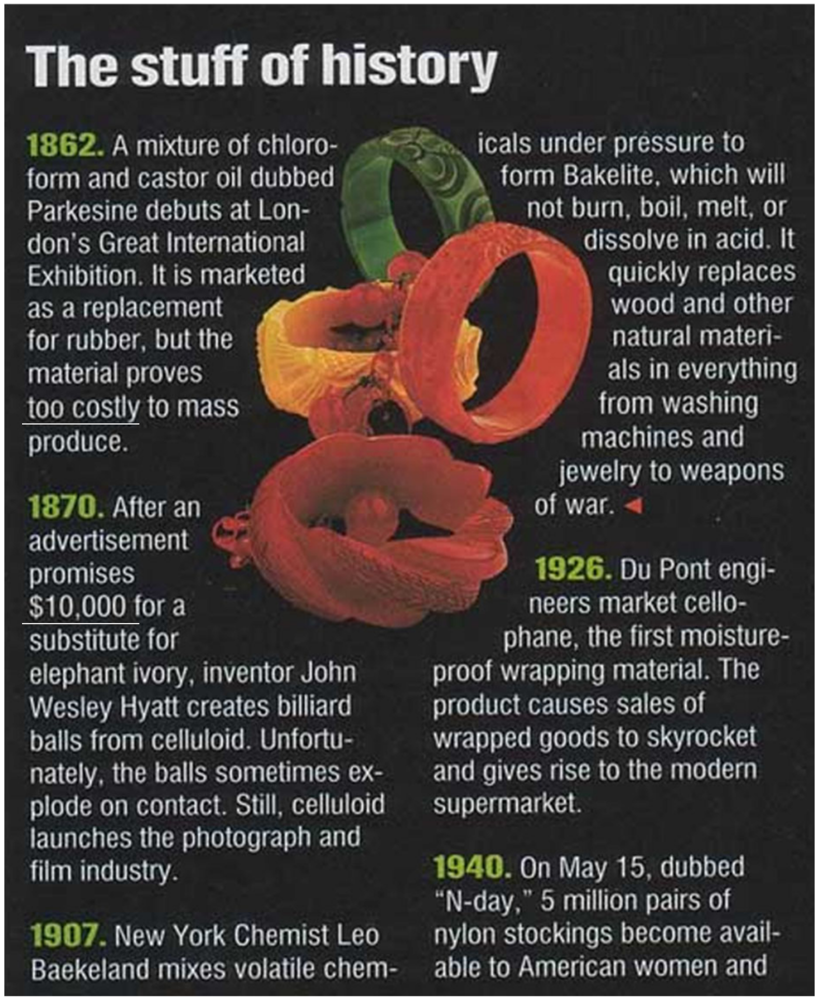


Viscose: Regenerated cellulose
(A viscous solution obtained by treating cellulose with sodium hydroxide and carbon disulfide).

The Beginning of Synthetic Polymers

1866: Materials to replace ivory billiard balls

>$300,000 in 2024
(only accounting for inflation)



The stuff of history

1862. A mixture of chloroform and castor oil dubbed Parkesine debuts at London's Great International Exhibition. It is marketed as a replacement for rubber, but the material proves too costly to mass produce.

1870. After an advertisement promises $10,000 for a substitute for elephant ivory, inventor John Wesley Hyatt creates billiard balls from celluloid. Unfortunately, the balls sometimes explode on contact. Still, celluloid launches the photograph and film industry.

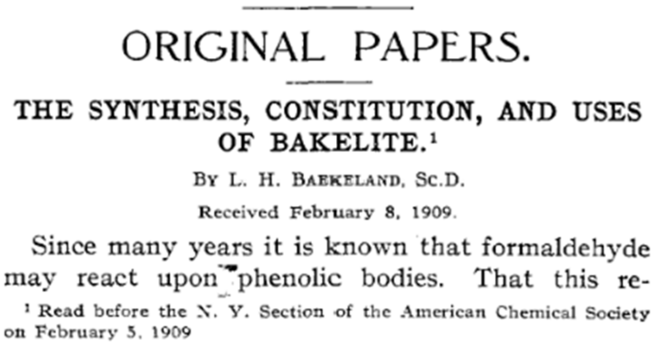
1907. New York Chemist Leo Baekeland mixes volatile chemicals under pressure to form Bakelite, which will not burn, boil, melt, or dissolve in acid. It quickly replaces wood and other natural materials in everything from washing machines and jewelry to weapons of war. ◀

1926. Du Pont engineers market cellophane, the first moisture-proof wrapping material. The product causes sales of wrapped goods to skyrocket and gives rise to the modern supermarket.

1940. On May 15, dubbed "N-day," 5 million pairs of nylon stockings become available to American women and

1907

courtesy Union Carbid



ORIGINAL PAPERS.

THE SYNTHESIS, CONSTITUTION, AND USES OF BAKELITE.[1]

By L. H. Baekeland, Sc.D.

Received February 8, 1909.

Since many years it is known that formaldehyde may react upon phenolic bodies. That this re-

[1] Read before the N. Y. Section of the American Chemical Society on February 5, 1909

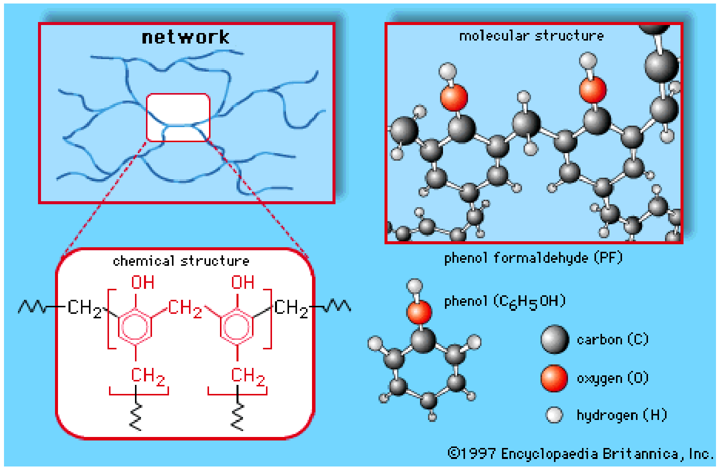
Baekeland 1909, The synthesis, constitution, and uses of Bakelite

The Beginning of Synthetic Polymers

1907. Bakelite: Phenol-formaldehyde resin

The first completely man-made substance.
The first thermoset plastic.

(Baekeland 1909, The synthesis, constitution, and uses of Bakelite. The Journal of Industrial and Engineering Chemistry. March 149-161)



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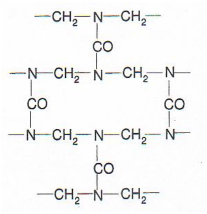
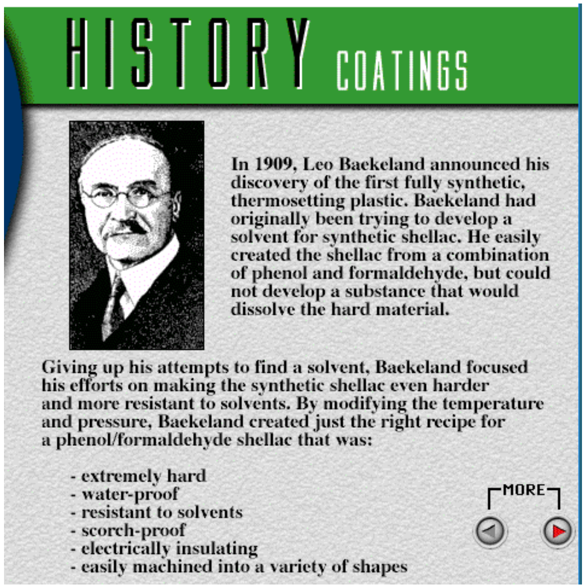


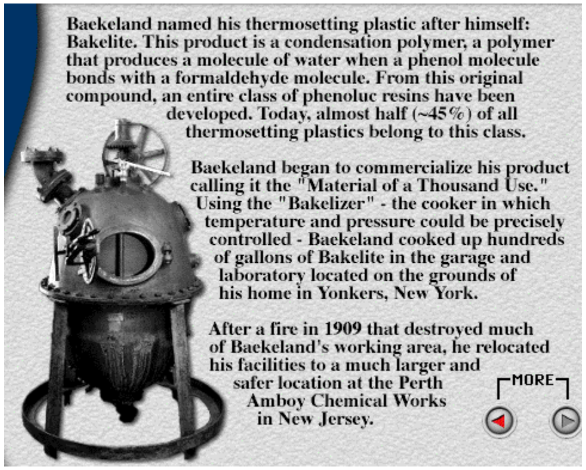
Urea-formaldehyde Resin (1929)



In 1909, Leo Baekeland announced his discovery of the first fully synthetic, thermosetting plastic. Baekeland had originally been trying to develop a solvent for synthetic shellac. He easily created the shellac from a combination of phenol and formaldehyde, but could not develop a substance that would dissolve the hard material.

Giving up his attempts to find a solvent, Baekeland focused his efforts on making the synthetic shellac even harder and more resistant to solvents. By modifying the temperature and pressure, Baekeland created just the right recipe for a phenol/formaldehyde shellac that was:

- extremely hard
- water-proof
- resistant to solvents
- scorch-proof
- electrically insulating
- easily machined into a variety of shapes



Baekeland named his thermosetting plastic after himself: Bakelite. This product is a condensation polymer, a polymer that produces a molecule of water when a phenol molecule bonds with a formaldehyde molecule. From this original compound, an entire class of phenoluc resins have been developed. Today, almost half (~45%) of all thermosetting plastics belong to this class.

Baekeland began to commercialize his product calling it the "Material of a Thousand Use." Using the "Bakelizer" - the cooker in which temperature and pressure could be precisely controlled - Baekeland cooked up hundreds of gallons of Bakelite in the garage and laboratory located on the grounds of his home in Yonkers, New York.

After a fire in 1909 that destroyed much of Baekeland's working area, he relocated his facilities to a much larger and safer location at the Perth Amboy Chemical Works in New Jersey.

1917

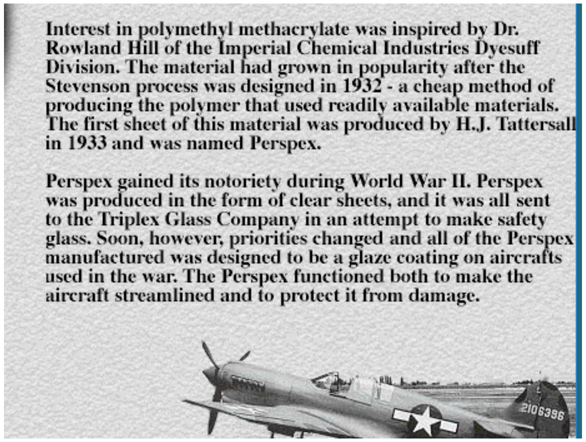
The material of a thousand uses

Born in 1863, Leo Baekeland (*above*) achieved success as both a chemist and entrepreneur. His first breakthrough came in the 1890s with "Volex," an improved photographic paper. He eventually sold the rights for one million dollars. Not content with this, Baekeland then set out to produce a cheap insulator for the electrical industry. Reacting phenol with formaldehyde, he developed not only an excellent insulator but also a moldable plastic, Bakelite. Bakelite became known as "the material of a thousand uses."

Plastic transforms household goods

Rolls Royce is going to launch another innovation to its new cars—this time it is not to be found in the engine but on the gear shift. The gear shift's handle will be made from Bakelite®, the world's first totally synthetic plastic. Ten years ago, Dr. Leo Baekeland discovered that under the right conditions the reaction of phenol with formaldehyde produced a hard, solid plastic. When heated, this plastic can be molded into any number of different objects. Once a mold has been created, the component can be mass-produced millions of times. Since its discovery, Bakelite has been used mainly as an insulator for electrical products, but now this versatile material looks as if it will revolutionize household goods.

▲ *Mass-produced plastic goods, such as this flask, are set to flood the market.*



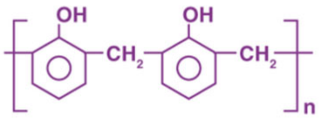
Interest in polymethyl methacrylate was inspired by Dr. Rowland Hill of the Imperial Chemical Industries Dyesuff Division. The material had grown in popularity after the Stevenson process was designed in 1932 - a cheap method of producing the polymer that used readily available materials. The first sheet of this material was produced by H.J. Tattersall in 1933 and was named Perspex.

Perspex gained its notoriety during World War II. Perspex was produced in the form of clear sheets, and it was all sent to the Triplex Glass Company in an attempt to make safety glass. Soon, however, priorities changed and all of the Perspex manufactured was designed to be a glaze coating on aircrafts used in the war. The Perspex functioned both to make the aircraft streamlined and to protect it from damage.

Bakelite Synthesis

Phenol > Formaldehyde

When the phenol is taken in excess and the reaction medium is made **acidic** (+HCl), the product of the condensation reaction obtained is acidic (Novolac).

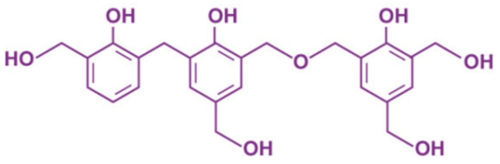


NOVOLAC

Novolac: Very strong

Formaldehyde > Phenol (1.5:1 mol conc)

When the quantity of formaldehyde taken is more than that of phenol in the reacting mixture, and the reaction occurs in a **basic** medium (+NaOH), the condensation product is known as Resol (**Stage A**).



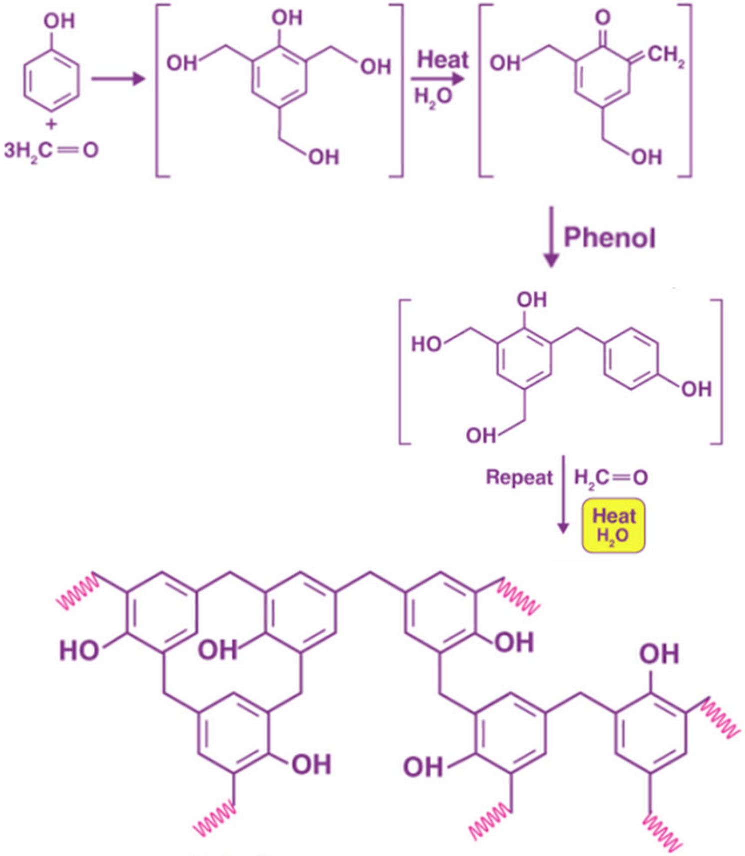
Resol

These intermediate condensation products are used as resins in different industries. Bakelite is obtained when **Novolac is allowed to undergo cross-linking in the presence of a cross-linking agent.** In general, phenol taken in excess acts as the cross-linking agent.

Hexamethylene tetraamine

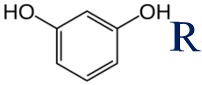
Hexamethylene tetraamine produces formaldehyde to crosslink Novolacs.

https://byjus.com/chemistry/bakelite-structure-properties-application/

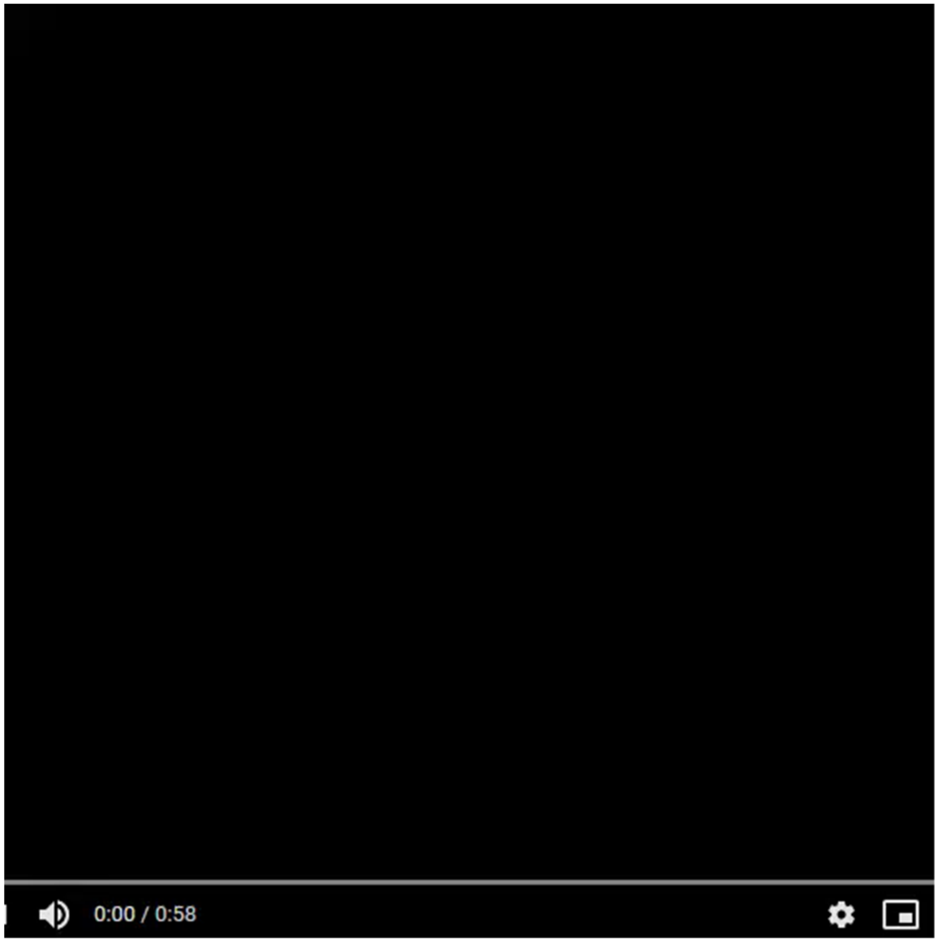


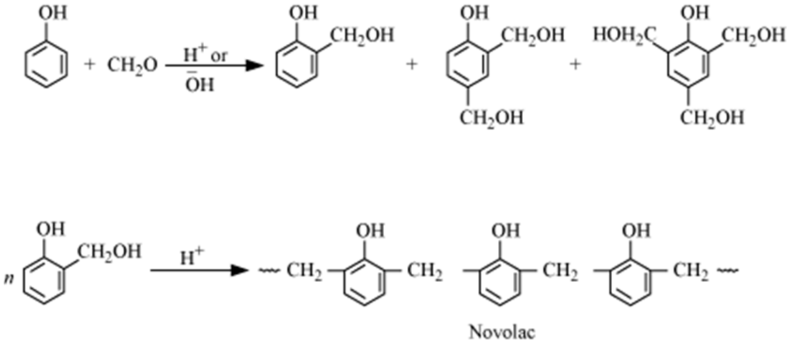
Bakelite (a cross-linked solid)

The Beginning of Synthetic Polymers



Resorcinol-formaldehyde resin.





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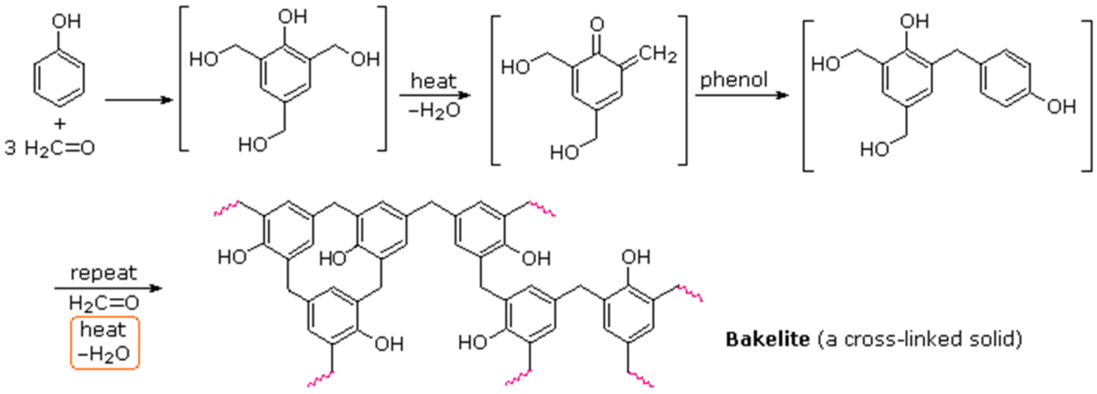
Phenol-Formaldehyde Resin



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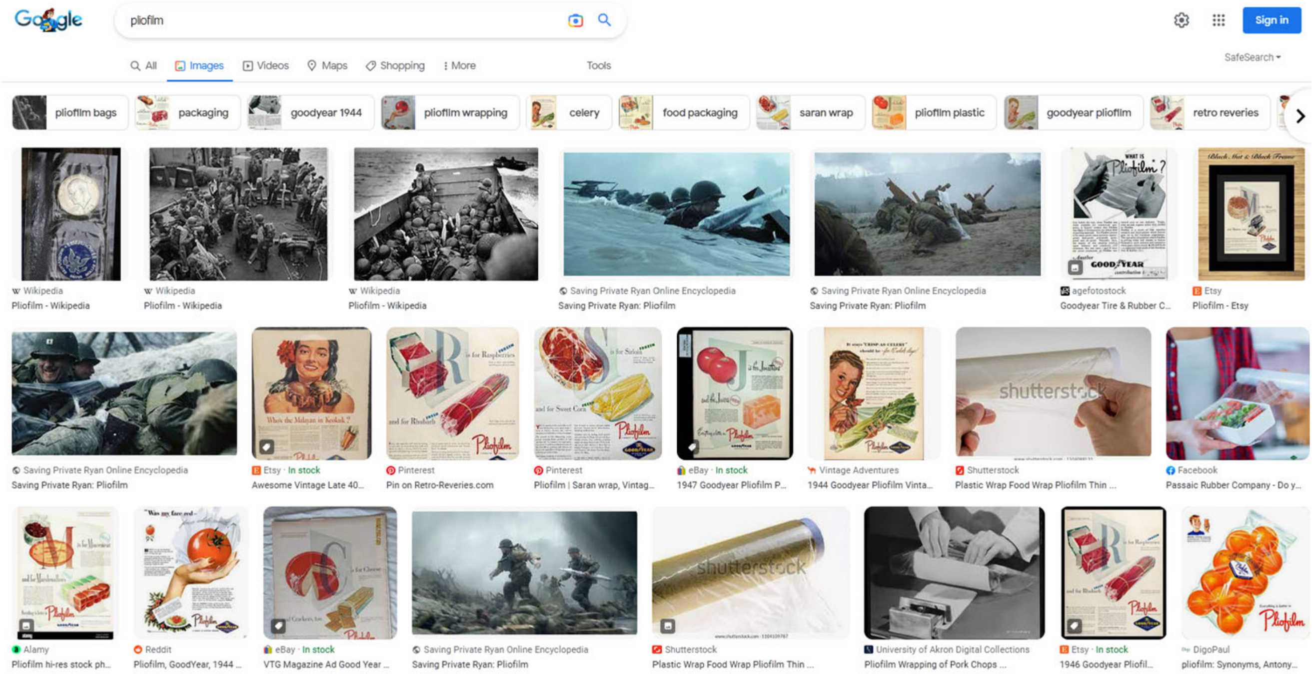
Chronological Development of Commercial Polymers

Date	Material
1926	Alkyd polyester (Kienle)
1927	Poly(vinyl chloride) (PVC) sheets wall covering
1927	Poly(vinyl butyral) (Matheson and Skirrow)
1927	Cellulose acetate sheet and rods
1927	Graft copolymers
1928	Nylon (Carothers at DuPont)
1929	Polysulfide synthetic elastomer (Thiokol; Patrick)
1929	Urea-formaldehyde resins
1930	Scotch tape, the first transparent sticky tape (3M)
1931	Poly(methyl methacrylate) (PMMA) plastics
1931	Polychloroprenc elastomer (Neoprene; Carothers)
1933	Poly(vinylidene chloride) (Saran) (Wiley, Dow)
1934	Epoxy resins (Schlack)
1935	Nylon-66 fibers (Carothers at DuPont)
1935	Ethylcellulose
1936	Poly(vinyl acetate)
1936	Poly(vinyl butyral) safety glass
1936	First production of aircraft canopies made from PMMA
1937	Polystyrene
1937	Styrene-butadiene (Buna·S) and styrene-acrylonitrile (Buna-N) copolymer elastomers
1938	Fluorocarbon resins (Teflon; Plunkett)
1939	Polycaprolactam (Nylon 6) (Schlack)
1939	Nitrile rubber
1939	Melamine-formaldehyde resins
1940	Polyacrylonitrile (PAN) (DuPont)
1940	Isobutylene-isoprene elastomers (butyl rubber; Sparks and Thomas)
1941	Low-density polyethylene (LDPE)
1941	Poly(ethylene terephthalate) (PET) (Whinfield and Dickson)
1942	Poly(methyl cyanoacrylate) (Superglue) (Coover at Eastman Kodak)
1942	Butyl rubber
1942	Unsaturated polyesters (Ellis and Rust)
1943	Silicones
1943	Polyurethanes (Baeyer)
1945	SBR
1946	Polysulfide rubber (Thiokol)
1947	Epoxy resins
1948	Copolymers of acrylonitrile, butadiene, and styrene (ABS)
1949	Cyanoacrylate (Goodrich)

Pliofilm



Pliofilm was a plastic wrap made by the Goodyear Tire and Rubber Company at plants in the US state of Ohio. Invented in the early 1930s, it was made by dissolving rubber in a benzene solvent and treating it with gaseous hydrochloric acid. Pliofilm was more stable in a range of humidities than earlier cellulose-based wraps and became popular as a food wrap. Its manufacture exposed workers to carcinogenic benzene and, when an additive was used to improve durability, caused dermatitis. Pliofilm is a transparent film made of rubber hydrochloride. It is impermeable to water and water vapour and non-flammable.

Pliofilm was manufactured by dissolving natural rubber in the solvent benzene. The solution was kept in a tank at around 10 °C (50 °F) and treated with gaseous hydrochloric acid. The material was then neutralised with an alkali.[3] The product was cast as a sheet on an endless belt which passed through a dryer that drove off the solvent. The finished product was around 30% chlorine.[4] It could be made thinner by stretching whilst being heated and thicknesses of 0.00075–0.025 inches (0.019–0.635 mm) were sold. Thicker sheets could be produced by laminating the product, combining several sheets with the use of rubber cement.

https://en.wikipedia.org/wiki/Pliofilm

Chronological Development of Commercial Polymers

Date	Material
1950	Polyester fibers (Whinfield and Dickson)
1950	Polyacrylonitrile fibers
1952	Block copolymers
1953	High impact polystyrene (HIPS)
1953	Polycarbonate (Schnell, Fox))
1955	Nylon 11
1956	Poly(ethylene-co-vinyl acetate) (DuPont)
1956	Poly(phenylene ether); Poly(phenylene oxide) (GE)
1956	Polyoxymethylene (acetals)
1957	High-density (linear) polyethylene (HDPE)
1957	Polypropylene
1958	Poly(dihydroxymethylcyclohexyl terephthalate) (Kodel, Eastman Kodak)
1959	cis-Polybutadiene and cis-polyisoprene elastomers
1960	Ethylene-propylene copolymer elastomers
1962	Polyimide resins
1964	Ionomers
1965	Poly(phenylene oxide)

Date	Material
1965	Polysulfones
1965	Styrene-butadiene block copolymers
1965	Polyester for injection moulding
1965	Nylon 12
1966	Liquid crystals
1970	Poly(butylene terephthalate); Thermoplastic elastomers
1971	Poly(phenylene sulfide)
1974	Polyacetylene
1974	Aramids-Aromatic polyamides
1974	Polyarylether-sulfones
1976	Aromatic Polyesters (Polyarylates)
1977	Polyaryletheretherketone (PEEK)
1982	Polyarylether-ketones
1982	Polyetherimides (GE)
1983	Polybenzimidazoles
1984	Thermotropic liquid crystal polyesters
1990	Polyethylene Ultra-High Molecular Weight
1990	Nylon 4,6

LDPE: Ethylene at 80-300 °C under 1,000-2,000 atm with peroxide initiator. Density = 0.91-0.94 g/cm^3. Low crystallinity
HDPE: Ethylene in a hydrocarbon solvent at 70 °C under 7 atm with Zeiglar Natta catalyst. Density = 0.95-0.97 g/cm^3. High crystallinity

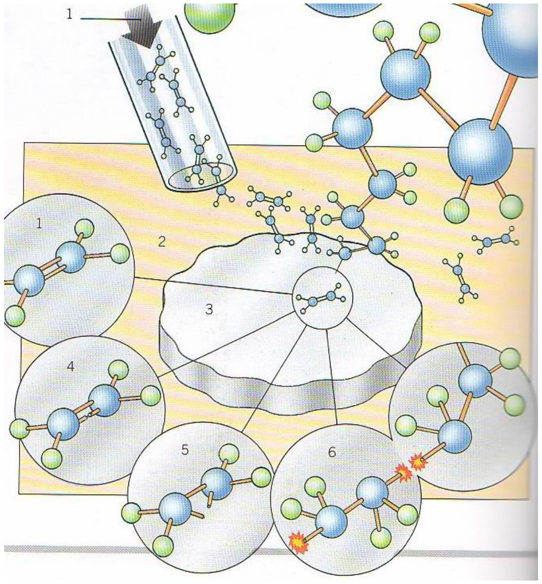
Polymer Synthesis: Chain Growth Polymerizations

2.1 Methods for Synthesis of Polymers

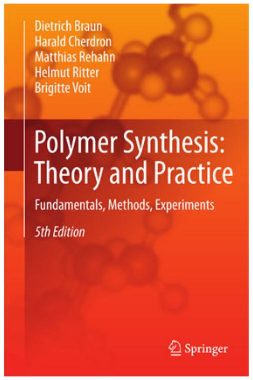
The chemical process of chain formation may be subdivided roughly into two classes.

2.1.1 Chain Growth Polymerizations

Chain growth polymerizations (also called addition polymerizations) are characterized by the occurrence of activated species (initiators)/active centers. They add one monomer molecule after the other in a way that at the terminus of each new species formed by a monomer addition step an activated center is created which again is able to add the next monomer molecule. Such species are formed from compounds which create radicals via homolytic bond scission, from metal complexes, or from ionic (or at least highly polarized) molecules in the initiating steps (2.1) and (2.2). From there the chain growth can start as a cascade reaction (propagation; 2.3) upon manifold repetition of the monomer addition and reestablishment of the active center at the end of the respective new product:



Vinyl Polymerization


Dietrich Braun
Harald Cherdron
Matthias Rehahn
Helmut Ritter
Brigitte Voit

Polymer Synthesis: Theory and Practice

Fundamentals, Methods, Experiments

5th Edition

Springer

$$I \longrightarrow I^* \tag{2.1}$$

$$I^* + M \longrightarrow I{-}M^* \tag{2.2}$$

$$I{-}M^* + n\,M \longrightarrow I{+}M{+}_{n}M^* \quad (=P^*) \tag{2.3}$$

BF Goodrich, 1954
(Prelinger Archives San Francisco,
www.prelinger.com)

Emulsion Polymerization

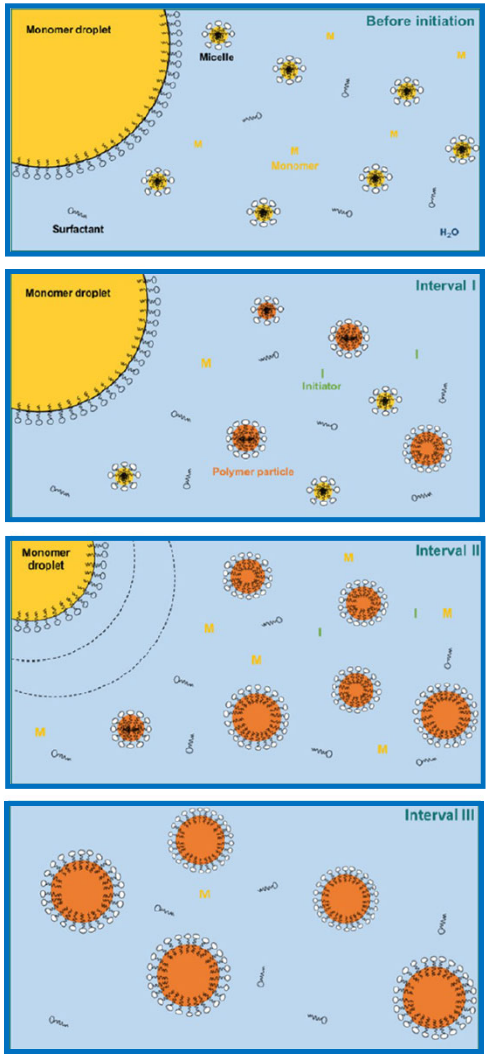


Figure 1. Schematic representation of an emulsion polymerization process.

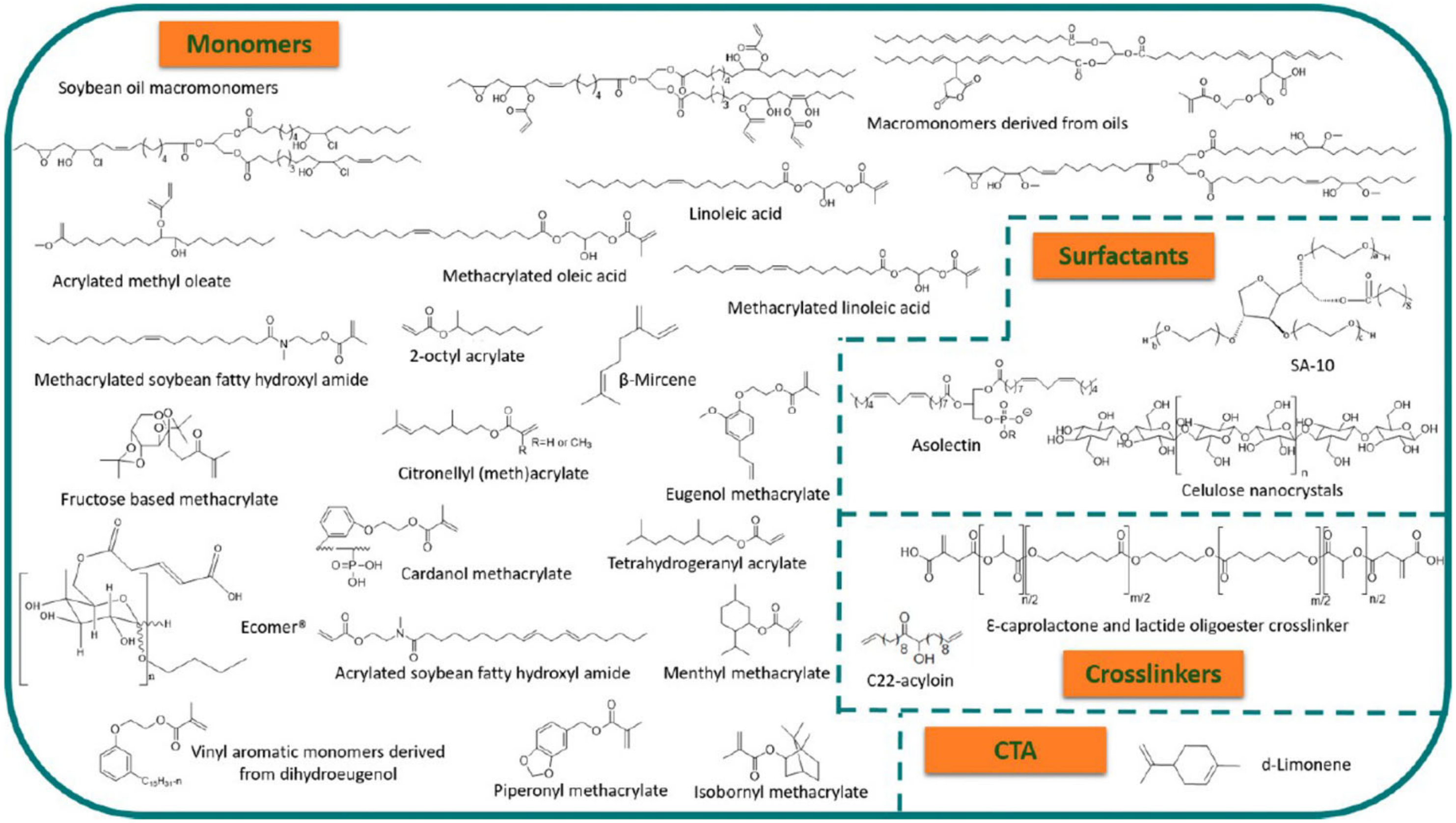


Figure 5. Biobased components for emulsion polymerization formulation: monomers, surfactants, cross-linkers, and chain transfer agent (CTA).

Aguirre 2023, Polymer colloids- Current challenges, emerging applications, and new developments

Radical Polymerization with Biocatalysts

Atom transfer radical polymerization (ATRP)
Reversible addition−fragmentation chain transfer (RAFT)
  RAFT polymerization with glucose oxidase (GOx) for in situ deoxygenation in 2014.
  RAFT polymerization with horseradish peroxidase (HRP) to initiate polymerization in 2015.
Reversible deactivation radical polymerization (RDRP)
Bio-RDRP with enzymes and bacteria

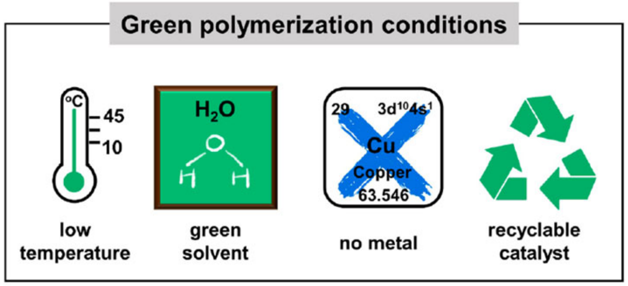


Figure 1. Bio-RDRP features green polymerization conditions.

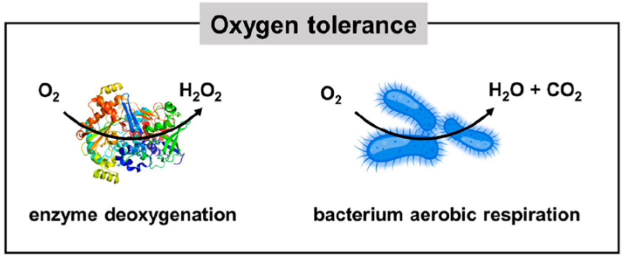


Figure 2. Enzymes and bacteria can be used to deoxygenate RDRP.

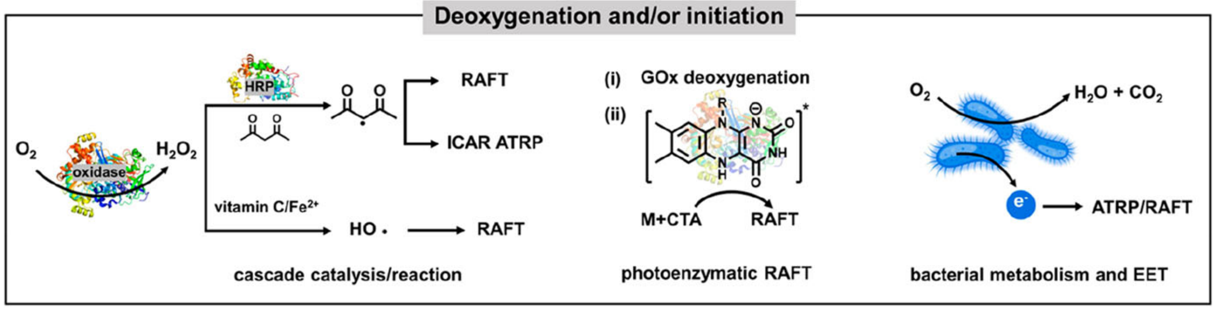


Figure 3. Coupling biodeoxygenation and initiation in a polymerization makes bio-RDRP oxygen tolerant.

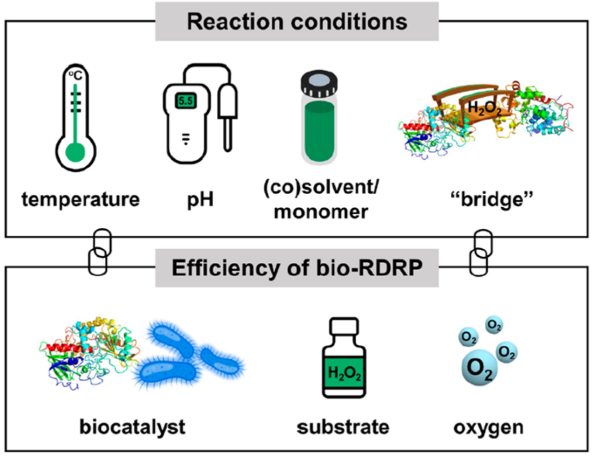


Figure 7. Key points that need to be considered when conducting bio-RDRP.

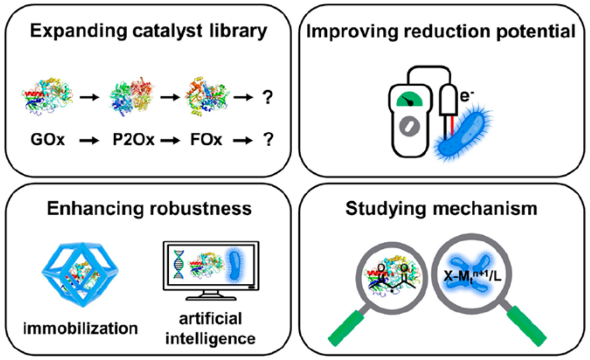


Figure 8. Challenges of bio-RDRP and future directions.

Li 2023, Controlling radical polymerization with biocatalysts

Sequence-Defined Polymers

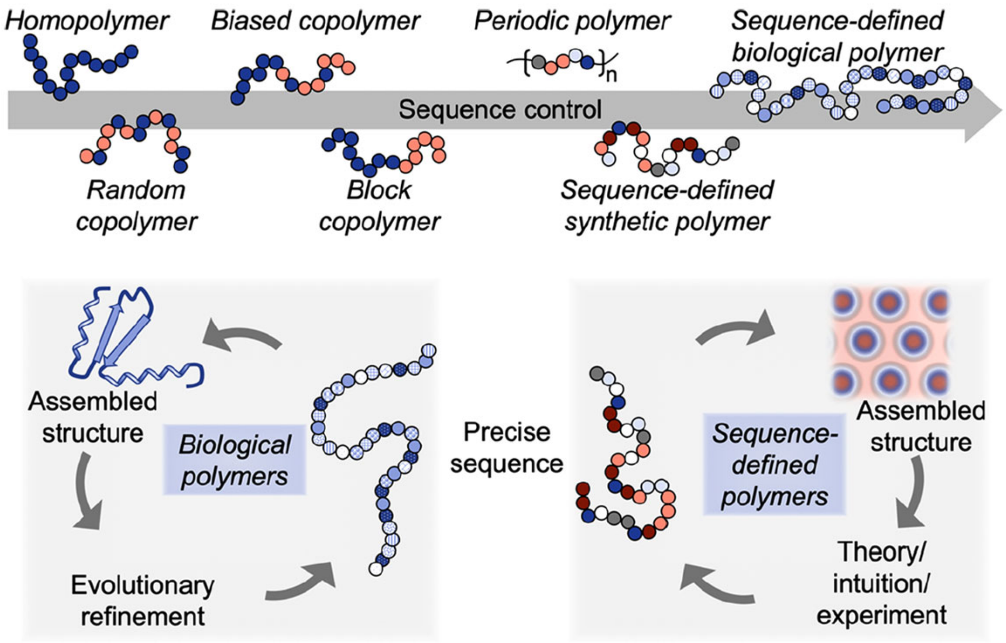


Figure 1. Sequence-defined polymers bridge biological and traditional synthetic polymers. Biological materials, such as proteins, and traditional synthetic polymers make up two well established classes of polymers. While traditional synthetic polymers feature broad molecular weight distributions with statistically controlled sequences, many biological polymers are characterized by precise monomer sequences. Synthetic sequence-defined polymers contain perfectly controlled monomer sequences, where the difference from chain-to-chain is comparable to that of protein or small molecule purity, but are capable of incorporating a broader range of functionalities. Depicted cycles represent that while many sequence-defined biological polymers evolve over many generations (in nature or in laboratories) to access precise architectures capable of achieving specific functions, sequences guiding synthetic polymer assembly and function are engineered through intuition, experiment, and, ultimately, theory. Advances in computational de novo protein design vastly accelerate this process, and development of similar tools for designing non-natural polymers will be transformative.

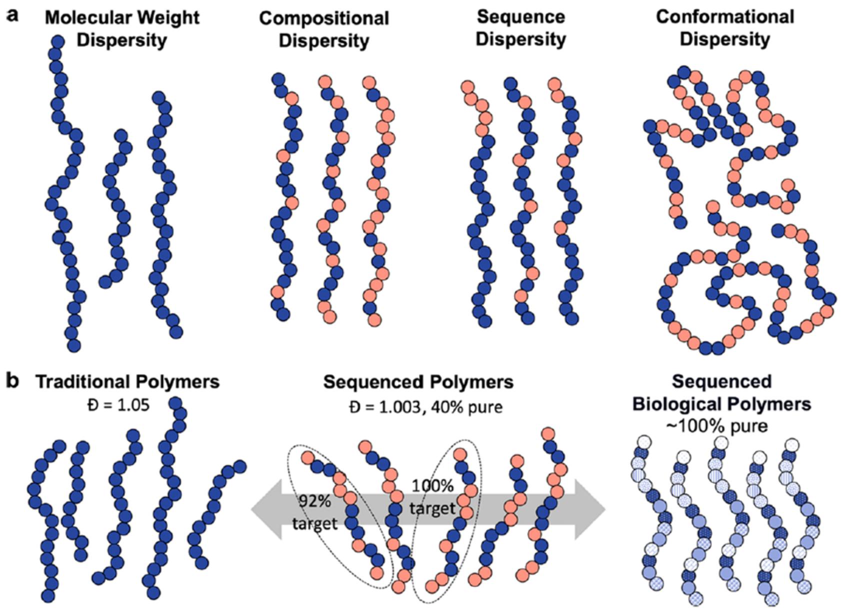


Figure 2. Describing precision in linear polymer chains. (a) Measures of dispersity often describe only the molecular weight distribution of a sample of polymer chains. In a population of chains with multiple monomers, the sample may be characterized by an overall fraction of monomer A and monomer B, but this composition may vary from chain to chain. Similarly, in a population of chains with an identical fraction of each monomer, the sequence of those monomers may not be constant. A population of chains with an identical sequence will still adopt a range of chain conformations whether in solution or in the bulk. (b) The presence of multiple forms of dispersity in sequence-defined polymers demands that we quantify dispersity in multiple ways and weigh the impact of dispersity on material performance. Sequenced polymers in which many chains have minor deviations (e.g., 1−2 deletions) still have Đ far closer to unity than is attainable for traditional polymers. In terms of a yield of perfect sequences, however, even one deletion renders that chain an impurity, leading to low yields of the target sequence.

Davidson 2021, Where biology and traditional polymers meet- the potential of associating sequence-defined polymers for materials science

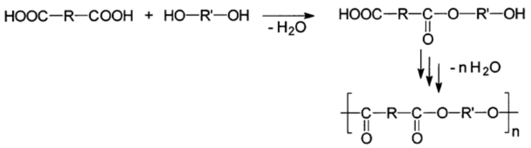
Polymer Synthesis: Condensation (Step-reaction) Polymerization

2.1 Methods for Synthesis of Polymers

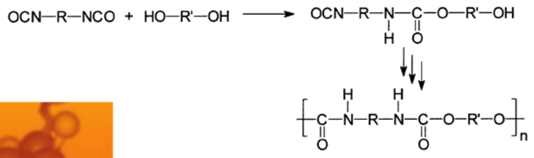
The chemical process of chain formation may be subdivided roughly into two classes.

2.1.2 Step Growth Polymerizations

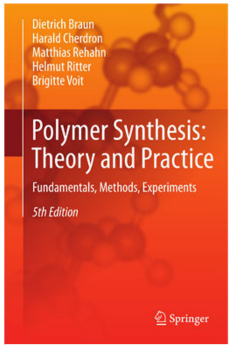
In step growth reactions, on the other hand, neither are specific activated centers present to force the connection of the monomers, nor does the process occur as a cascade reaction. Instead, the monomers are tied together in discreet, independent steps via conventional organic reactions such as ester-, ether-, amide-, or urethane formation. Depending on whether small molecules are set free in the connection step, one distinguishes between polycondensations Eq. 2.9 and polyadditions Eq. 2.10.



$$\mathrm{HOOC{-}R{-}COOH} + \mathrm{HO{-}R'{-}OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{HOOC{-}R{-}}\underset{\underset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}O{-}R'{-}OH} \;\; \downarrow\downarrow\downarrow\, -n\mathrm{H_2O} \;\; \left[\underset{\underset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}R{-}}\underset{\underset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}O{-}R'{-}O}\right]_n \qquad (2.9)$$



$$\mathrm{OCN{-}R{-}NCO} + \mathrm{HO{-}R'{-}OH} \longrightarrow \mathrm{OCN{-}R{-}}\underset{\displaystyle H}{\mathrm{N}}\mathrm{{-}}\underset{\underset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}O{-}R'{-}OH} \;\; \downarrow\downarrow\downarrow \;\; \left[\underset{\underset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}}\overset{\displaystyle H}{\mathrm{N}}\mathrm{{-}R{-}}\overset{\displaystyle H}{\mathrm{N}}\mathrm{{-}}\underset{\underset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}O{-}R'{-}O}\right]_n \qquad (2.10)$$



Dietrich Braun
Harald Cherdron
Matthias Rehahn
Helmut Ritter
Brigitte Voit

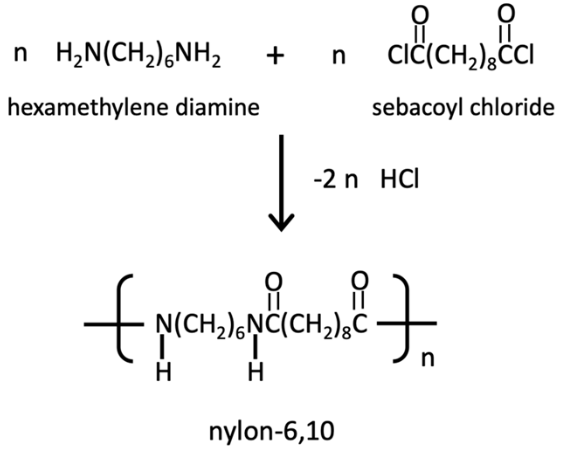
Polymer Synthesis: Theory and Practice

Fundamentals, Methods, Experiments

5th Edition

Springer

Nylon 6,10

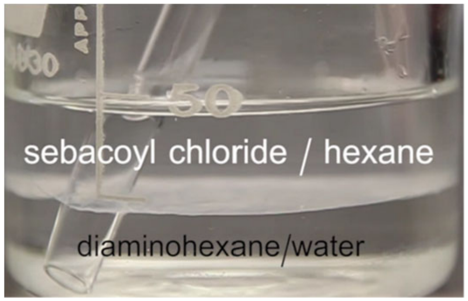


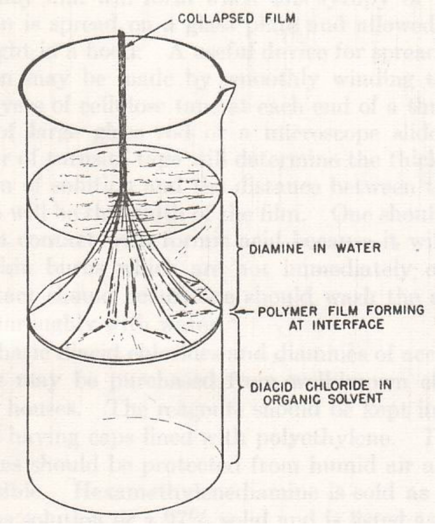
$$n\ \mathrm{H_2N(CH_2)_6NH_2} + n\ \mathrm{Cl}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{(CH_2)_8}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{Cl} \xrightarrow{-2n\ \mathrm{HCl}} \left[\underset{\underset{\displaystyle H}{|}}{\mathrm{N}}\mathrm{(CH_2)_6}\underset{\underset{\displaystyle H}{|}}{\mathrm{N}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{(CH_2)_8}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\right]_n$$

hexamethylene diamine

sebacoyl chloride

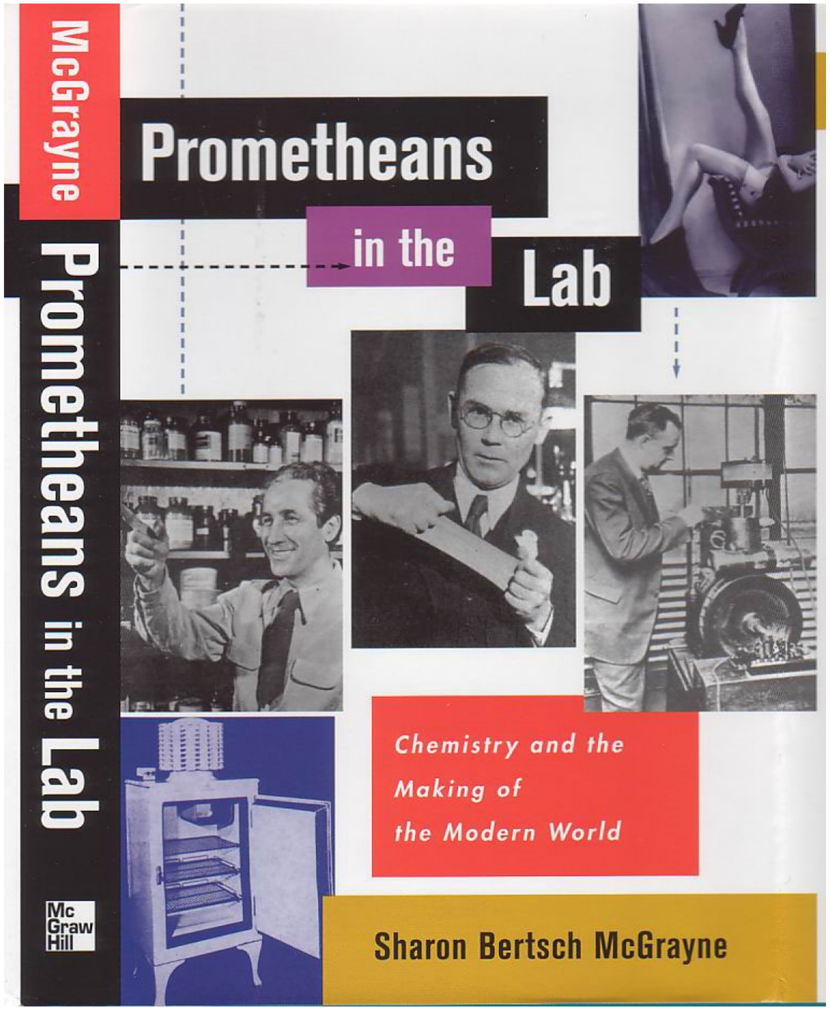
nylon-6,10





https://en.wikipedia.org/wiki/Nylon_rope_trick

Nylon



1940. On May 15, dubbed "N-day," 5 million pairs of nylon stockings become available to American women and sell out in hours. For years, hucksters fraudulently pass silk stockings off as the more popular nylon hosiery because it commands a higher price. ▲

1949. General Electric engineers mix silicone oil with boric acid and produce Silly Putty. The $6 million in sales that year tops any previous toy.

1982. Doctors implant the first artificial heart, the plastic Jarvik-7, which continues to be used for transplants through the turn of the century.

2000. A Dearborn, Mich., company announces development of the first plastic fuel-tank system, which will enable autos to eliminate tailpipe emissions.

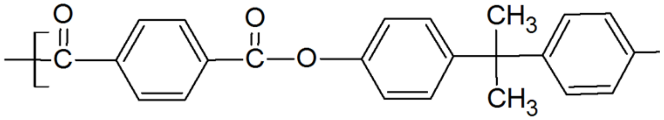
2001. Lucent Technologies researchers create the world's first plastic superconductor, paving the way for ultra-high-speed trains and a new era of quantum computing. ▼

Polyarylates (Aromatic Polyesters)

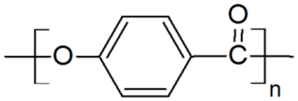
Polyarylates are a family of aromatic polyesters. The repeat units consists of ester groups (chemical formula -CO-O-) and aromatic rings. They are produced by polycondensation of a diacid chloride derivative of a dicarboxylic acid with a phenolic compound. The dicarboxylic acid is usually terephthalic or isophthalic acids and the phenol is Bisphenol A or a derivate of it. The bulky aromatic rings and the absence of methylene groups in the polymer backbone greatly stiffen the polymer chain by interfering with the rotation of the repeat units around the ester linkages. The two most common polyarylates are poly(-p-hydroxybenzoate) and polybisphenol-A terephthalate. The chemical structure of these arylates is given below.

Polybisphenol-A terephthalate is the most common polyarylate. It has one of the highest-levels of heat resistance among transparent resins. For example, its deflection temperature under 1.8 MPa load is about 175 °C (345 °F) (Ardel Polyarylate). It also has high transparency and excellent resistance to degradation from ultraviolet radiation. The material undergoes a molecular rearrangement resulting in the formation of a protective layer that essentially serves as a UV stabilizer. Because UV irradiation increases the UV-blocking property of the polymer, it exhibits excellent weather resistance without addition of any stabilizers. (Although some yellowing occurs, there is hardly any change in physical properties.) Arylates have a transparency as high as PC or PMMA, transmitting almost 90% light. The polymer exhibits excellent elastic recovery and has a high tolerable strain ratio. It also has excellent creep resistance and retains its properties for an ex

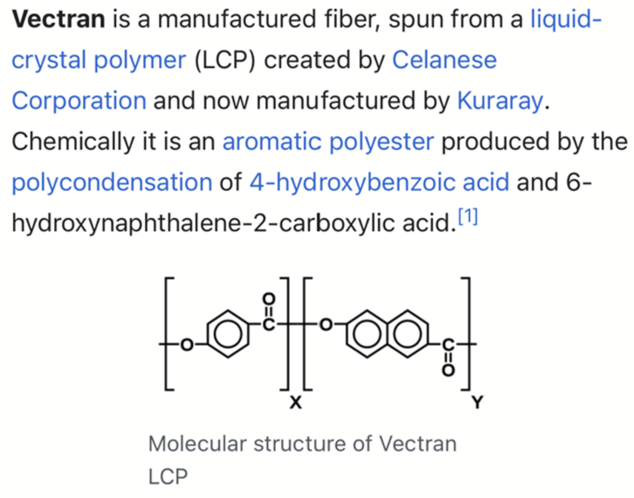
ymer can be used as springs.



Poly(bisphenol-A-terephthalate)



Poly(4-hydroxybenzoate)



Vectran is a manufactured fiber, spun from a liquid-crystal polymer (LCP) created by Celanese Corporation and now manufactured by Kuraray. Chemically it is an aromatic polyester produced by the polycondensation of 4-hydroxybenzoic acid and 6-hydroxynaphthalene-2-carboxylic acid.[1]

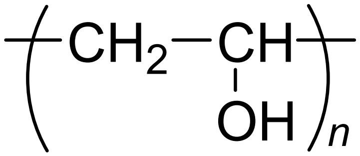
Molecular structure of Vectran LCP

ɔmers are 4-acetoxybenzoic acid, 4-hydroxybenzoic
ʼlic acid, and 4-pivaloyloxybenzoic acid. The polymer
s based on 4-hydroxybenzoic acid. It is a highly
mer with no melting point and virtually no creep below
ɪmperatures up to 315 °C and, at temperatures around
ɪransition and becomes malleable and can be forged
erties are high heat resistance, dielectric strength,
y, and good resistance to wear and solvents. It is also
zoate) can be blended with polytetrafluoroethylene
self-lubricating and has excellent temperature and wear
ylate is the Vectran fiber, manufactured by Kuraray. It
is produced by polycondensation of 4-hydroxybenzoic acid and 6-hydroxynaphthalene-2-carboxylic acid and has similar good properties.

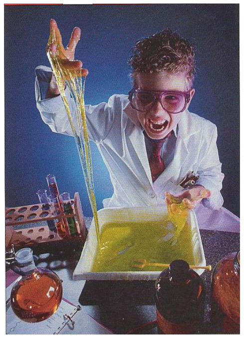
https://polymerdatabase.com/polymer%20classes/Polyarylate%20type.html

Poly(vinyl alcohol)

1924



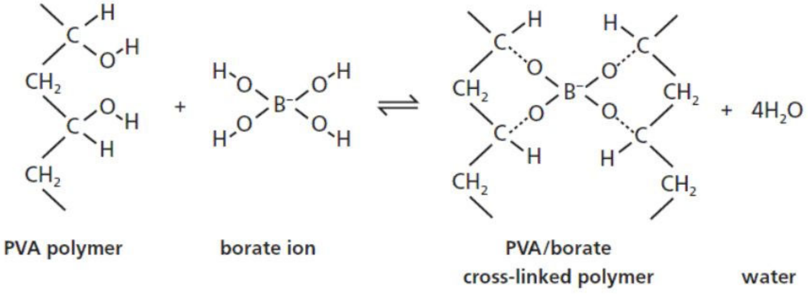
$$\left(-CH_2-\underset{OH}{\underset{|}{CH}}-\right)_n$$

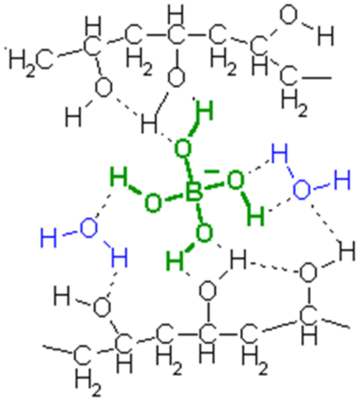


Poly(vinyl alcohol) has been available since around 1924, when its synthesis via the saponification of poly(vinyl acetate) was first described by Herman and Haehnel. In the early years, the principal application for PVOH was in textile sizing (filler).

Today, much of the PVOH produced is used as a protective colloid in the manufacture of polymer emulsions. It is also found in many other applications, including the binding of pigments and fibres, dip coated articles, protective strippable coatings, the production of detergents and cleansing agents, adhesives, emulsion paints and solution cast film.

All of these applications involve the use of the polymer in solution, since the thermal degradation characteristics of PVOH limit its ability to be used as a conventional thermoplastic. Unplasticised PVOH thermally degrades at temperatures of about 150 °C, with the release of water and the formation of conjugated double bonds. As the crystalline melting point of PVOH ranges from 180 °C to 240 °C, its use as a thermoplastic, processable on conventional thermoplastic processing equipment, is limited unless it can be plasticised to such an extent that thermal dehydration is avoided. In practice, the amount of plasticiser necessary to achieve this is so high that many of the useful properties of PVOH are sacrificed.





Poly Vinyl Alcohol chain - black.

Borate ion - green

Water molecules - blue

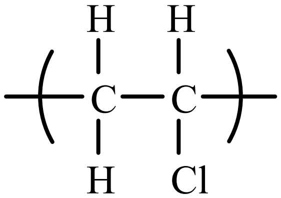
Hydrogen bonds - dashed lines

Poly Vinyl Alcohol chain - black.

http://www.wacker.com/cms/en/wacker_group/wacker_facts/history/history.jsp
http://www.azom.com/article.aspx?ArticleID=266
https://www.carolina.com/knowledge/2020/09/29/how-to-make-slime-2
https://myzlog.blogspot.com/2011/09/slime-is-mixture-of-pva-and-borax.html

Poly(vinyl chloride)

1927

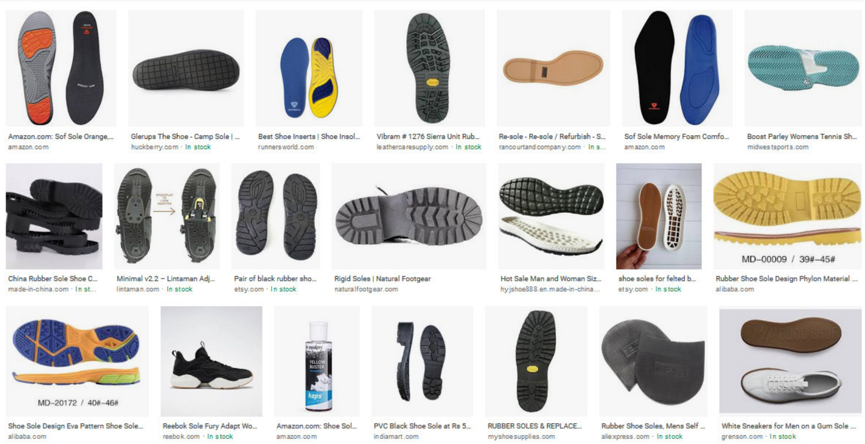


$$-\!\!\left[\mathrm{CH_2{-}CHCl}\right]\!\!-$$

Hard

Soft

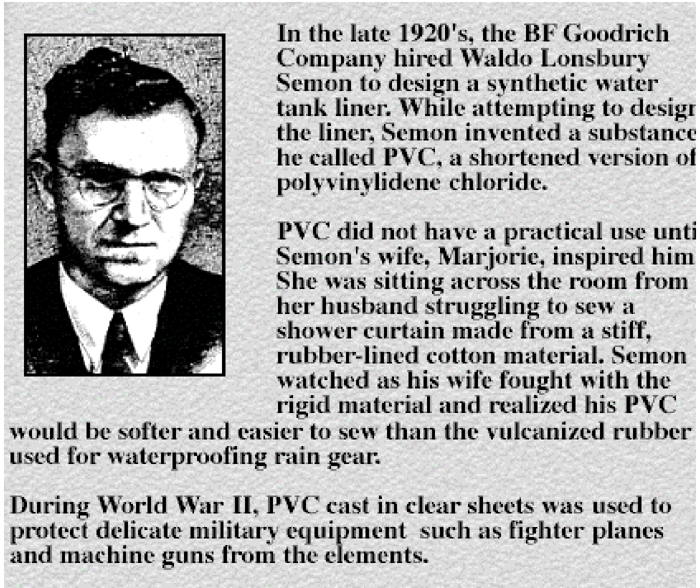
Plasticizer



The chloride atoms increase attractions between polymer chains, making a stronger plastic.

Properties: flame resistant, water resistant, durable, light weight, rigid, elastic, inexpensive, resistant to biological attack.

Used in bottle, piping, shoe soles, cables, rain coats, linoleum shower curtains, table cloths.

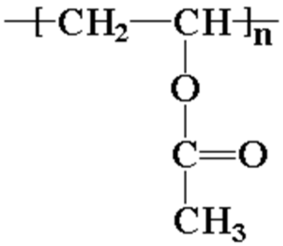


In the late 1920's, the BF Goodrich Company hired Waldo Lonsbury Semon to design a synthetic water tank liner. While attempting to design the liner, Semon invented a substance he called PVC, a shortened version of polyvinylidene chloride.

PVC did not have a practical use unti Semon's wife, Marjorie, inspired him She was sitting across the room from her husband struggling to sew a shower curtain made from a stiff, rubber-lined cotton material. Semon watched as his wife fought with the rigid material and realized his PVC would be softer and easier to sew than the vulcanized rubber used for waterproofing rain gear.

During World War II, PVC cast in clear sheets was used to protect delicate military equipment such as fighter planes and machine guns from the elements.

Poly(vinylidene chloride)



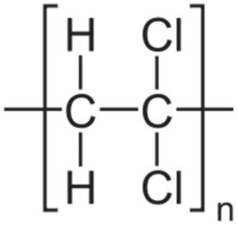
$$-\left[CH_2-\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{\underset{|}{\overset{}{CH}}}\!\!\!\!\!\!\!\!\!\!\!\!\right]_n-$$

$-[CH_2-CH(O-C(=O)-CH_3)]_n-$

Vinylite: a copolymer of vinyl chloride and vinyl acetate

1930 the Union Carbide Corporation introduced the trademarked polymer Vinylite that became the standard material of long-playing phonograph records.

1933



$$\left[-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}-\right]_n$$

From 2004, polyethylene

Keglined™ (1934)
Beer can lining (American Can Co.)

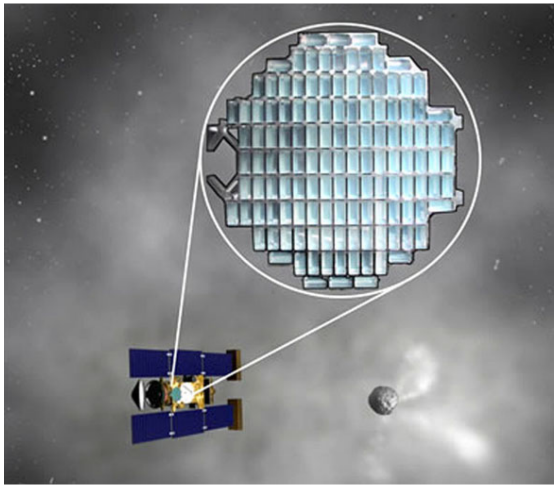
Early 1935: 1st Beer Can Set

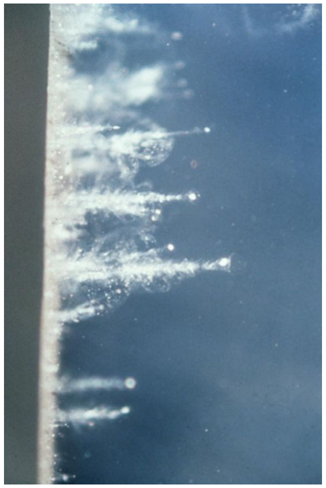
https://breweriana.com/beer-can-appraisal/history-of-beer-cans.html

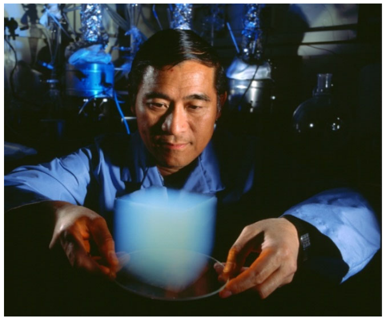
Aerogel = Silica Aerogel (1931)

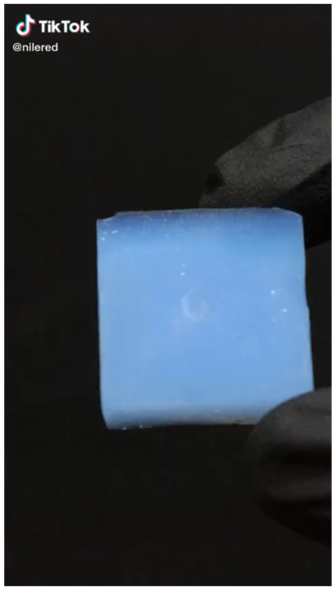
Once called “frozen smoke,” aerogels were invented in 1931 when two chemists challenged each other to remove water from pectin, a gelatin, without shrinking the volume. They are among the least dense solids and act as good insulators. Traditional aerogels, however, made from silica, are brittle. The new aerogels, made with polymers, are strong, flexible, and hold up well against folding, creasing, and crushing.

Since their invention, aerogels have primarily been made of silica. The silica is combined with a solvent to create a gel. This gel is then subjected to supercritical fluid extraction. This supercritical fluid extraction involves introducing liquid carbon dioxide into the gel. The carbon dioxide surpasses its super critical point, where it can be either a gas or a liquid, and then is vented out. This exchange is performed multiple times to ensure that all liquids are removed from the gel. The resulting material is aerogel.









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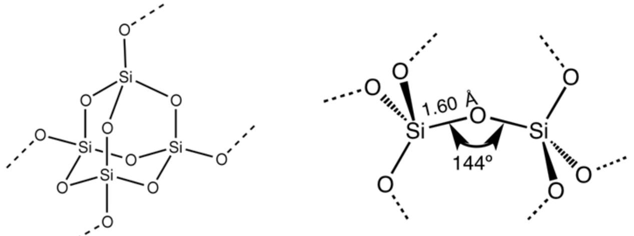
The team of researchers tried a cross-linking approach, where linear polyamides were reacted with a bridging compound to form a three-dimensional covalent polymer. The resulting density of the polymer aerogel was 0.14 g/cc, with 90% porosity. Silica gels were made with much better specs, but the polymer more than makes up for scale in strength.

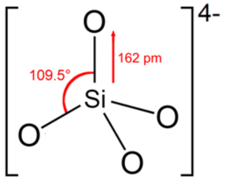
http://www.nasa.gov/topics/technology/features/aerogels.html
https://stardust.jpl.nasa.gov/tech/aerogel.html
https://astrobob.areavoices.com/2014/04/02/stardust-capturesSilica Aerogel-7-precious-pieces-of-cosmic-dust/
https://airandspace.si.edu/newsroom/press-releases/stardust-comet-sample-return-mission-team-and-col-joseph-kittinger-are-2008

Silica, Silicon, & Silicone

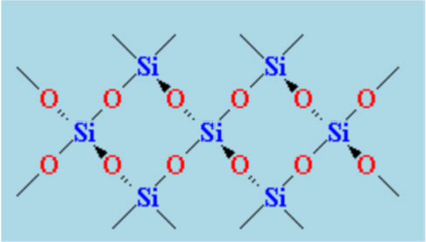
Silica is an oxide of silicon, silicon dioxide (SiO_2). (Glass)



Each silicon atom is covalently bonded in a tetrahedral manner to 4 oxygen atoms.

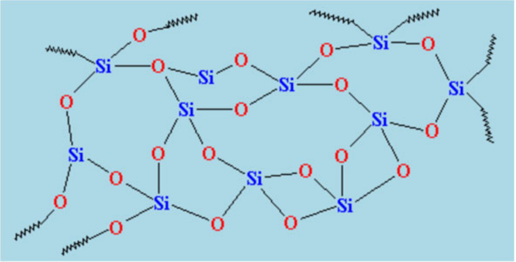


Structure of the orthosilicate anion SiO_4^{4-}

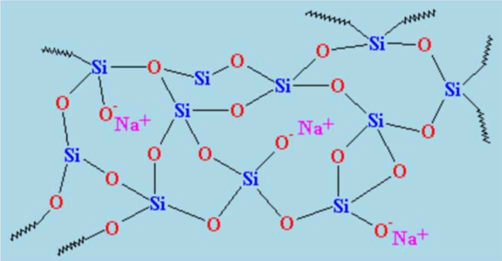


SiO_2 in its crystalline form, quartz.

https://www.pslc.ws/mactest/glass.htm



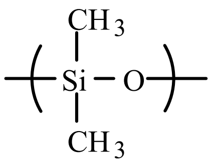
SiO_2 in its amorphous form. Brittle.



Most glass is made from sand with added sodium carbonate.

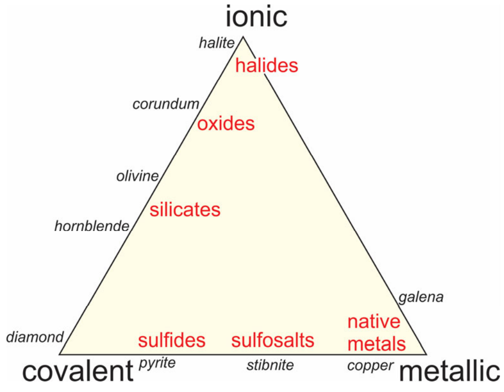
Is Silica a polymer or not?

Silicon (Si) is a nonmetallic chemical element in the carbon family.
Silicones are polysiloxane chains made of alternating silicon and oxygen atoms.
The most common silicone compound is poly(dimethyl siloxane).



$$-\!\left(\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array}\right)\!-$$

Different kinds of bonds in different minerals.



Bonding in most minerals is neither 100% ionic, 100% covalent, nor 100% metallic, but some come close. Most minerals contain combinations of ionic and covalent bonding. Metallic ore minerals such as pyrite (FeS_2), stibnite (Sb_2S_3), and copper (Cu) generally have little ionic character. Most of them, especially those in the sulfide and sulfosalt groups, contain combinations of covalent and metallic bonding. Metallic and ionic bonds do not often combine, although galena (PbS) may be one example in which they do to a limited extent.

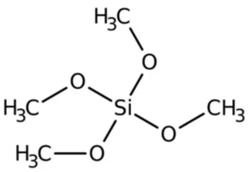
The degree to which a bond is ionic depends on both elements involved. For example, because alkali elements (group 1) have a very strong tendency to become cations, and halogens (group 17) have an equal tendency to become anions, halite (NaCl) and other alkali halides form crystals in which bonds are nearly 100% ionic. Fluorite (CaF_2), too, is nearly completely ionic. Alkaline earth oxides such as periclase (MgO) or lime (CaO), involving cations from group 2 and oxygen from group 16, are about 75% ionic. Many other oxides too, are mostly ionic. Silicates, the most common kind of mineral in Earth's crust, are generally about 50% ionic and 50% covalent. And, bonds in diamond (C) are entirely covalent.

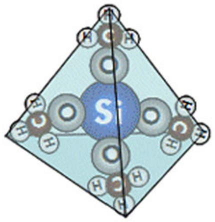
https://geo.libretexts.org/Bookshelves/Geology/Mineralogy_(Perkins_et_al.)/02%3A_Mineral_Chemistry/2.04%3A_Bonding_in_Minerals/2.4.05%3A_Ionic_Covalent_and_Metallic_Crystals

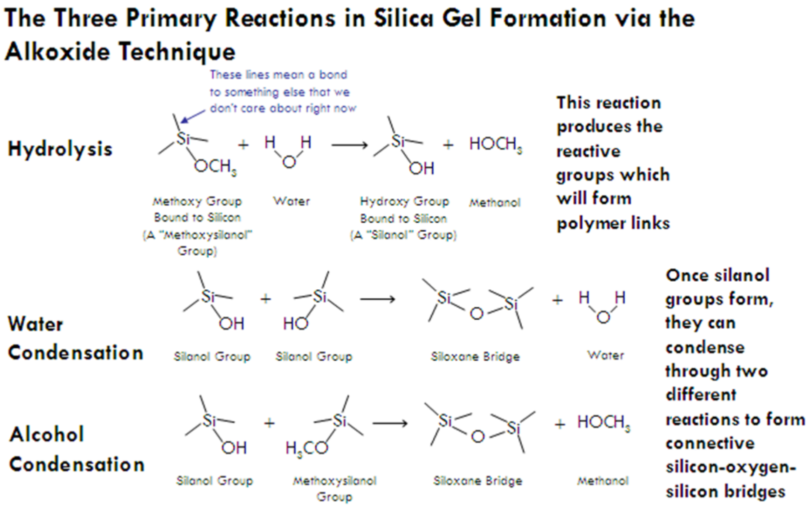
Silica Aerogel

Formation of a Silica Gel from a Silica Sol

silica alcogel





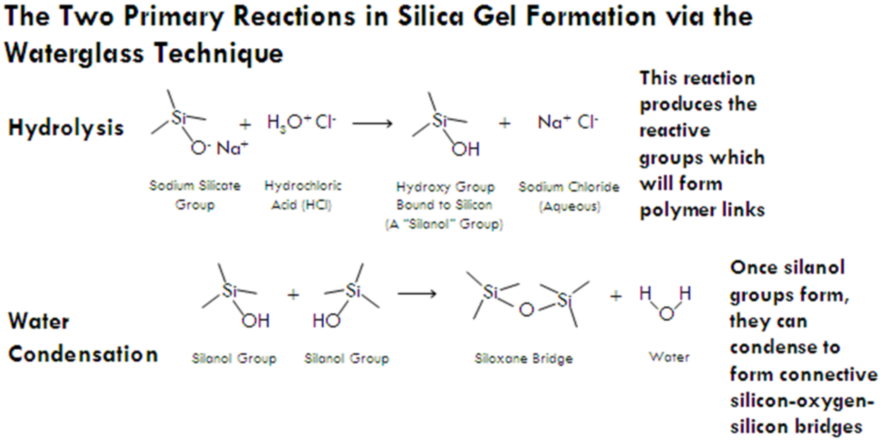


The Three Primary Reactions in Silica Gel Formation via the Alkoxide Technique

This reaction produces the reactive groups which will form polymer links

Once silanol groups form, they can condense through two different reactions to form connective silicon-oxygen-silicon bridges

Tetramethoxysilane (TMOS) = tetramethyl orthosilicate



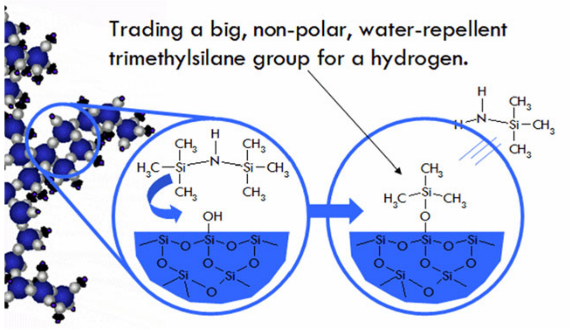
The Two Primary Reactions in Silica Gel Formation via the Waterglass Technique

This reaction produces the reactive groups which will form polymer links

Once silanol groups form, they can condense to form connective silicon-oxygen-silicon bridges

Waterglass Gelation: A Cheaper Alternative to Alkoxides
Silica gels can also be produced through a less expensive method involving an aqueous solution of sodium silicate. Sodium silicate is an inexpensive white solid with a range of possible stoichiometries (which each have different names)—Na_2SiO_3 or sodium metasilicate, sodium polysilicate or $(Na_2SiO_3)_n$, sodium orthosilicate Na_4SiO_4, and others. Sodium silicates are soluble in water, and when dissolved the resulting solution is referred to as waterglass or liquid glass.

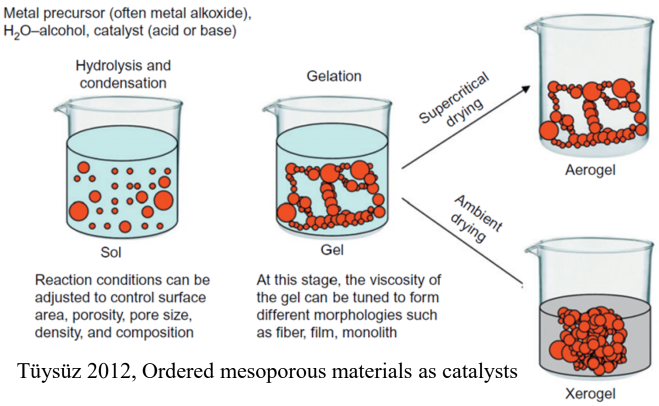
Water-Proofing and Functionalizing Silica Aerogels



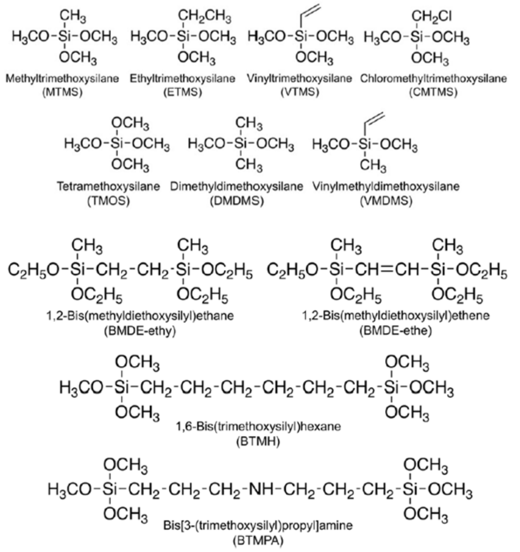
Trading a big, non-polar, water-repellent trimethylsilane group for a hydrogen.

http://www.aerogel.org/?p=16

Aerogels and Xerogels



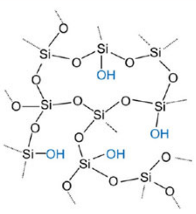
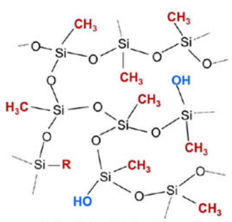
Tüysüz 2012, Ordered mesoporous materials as catalysts



Kanamori 2019, Hybrid silicone aerogels toward unusual flexibility, functionality, and extended applications

2.2. Xerogels and aerogels

Xerogels and aerogels can be described as dried gels that retain—at least in part—their porous texture after the drying. The attractive properties of such porous gels arise from the extraordinary flexibility of the sol–gel processing, which can be combined with various drying techniques that lead to aerogels (supercritical drying) or xerogels (ambient drying). Moreover, gels can be directly synthesized in the desired shape. Xerogels and aerogels are probably the closest relatives of ordered mesoporous materials. Their structures and morphologies can be easily controlled in the synthesis and drying process. Xero- and aerogels have the same kind of disorder in the wall structure as OMMs; they can be synthesized with approximately the same range of compositions; and they have high porosities.

Silica aerogel		PMSQ xerogel
TMOS Water glass	**Precursor**	MTMS
 Low strength Hydrophilic (silylation required)	**Network structure & properties**	 Flexible, high strength Hydrophobic
Supercritical (> 100 atm)	**Drying**	Ambient (1 atm)
>12 mW m^{-1} K^{-1}	**Thermal conductivity**	>13 mW m^{-1} K^{-1}

The resultant PMSQ aerogels and xerogels show similar properties in bulk density, transparency, pore size and volume, specific surface area, and thermal conductivity, which are also comparable with conventional silica aerogels. Although it had been difficult to realize monolithicity, transparency, and low thermal conductivity in a single xerogel material in spite of the efforts and progresses in a hydrophobized silica system [16], it is now facilitated in the PMSQ network. Other material formats such as granules/powders, sheets/films, and composites can also be prepared by APD. However, since some issues still remain in the PMSQ material, further extended research is ongoing as mentioned in the following section.

Polymethylsilsesquioxane (PMSQ) $CH_3SiO_{3/2}$	MTMS
Polyethylsilsesquioxane (PESQ) $CH_3CH_2SiO_{3/2}$	ETMS
Polyvinylsilsesquioxane (PVSQ) $CH_2{=}CHSiO_{3/2}$	VTMS
Polychloromethylsilsesquioxane (PCMSQ) $ClCH_2SiO_{3/2}$	CMTMS
Hexylene-bridged polysilsesquioxane (HBPSQ) $O_{3/2}Si–(CH_2)_6–SiO_{3/2}$	BTMH
Ethylene-bridged polymethylsiloxane (Ethy-BPMS) $O_{2/2}(CH_3)Si–(CH_2)_2–Si(CH_3)O_{2/2}$	BMDE-ethy
Ethenylene-bridged polymethylsiloxane (Ethe-BPMS) $O_{2/2}(CH_3)Si–CH{=}CH–Si(CH_3)O_{2/2}$	BMDE-ethe
Polyvinylpolymethylsiloxane (PVPMS) $[CH_2CH(Si(CH_3)O_{2/2})]_n$	VMDMS

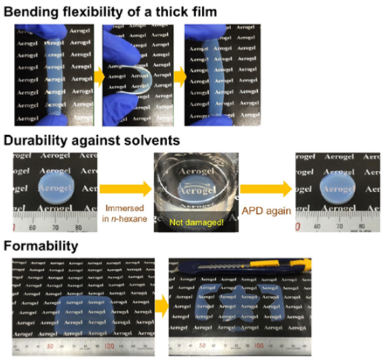
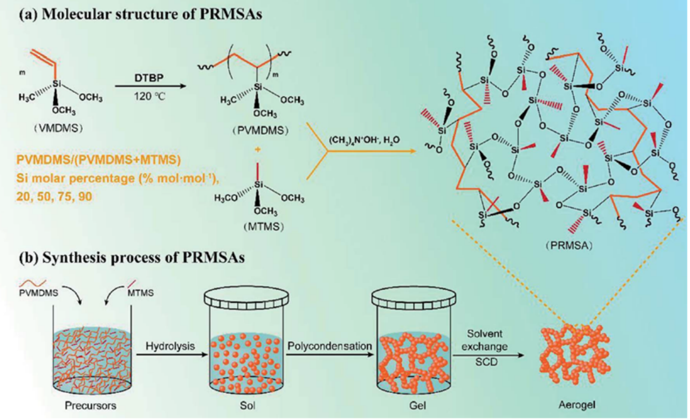


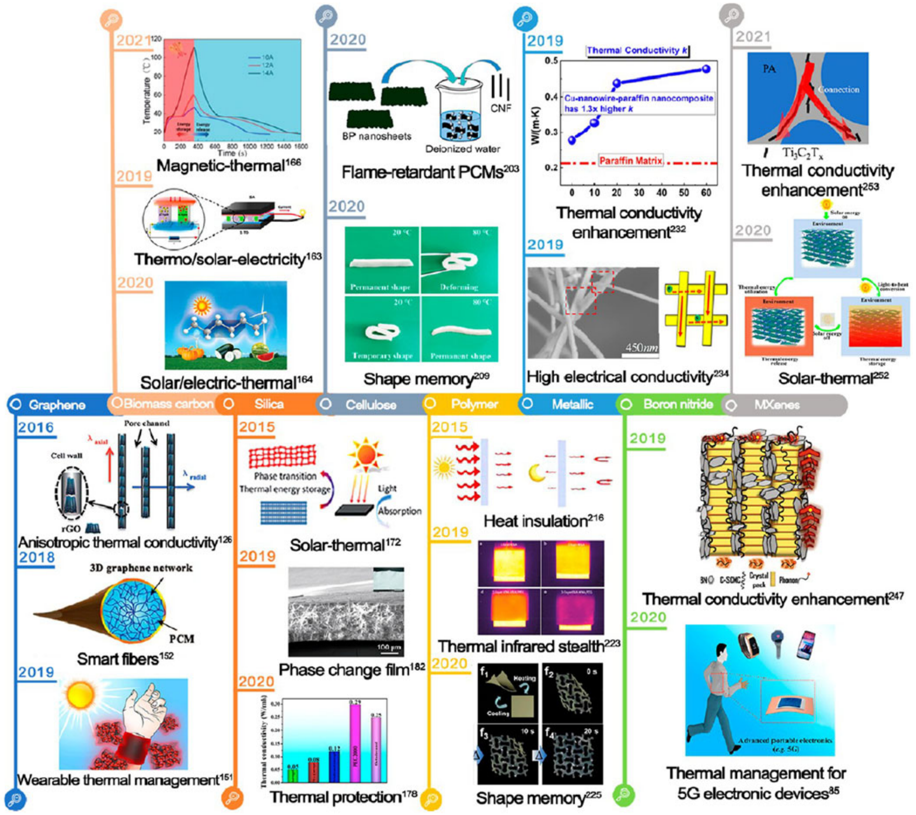
Fig. 4 Outstanding bendability, durability against solvents, and formability of doubly cross-linked PVPMS xerogels.



Wang 2019, Elastic methyltrimethoxysilane based silica aerogels reinforced with polyvinylmethyldimethoxysilane.

Pal 2018, Polymeric Gels

Polymer Aerogels



Timeline of major breakthroughs of aerogel-based composite phase change materials (PCMs) in recent years.

Liu 2022, Aerogels meet phase change materials- Fundamentals, advances, and beyond

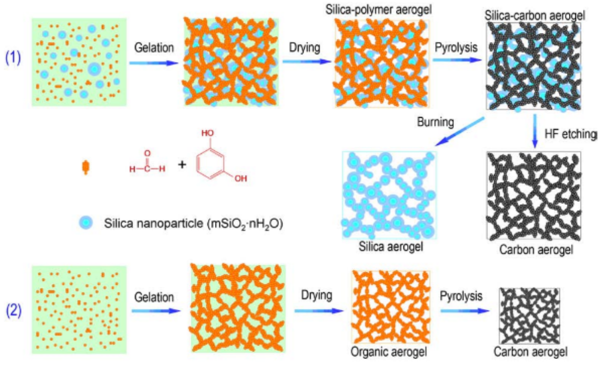
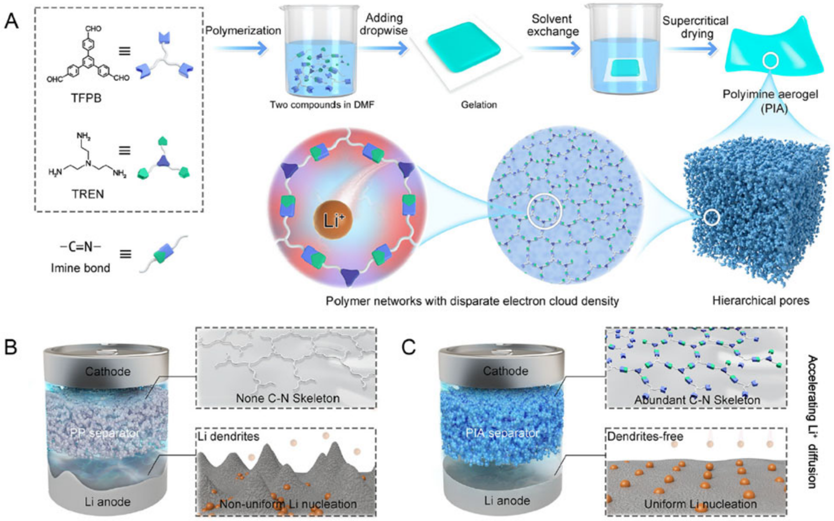


Fig. 3. The schematic representation of preparation of carbon aerogels with (1) or without (2) colloidal silica nanoparticles.

Qingjun Chen, Donghui Long, Liang Chen, Xiaojun Liu, Xiaoyi Liang, Wenming Qiao, Licheng Ling. Synthesis of ultrahigh-pore-volume carbon aerogels through a "reinforced-concrete" modified sol–gel process. Journal of Non-Crystalline Solids. 357 (1); 232-235, 2011

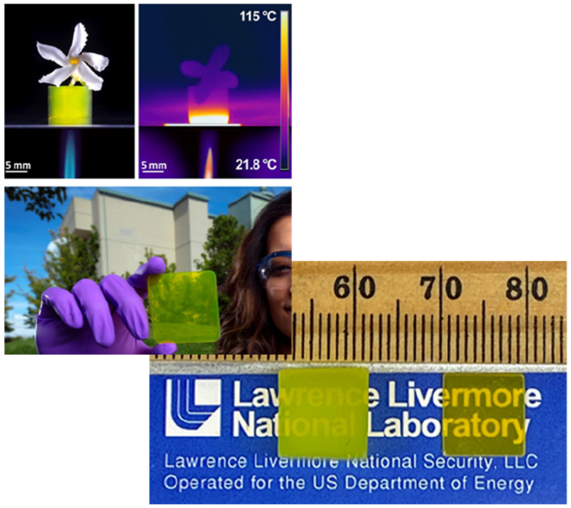
https://www.polymersolutions.com/blog/polymer-aerogel-super-insulating-strong/



Ding 2023, A polyimine aerogel separator with electron cloud design to boost Li- ion transport for stable Li metal batteries

Polymer Aerogels

Merillas 2021, Transparent polyisocyanurate-polyurethane-based aerogels- Key aspects on the synthesis and their porous structures



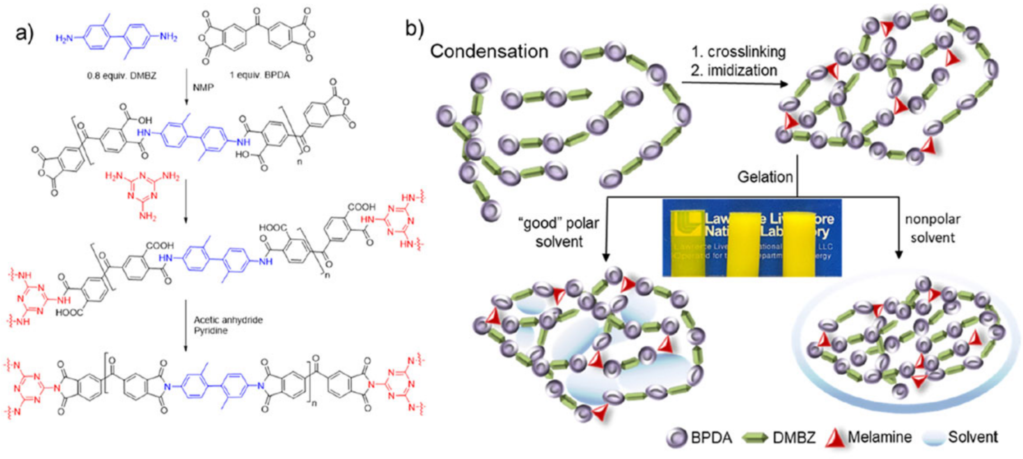
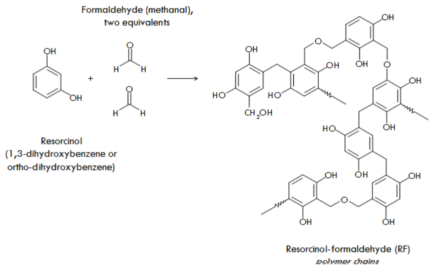
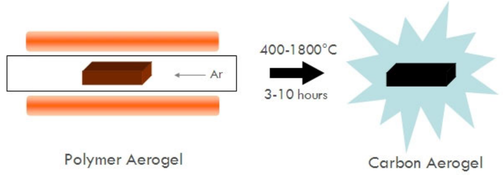


Figure 1. (a) Reaction conditions of PI aerogel used in this study and (b) proposed scheme of gelation steps for transparent and opaque PI aerogels. Inset: 2 cm molded aerogel cylinder with pure NMP, 25% toluene, and 50% toluene (left to right) after supercritical drying.

Mettry 2022, Transparent polyimide aerogels

Organic RF Polymer aerogels made of resorcinol-formaldehyde polymer





http://www.aerogel.org/?p=71

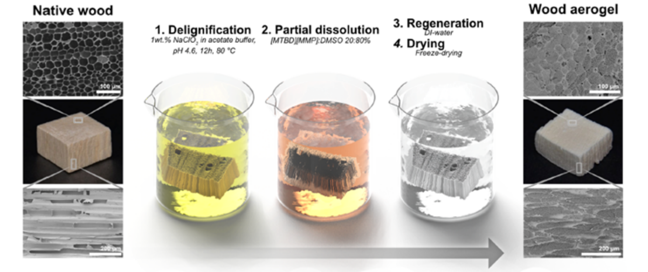


Figure 2. Synthesis of wood aerogels. Top left-hand side, Native wood (NW) exhibits its neighboring fibers with empty centers (up) and bottom image shows the long empty fibers in the axial direction of wood. The following are illustrations of NW treatment. In the upper right-hand side image, nanofibril networks homogeneously fill the fiber centers in wood. Bottom right-hand side image shows complete filling of all fibers in axial direction of the wood aerogel.

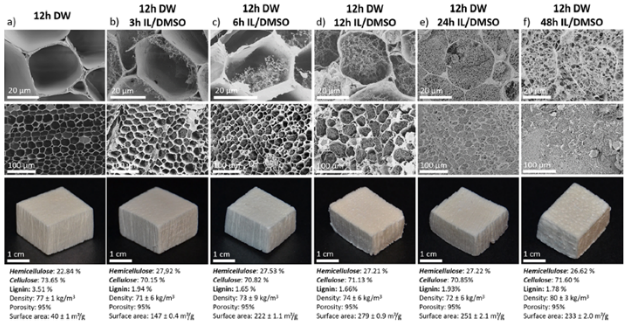
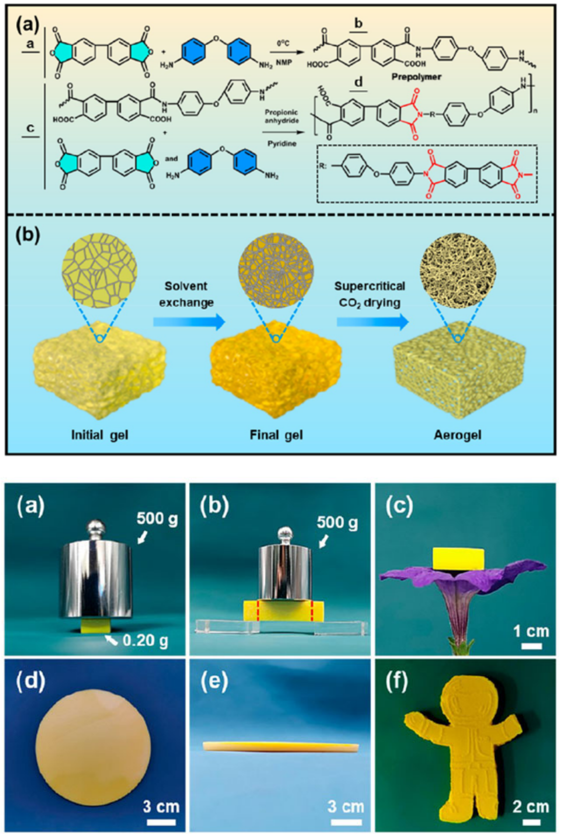


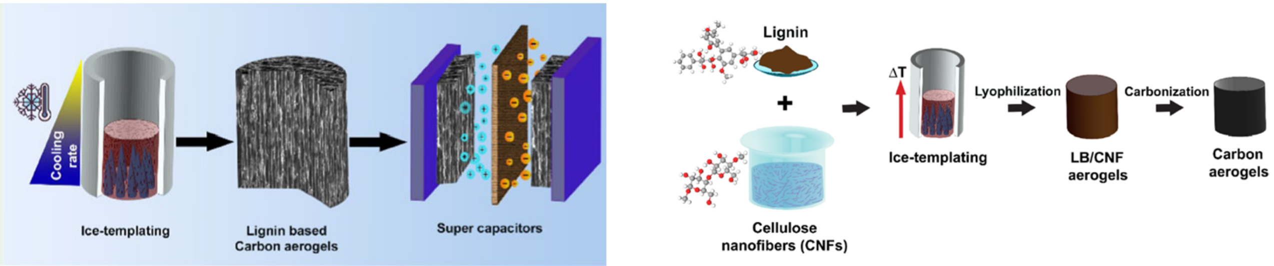
Figure 3. SEM of cross sections of DW after 12 h delignification (a), followed by IL treatment of 12h DW for (b) 3 h, (c) 6 h, (d) 12 h, (e) 24 h, and (f) 48 h. The second row shows lower magnification SEM images of homogeneous structures. The third row represents the wood specimen from which the SEM images were obtained.

Garemark 2022, Nanostructurally controllable strong wood aerogel toward efficient thermal insulation

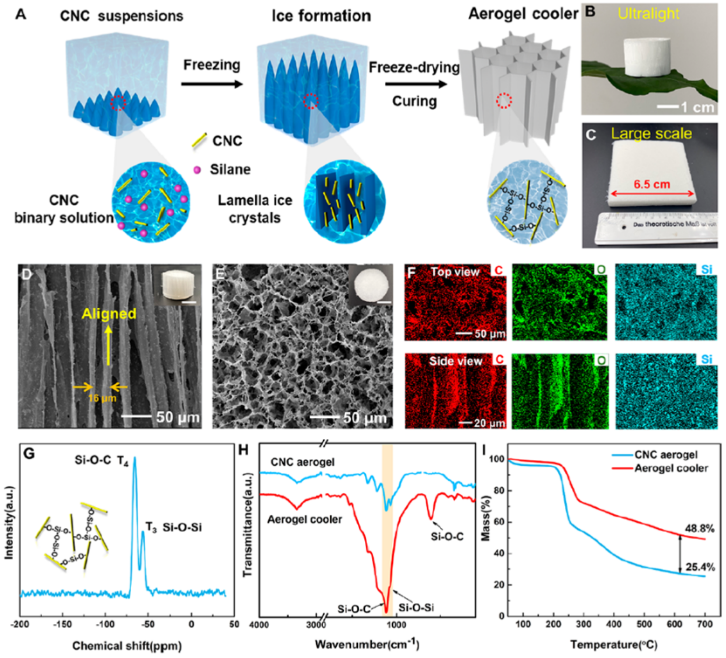
Polymer Aerogels



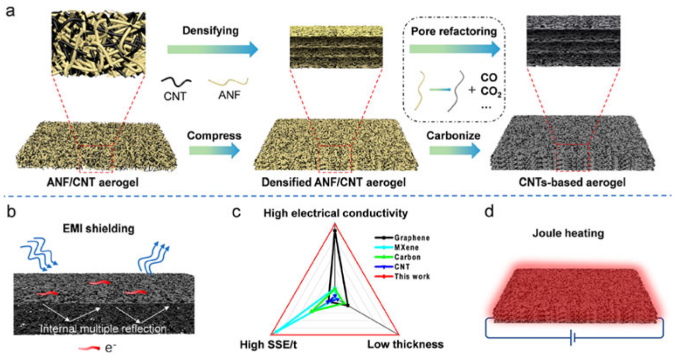
Zhang 2022, Polyimide aerogels with excellent thermal insulation, hydrophobicity, machinability, and strength evolution at extreme conditions



Thomas 2022, Ice-templating of lignin and cellulose nanofiber-based carbon aerogels



Cai 2022, Dynamically tunable all-weather daytime cellulose aerogel radiative supercooler for energy-saving building



Schematic Illustration of the Fabrication Procedure and Features of the CNT-Based Aerogel Film (a) ANF/CNT aerogel film can be formed with a three-dimensional fiber network. By directional compressing, the lamination structure can be generated. Following carbonization, CNT-based aerogel film with a dense fiber layer and laminated structure can be obtained as well as pore refactoring in between the layers. (b) Schematic illustration of EMI shielding behavior of the CNT-based aerogel film. (c) Radical plot comparing the thickness, density, and SSE/t for CNT-based aerogel film and other aerogel materials including graphene, CNT, and MXene. (d) Schematic illustration of Joule heating performance of the CNT-based aerogel film.

Fu 2022, Laminated structural engineering strategy toward carbon nanotube-based aerogel

PVA Aerogels

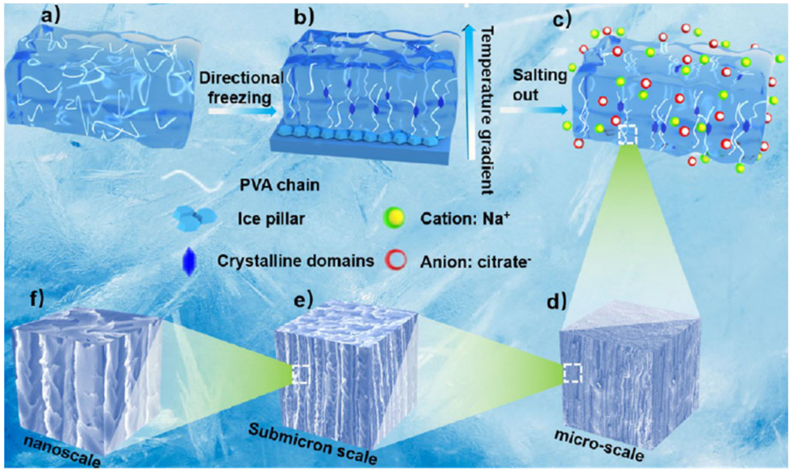


Figure 1. Fabrication of the multiscale hierarchical structure and anisotropic PVA hydrogel based on the directional freezing-assisted salting-out effect. (a) Disorderly distributed PVA solution; (b) PVA molecular chains arranged in order after directional freezing; (c) adjustment of PVA aggregation for the salting-out effect; (d) micrometer-scale structure diagram; (e) submicrometer-scale structure diagram; (f) nanoscale structure diagram.

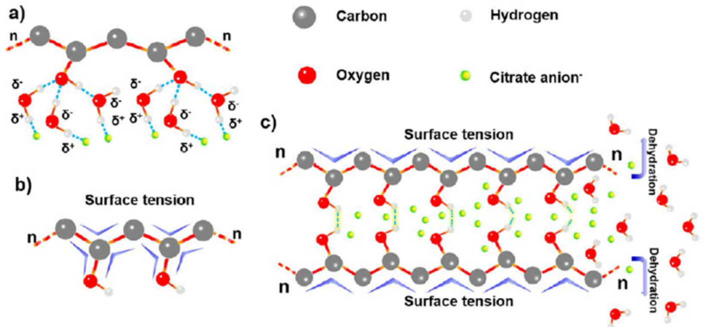


Figure 2. Regulation principle of the PVA molecular chain structure induced by the citrate anion due to the salting-out effect. (a) Interaction between the PVA chain and the water molecule; (b) interaction between the citrate anion and the PVA chain; (c) principle of aggregation among the PVA chain, citrate anion, and water molecule.

2.2. Specimen Preparation.

2.2.1. Fabrication of the Multiscale Hierarchical Anisotropic Hydrogel (DS-PVA). (Directional freezing salting out)

First, PVA-124 was dissolved into demi water to prepare the PVA solution (2, 5, and 10%). Then, the PVA solution was poured into a container made of PTFE (insulation layer) and copper bottom (heat transfer layer), which was placed on the top of the copper block, and the top exposed 1 cm of liquid nitrogen. The rest was immersed in liquid nitrogen and frozen in the direction for 30 min (Figure S1). Finally, the frozen samples were immersed in sodium citrate solution with 10, 15, 20, 25, 30, and 40% concentrations for 24 h to get the hydrogels.

2.2.2. Fabrication of the Cyclic Freeze−Thaw Hydrogel (CT-PVA). (Cyclic freezing-thawing)

The PVA-124 was dissolved into demi water to prepare a 5% PVA solution. Then, the solution was cast into the module and froze for 30 min. After that, the module was removed for thawing for 2 h. This cycle was operated five times to prepare the CT-PVA.

A PVA conductive hydrogel with an anisotropic multiscale hierarchical structure by directional freezing versus citrate solution salting-out effect (DS-PVA). The PVA molecular chain occurred at orientation with loading the temperature gradient field, resulting in a millimeter-scale, micron-level aggregate orientation structure. Then, under the anion salting-out effect (Hofmeister effect), the PVA aggregation states would be further altered, resulting in PVA molecular chains self-coalesced, forming the nanofibrils.

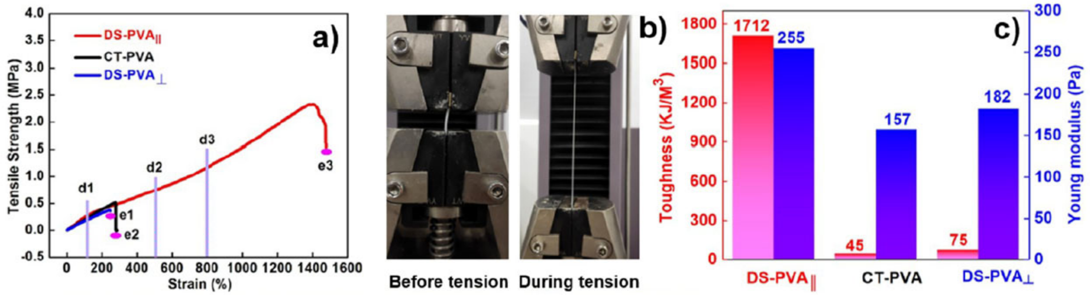
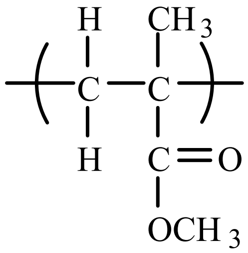


Figure 6. Mechanical performance of anisotropic (DS-PVA) and isotropic (CT-PVA) hydrogels prepared by directional freezing salting-out and cyclic freezing−thawing processes. (a) Stress−strain cures of hydrogels; (b) photograph of the DS-PVA∥ before and after tension; (c) toughness and Young's modulus of hydrogels.

Fu 2023, Anisotropic hydrogels with multiscale hierarchy based on ionic conductivity for flexible sensors

Poly(methyl methacrylate) (PMMA) Poly(hydroxyethyl Methacrylate) (PHEMA)

1931

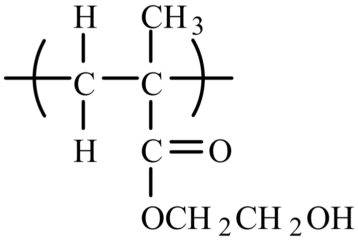

$\left(\mathrm{CH_2-C(CH_3)(C{=}O)OCH_3}\right)$

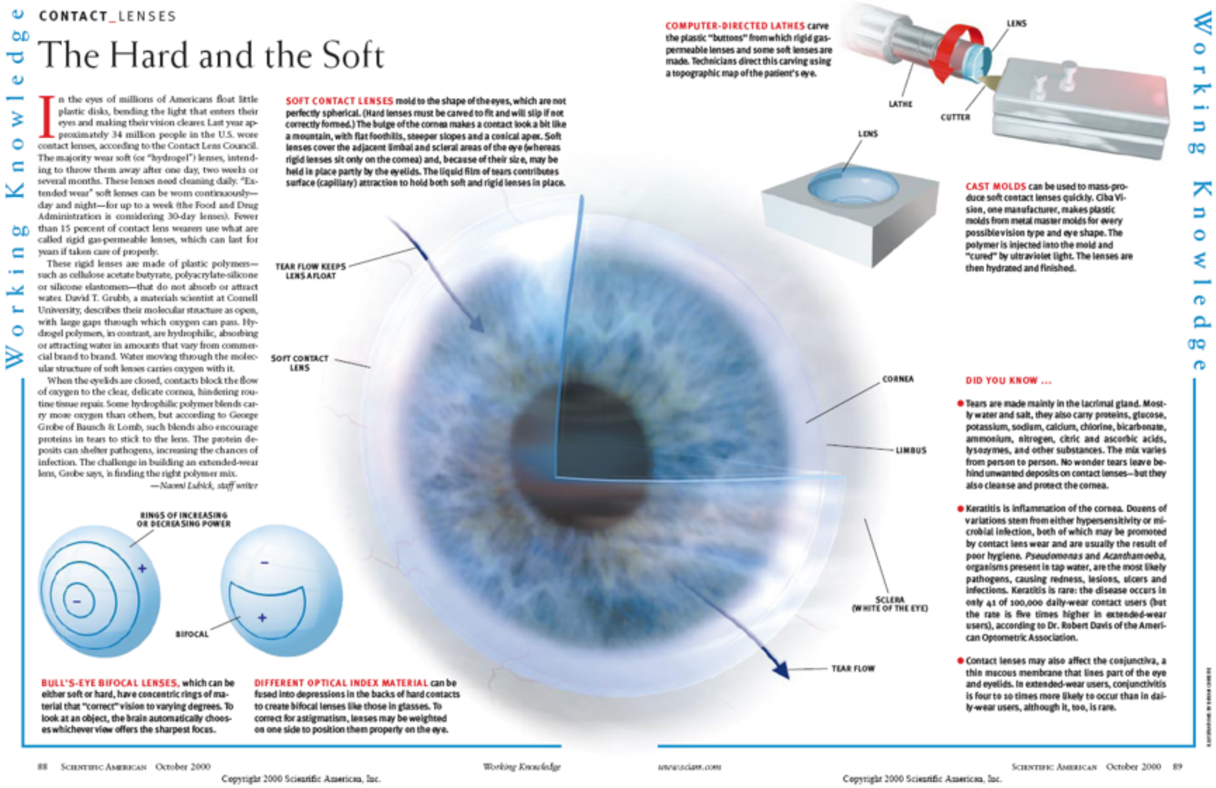
(Plexiglas, Lucite)

1936 Hard Contact Lens

FINALLY, A COLOR CONTACT LENS
GOOD ENOUGH TO BE CALLED ACUVUE

1960


$\left(\mathrm{CH_2-C(CH_3)(C{=}O)OCH_2CH_2OH}\right)$



CONTACT_LENSES

The Hard and the Soft

In the eyes of millions of Americans float little plastic disks, bending the light that enters their eyes and making their vision clearer. Last year approximately 34 million people in the U.S. wore contact lenses, according to the Contact Lens Council. The majority wear soft (or "hydrogel") lenses, intending to throw them away after one day, two weeks or several months. These lenses need cleaning daily. "Extended wear" soft lenses can be worn continuously—day and night—for up to a week (the Food and Drug Administration is considering 30-day lenses). Fewer than 15 percent of contact lens wearers use what are called rigid gas-permeable lenses, which can last for years if taken care of properly.

These rigid lenses are made of plastic polymers—such as cellulose acetate butyrate, polyacrylate-silicone or silicone elastomers—that do not absorb or attract water. David T. Grubb, a materials scientist at Cornell University, describes their molecular structure as open, with large gaps through which oxygen can pass. Hydrogel polymers, in contrast, are hydrophilic, absorbing or attracting water in amounts that vary from commercial brand to brand. Water moving through the molecular structure of soft lenses carries oxygen with it.

When the eyelids are closed, contacts block the flow of oxygen to the clear, delicate cornea, hindering routine tissue repair. Some hydrophilic polymer blends carry more oxygen than others, but according to George Grobe of Bausch & Lomb, such blends also encourage proteins in tears to stick to the lens. The protein deposits can shelter pathogens, increasing the chances of infection. The challenge in building an extended-wear lens, Grobe says, is finding the right polymer mix.

—Naomi Lubick, staff writer

SOFT CONTACT LENSES mold to the shape of the eyes, which are not perfectly spherical. (Hard lenses must be carved to fit and will slip if not correctly formed.) The bulge of the cornea makes a contact look a bit like a mountain, with flat foothills, steeper slopes and a conical apex. Soft lenses cover the adjacent limbal and scleral areas of the eye (whereas rigid lenses sit only on the cornea) and, because of their size, may be held in place partly by the eyelids. The liquid film of tears contributes surface (capillary) attraction to hold both soft and rigid lenses in place.

COMPUTER-DIRECTED LATHES carve the plastic "buttons" from which rigid gas-permeable lenses and some soft lenses are made. Technicians direct this carving using a topographic map of the patient's eye.

CAST MOLDS can be used to mass-produce soft contact lenses quickly. Ciba Vision, one manufacturer, makes plastic molds from metal master molds for every possible vision type and eye shape. The polymer is injected into the mold and "cured" by ultraviolet light. The lenses are then hydrated and finished.

BULL'S-EYE BIFOCAL LENSES, which can be either soft or hard, have concentric rings of material that "correct" vision to varying degrees. To look at an object, the brain automatically chooses whichever view offers the sharpest focus.

DIFFERENT OPTICAL INDEX MATERIAL can be fused into depressions in the backs of hard contacts to create bifocal lenses like those in glasses. To correct for astigmatism, lenses may be weighted on one side to position them properly on the eye.

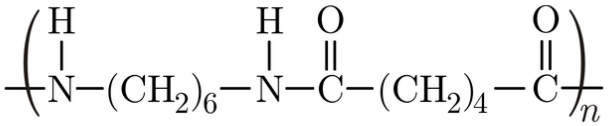
DID YOU KNOW ...

- Tears are made mainly in the lacrimal gland. Mostly water and salt, they also carry proteins, glucose, potassium, sodium, calcium, chlorine, bicarbonate, ammonium, nitrogen, citric and ascorbic acids, lysozymes, and other substances. The mix varies from person to person. No wonder tears leave behind unwanted deposits on contact lenses—but they also cleanse and protect the cornea.
- Keratitis is inflammation of the cornea. Dozens of variations stem from either hypersensitivity or microbial infection, both of which may be promoted by contact lens wear and are usually the result of poor hygiene. *Pseudomonas* and *Acanthamoeba*, organisms present in tap water, are the most likely pathogens, causing redness, lesions, ulcers and infections. Keratitis is rare: the disease occurs in only 41 of 100,000 daily-wear contact users (but the rate is five times higher in extended-wear users), according to Dr. Robert Davis of the American Optometric Association.
- Contact lenses may also affect the conjunctiva, a thin mucous membrane that lines part of the eye and eyelids. In extended-wear users, conjunctivitis is four to 10 times more likely to occur than in daily-wear users, although it, too, is rare.

Nylon

Polyamides are polymers made of monomers containing nitrogen.

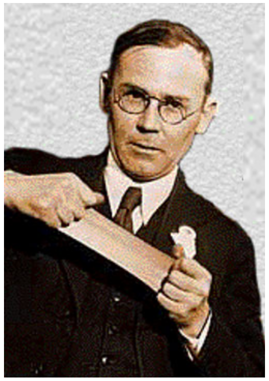
1934 Need for new tough plastic, replacing silk.
Synthesis of nylon based on Staudinger's theory on polymeric nature of plastics (1920).



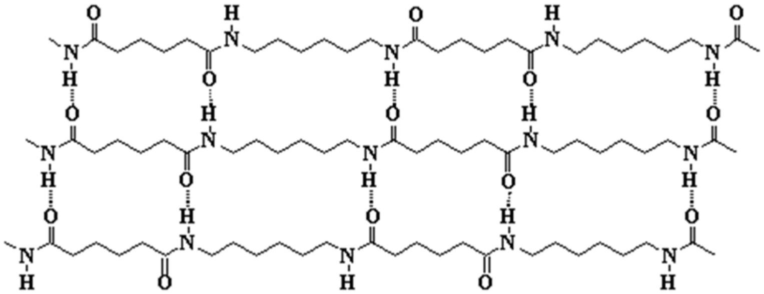
$$\left(\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right)_n$$

Nylon 6-6

Wallace Carothers and his group at Du Pont invented nylon. It was the highest molecular weight polymer made at that time and was called Fiber 66 because two monomers that react to form nylon each contain six carbon atoms.

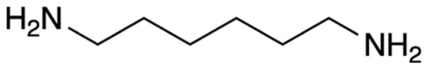


Wallace Hume Carothers

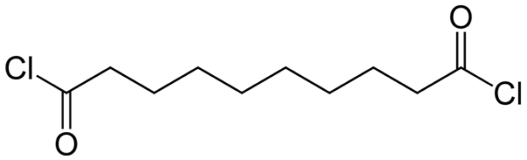


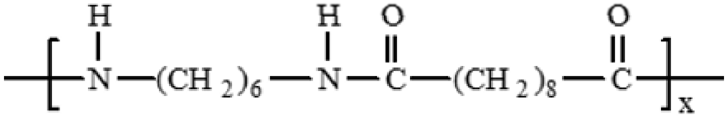
In nylon 6,6, the carbonyl oxygens and amide hydrogens can hydrogen bond with each other. This allows the chains to line up in an orderly fashion to form fibers.

Hexamethylenediamine in water



Sebacoyl chloride in tetrachloroethylene 1.62 g/cm³

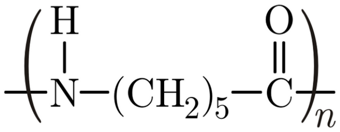




$$\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}\right]_x$$

Nylon 6-10

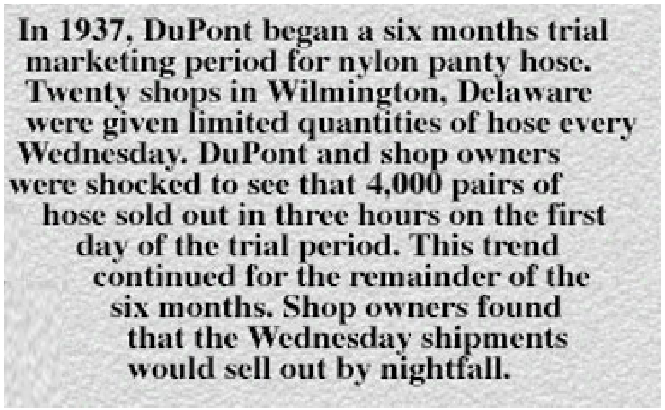
Nylon 6



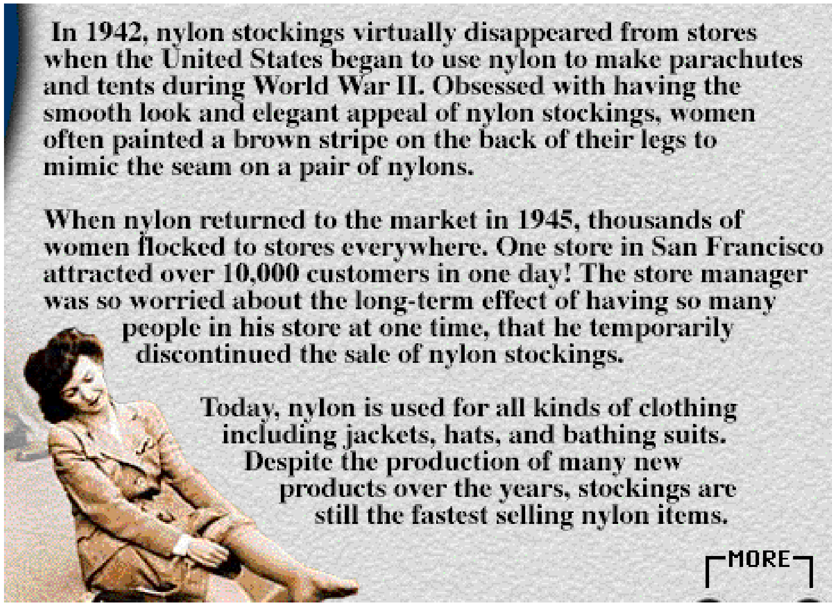
$$\left(\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right)_n$$

Strong, stiff, tensile, elastic, abrasion resistant, heat resistant, chemical resistant, wear resistant.
Used in textiles, netting, rope, pantyhose, brush bristles, collars, leashes, fasteners, guitar strings.

Nylon during World War II



In 1937, DuPont began a six months trial marketing period for nylon panty hose. Twenty shops in Wilmington, Delaware were given limited quantities of hose every Wednesday. DuPont and shop owners were shocked to see that 4,000 pairs of hose sold out in three hours on the first day of the trial period. This trend continued for the remainder of the six months. Shop owners found that the Wednesday shipments would sell out by nightfall.



In 1942, nylon stockings virtually disappeared from stores when the United States began to use nylon to make parachutes and tents during World War II. Obsessed with having the smooth look and elegant appeal of nylon stockings, women often painted a brown stripe on the back of their legs to mimic the seam on a pair of nylons.

When nylon returned to the market in 1945, thousands of women flocked to stores everywhere. One store in San Francisco attracted over 10,000 customers in one day! The store manager was so worried about the long-term effect of having so many people in his store at one time, that he temporarily discontinued the sale of nylon stockings.

Today, nylon is used for all kinds of clothing including jackets, hats, and bathing suits. Despite the production of many new products over the years, stockings are still the fastest selling nylon items.

1942

A GLANCE AT THE PAST

MILITARY TECHNOLOGY

Nylon is used for parachutes

The American military has adapted the synthetic fiber nylon to use for making parachutes. Parachutes have become an essential part of modern warfare, used by pilots for escaping from damaged aircraft, dropping spies behind enemy lines, and landing supplies and troops. Until now all parachutes have been made from silk spun by silk worms. Silk production is slow and costly. Nylon parachutes can be manufactured cheaply and on a massive scale to aid the Allied war effort.

A parachute canopy is made of many separate panels, which makes it extraordinarily strong, and confines any tears to only one part of the parachute. ▼

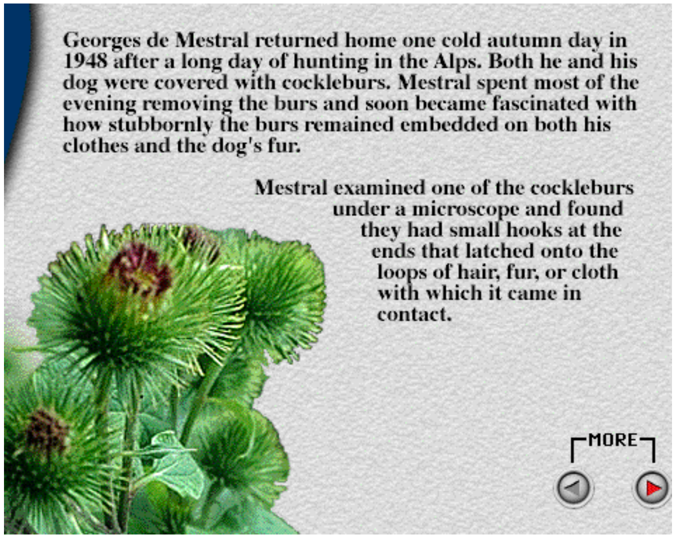
The history of the parachute

Leonardo da Vinci first recognized the principle of parachute descent in the 16th century, but Frenchman Louis-Sébastien Lenormand gave the first practical demonstration in 1783. His fellow countryman, André-Jacques Garnerin, made some exhibition jumps from 8,000 feet (2,400 meters) in England in 1802.

1940

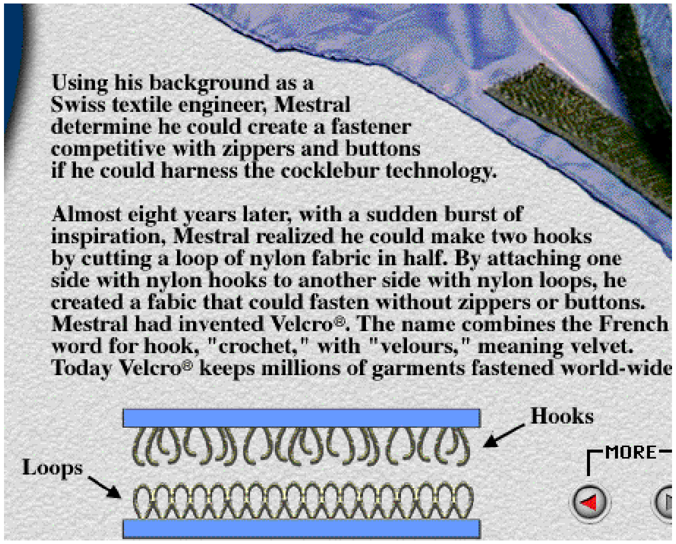
On May 15, crowds wait to purchase nylon stockings; 4 million pairs sold in a few hours.

Velcro



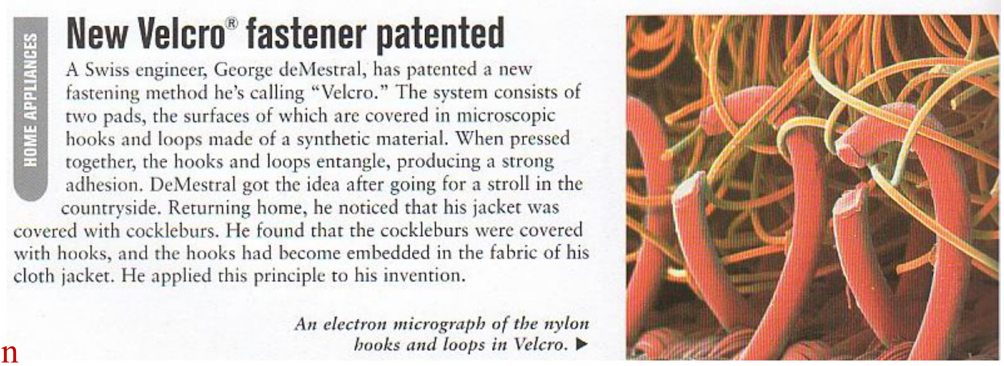
Georges de Mestral returned home one cold autumn day in 1948 after a long day of hunting in the Alps. Both he and his dog were covered with cocklebururs. Mestral spent most of the evening removing the burs and soon became fascinated with how stubbornly the burs remained embedded on both his clothes and the dog's fur.

Mestral examined one of the cockleburs under a microscope and found they had small hooks at the ends that latched onto the loops of hair, fur, or cloth with which it came in contact.



Using his background as a Swiss textile engineer, Mestral determine he could create a fastener competitive with zippers and buttons if he could harness the cocklebur technology.

Almost eight years later, with a sudden burst of inspiration, Mestral realized he could make two hooks by cutting a loop of nylon fabric in half. By attaching one side with nylon hooks to another side with nylon loops, he created a fabic that could fasten without zippers or buttons. Mestral had invented Velcro®. The name combines the French word for hook, "crochet," with "velours," meaning velvet. Today Velcro® keeps millions of garments fastened world-wide



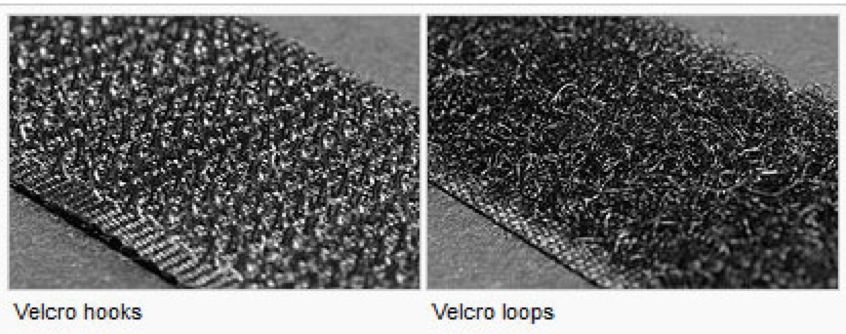
HOME APPLIANCES

New Velcro® fastener patented

A Swiss engineer, George deMestral, has patented a new fastening method he's calling "Velcro." The system consists of two pads, the surfaces of which are covered in microscopic hooks and loops made of a synthetic material. When pressed together, the hooks and loops entangle, producing a strong adhesion. DeMestral got the idea after going for a stroll in the countryside. Returning home, he noticed that his jacket was covered with cockleburs. He found that the cockleburs were covered with hooks, and the hooks had become embedded in the fabric of his cloth jacket. He applied this principle to his invention.

An electron micrograph of the nylon hooks and loops in Velcro. ▶

Nylon, Polyesters, Teflon

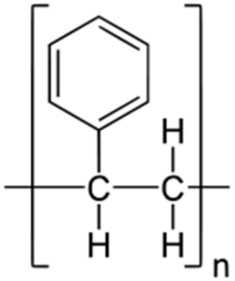


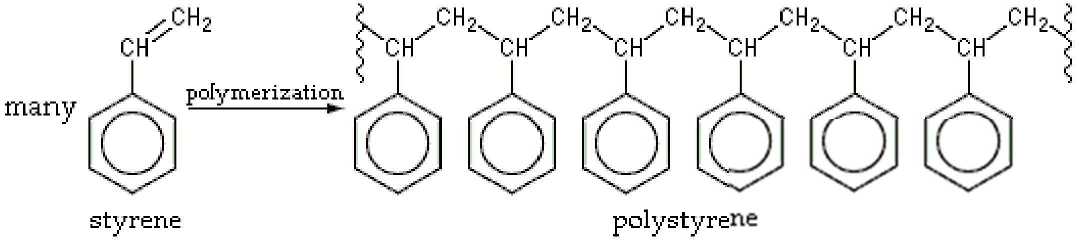
Velcro hooks

Velcro loops

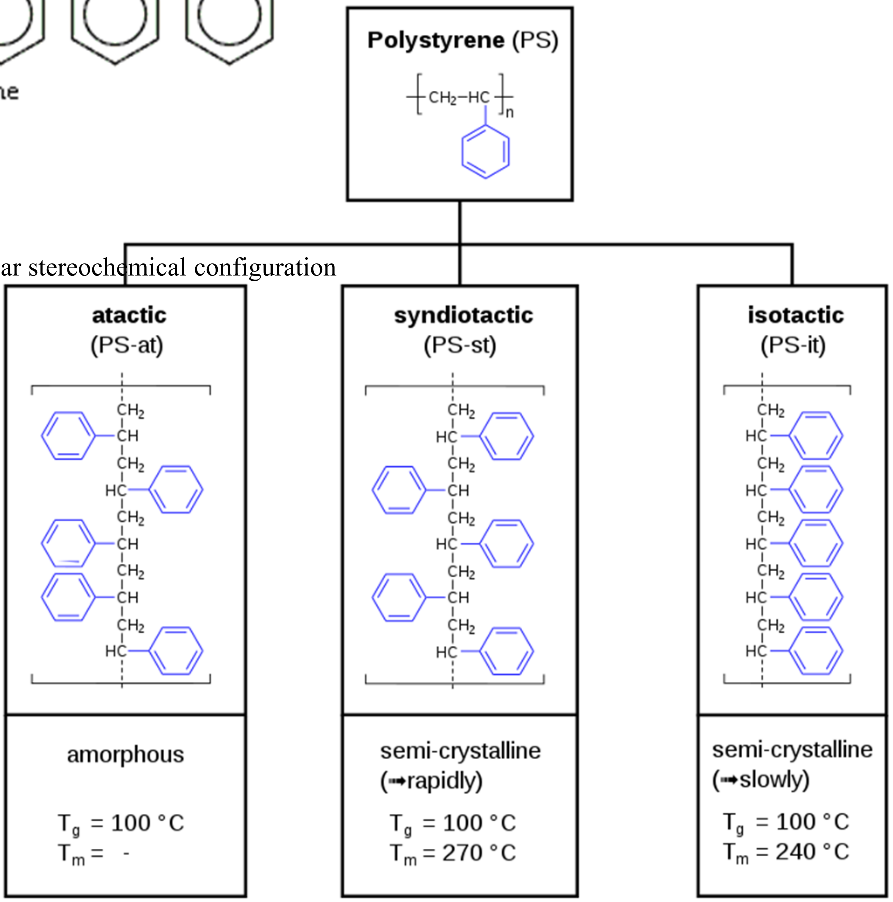
Polystyrene

1937





https://en.wikipedia.org/wiki/Polystyrene

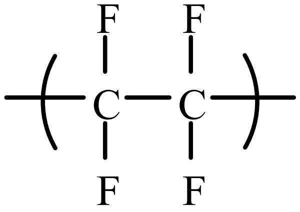


No regular stereochemical configuration

Polystyrene is ideal for disposable applications, because of its low price, rigid structural properties, and its transparency.
Properties: Light weight, stiff, easily processed thermally stable, transparency.
Used in insulating materials, packaging materials, housewares, luggage, toys.

Poly(tetrafluoro ethylene)

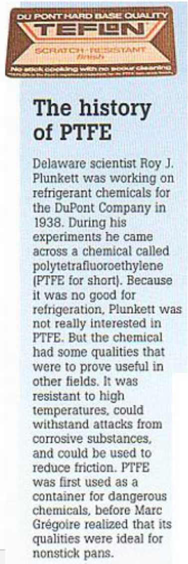
1938



$$-\!\left(\mathrm{CF_2-CF_2}\right)\!-$$

During World War II, designers of the atomic bomb utilized Teflon to manufacture gaskets and linings that could resist the bomb's corrosive uranium hexafluorides.

Properties: Non-stick, heat resistant, abrasion resistant, corrosion and chemical resistant, hydrophobic.
Used in automotive fasteners, lubricants, valves, pump linings, gaskets, frying pans, garden tools.



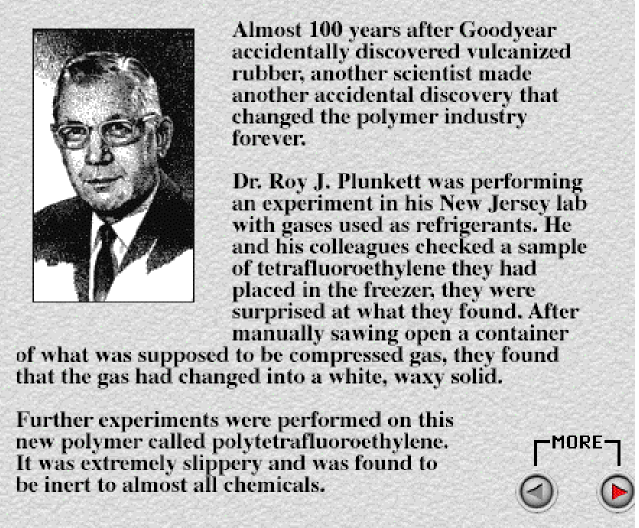
The history of PTFE

Delaware scientist Roy J. Plunkett was working on refrigerant chemicals for the DuPont Company in 1938. During his experiments he came across a chemical called polytetrafluoroethylene (PTFE for short). Because it was no good for refrigeration, Plunkett was not really interested in PTFE. But the chemical had some qualities that were to prove useful in other fields. It was resistant to high temperatures, could withstand attacks from corrosive substances, and could be used to reduce friction. PTFE was first used as a container for dangerous chemicals, before Marc Grégoire realized that its qualities were ideal for nonstick pans.

Nonstick (Teflon®-coated) pans introduced 1955

French engineer Marc Grégoire has come up with a winner for the kitchen. Aware that the chemical PTFE could be used to reduce friction, Grégoire used it to stop his fishing line from sticking. He came up with a PTFE coating for pans when his wife asked if he could stop food from sticking to her saucepans. The couple believe that cooks everywhere will want to use nonstick saucepans, and so they have founded a company, called Tefal®, to manufacture them.

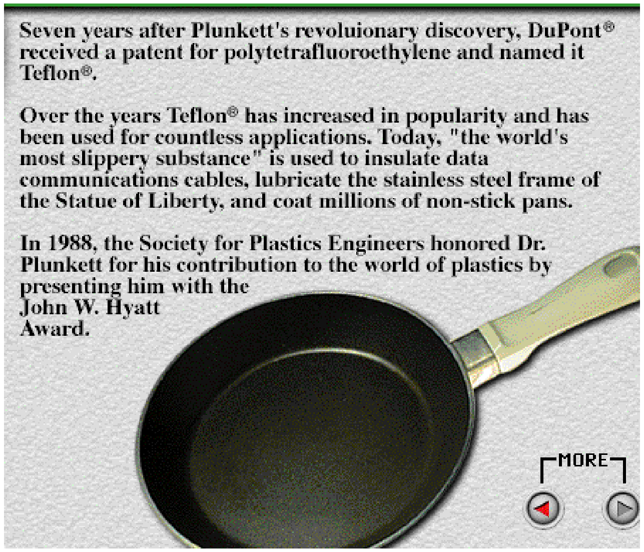
▲ *Grégoire is already selling millions of his Teflon-coated pans.*



Almost 100 years after Goodyear accidentally discovered vulcanized rubber, another scientist made another accidental discovery that changed the polymer industry forever.

Dr. Roy J. Plunkett was performing an experiment in his New Jersey lab with gases used as refrigerants. He and his colleagues checked a sample of tetrafluoroethylene they had placed in the freezer, they were surprised at what they found. After manually sawing open a container of what was supposed to be compressed gas, they found that the gas had changed into a white, waxy solid.

Further experiments were performed on this new polymer called polytetrafluoroethylene. It was extremely slippery and was found to be inert to almost all chemicals.

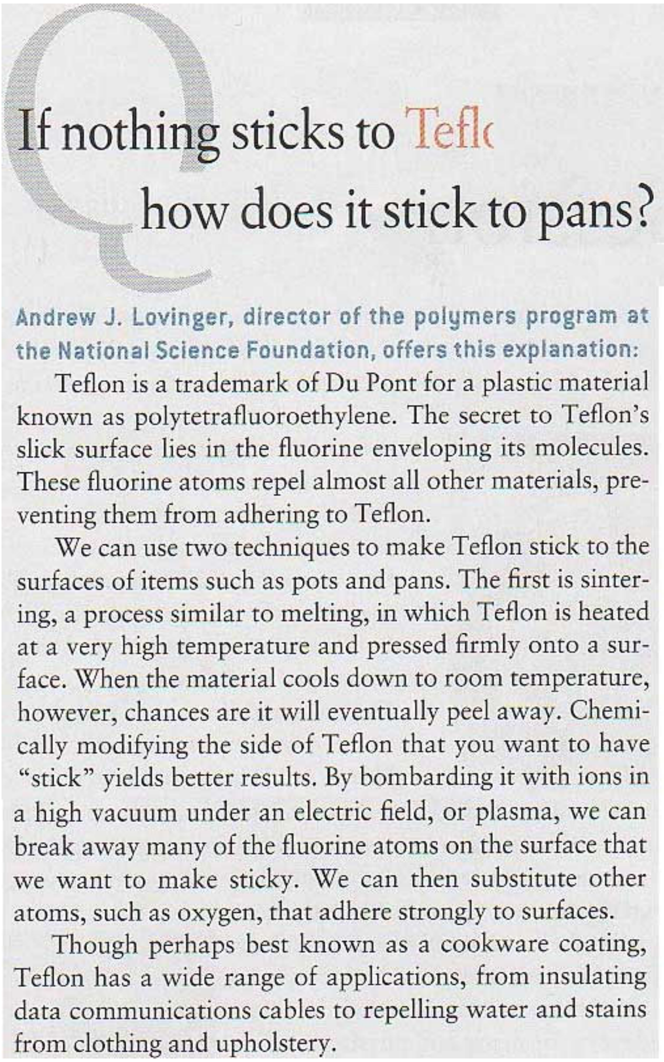


Seven years after Plunkett's revoluionary discovery, DuPont® received a patent for polytetrafluoroethylene and named it Teflon®.

Over the years Teflon® has increased in popularity and has been used for countless applications. Today, "the world's most slippery substance" is used to insulate data communications cables, lubricate the stainless steel frame of the Statue of Liberty, and coat millions of non-stick pans.

In 1988, the Society for Plastics Engineers honored Dr. Plunkett for his contribution to the world of plastics by presenting him with the John W. Hyatt Award.

Poly(tetrafluoro ethylene)



If nothing sticks to Tefl
how does it stick to pans?

Andrew J. Lovinger, director of the polymers program at the National Science Foundation, offers this explanation:

Teflon is a trademark of Du Pont for a plastic material known as polytetrafluoroethylene. The secret to Teflon's slick surface lies in the fluorine enveloping its molecules. These fluorine atoms repel almost all other materials, preventing them from adhering to Teflon.

We can use two techniques to make Teflon stick to the surfaces of items such as pots and pans. The first is sintering, a process similar to melting, in which Teflon is heated at a very high temperature and pressed firmly onto a surface. When the material cools down to room temperature, however, chances are it will eventually peel away. Chemically modifying the side of Teflon that you want to have "stick" yields better results. By bombarding it with ions in a high vacuum under an electric field, or plasma, we can break away many of the fluorine atoms on the surface that we want to make sticky. We can then substitute other atoms, such as oxygen, that adhere strongly to surfaces.

Though perhaps best known as a cookware coating, Teflon has a wide range of applications, from insulating data communications cables to repelling water and stains from clothing and upholstery.

This Is How Teflon Is Coated On Utensils To Make Non-Stick Cookware (Aayesha Arif . March 27, 2017) Teflon coated pans are any cooks heaven; saving them from scraping, scratching, scrubbing, and crying. Crying, of course! No one wants to wash sticky, burnt pans. Non-stick utensils have been around for 50 years now. Teflon is a unique polymer that repels most things, so the question is, how do the manufacturers get it to stick to the pans? The Teflon coating process uses sand, heat, vacuum, and some other chemicals.

Teflon was a polymer that resulted as an accident in 1938 at Dupont's Jackson Lab. Dr. Roy J. Plunkett was experimenting with refrigerants and froze a sample of tetrafluoroethylene which polymerized spontaneously. The polymer was called polytetrafluoroethylene (PTFE) and was known as the most slippery material in existence. Several years later, it came to be known as Teflon. PTFE is amazing for use on utensils to keep them non-stick, but a long chain of the carbon-fluorine mesh molecules in the strongest of bonds makes it practically inert. In addition to the super strength of the carbon-fluorine bond, fluorine is a natural repellant of most elements. These properties make the material both inert and non-stick.

Several different methods are used to make Teflon stick to pans.

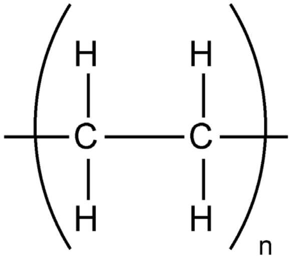
1. Dupont's Silverstone brand uses a method that begins with sandblasting the pans. This causes the surface to become uneven thus favoring adherence. On the sandblasted metal, a layer of Teflon is sprayed which is then baked at extremely high heat making the Teflon get a mechanical grip on the metal. Until an even thick layer is achieved, the process is repeated several times. This is not a chemical process as it only involves mechanical sticking of the polymer to the metal.
2. Another method called "sintering" also uses heat to make the Teflon stick, but the first step is different. The metal is first bombarded with ions in a high-vacuum electric field. The ions cause some fluorine bonds to break that allows the carbon atoms to bond with other materials, making it stick to the metal.
3. The third method makes use of chemicals. Instead of bombarding with ions, one surface of Teflon is treated with a reducing agent, thus breaking the strong carbon-fluorine bonds. The free carbon forms into unsaturated hydrocarbons that get the polymer to adhere to the pan.

Watch how a pan is made from scratch and how it is treated to make it non-stick.

https://wonderfulengineering.com/teflon-sticks-pans/

Polyethylene

1941



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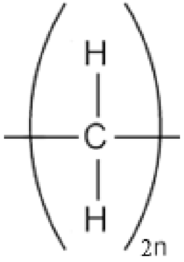
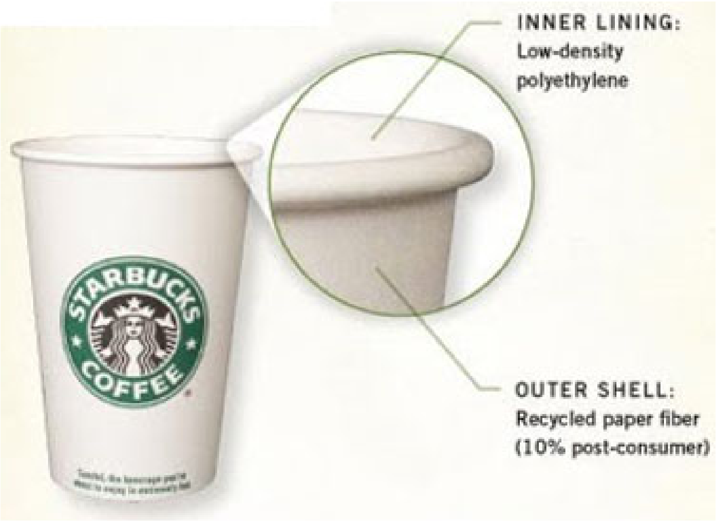


Polyethylene was developed in England for military purposes.

Properties: Break resistant, stiff, water resistant, nontoxic, sealable, odorless

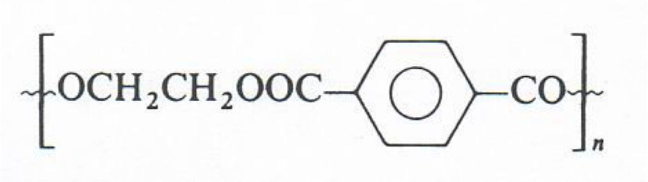
Used in packaging material, textiles, break resistant containers, bottles, toys, cables, greenhouse film.

Lining of paper milk cartons



Poly(ethylene Terephthalate) (PET)

1941



Dacron, Vycron (Fibers). Mylar (Films)

Shatter proof glass
Tossware

Polyester resins are a very large and diverse group of synthetic resins that can be obtained from many different starting materials,

Properties: Stiff, strong, abrasion resistant, chemical resistant, opaque, heat resistant.

Used in VCR and cassette tape, adhesive tape, textiles, plastic bottles, typewriter and computer keys, headlight brackets.

Beer in Plastic Bottles? Mitsubishi Plastics Works to Make it Happen.
Jun Hongo. Aug 20, 2015.

Plastic bottles are lighter and more durable than glass bottles, but are also known to allow permeation of gases including oxygen and carbon, which affect the taste of beer. Mitsubishi Plastic’s new bottles use a thin carbon film on the inside that makes them 10 times better at preventing the loss of oxygen, the spokesman said.

Beer

http://blogs.wsj.com/japanrealtime/2015/08/20/beer-in-plastic-bottles-mitsubishi-plastics-works-to-make-it-happen/

Rubber Balloons vs. Polyester Balloons

Which type of balloon floats longer?

Rubber latex

Diffusion of helium gas through polymer membranes

Polyester

Mylar® and Dacron ®, both by DuPont, are made by reacting terephthalic acid and ethylene glycol.

Properties: Mylar-Light resistant, heat resistant, chemical resistant,
Dacron-stiff, strong, wrinkle resistant.

Mylar- used in balloons, plastic wrap, bottles, seals, food packaging, medical packaging.
Dacron-Textiles.

Kapton

Kapton is a polyimide film used in flexible printed circuits (flexible electronics) and space blankets, which are used on spacecraft, satellites, and various space instruments. Invented by the DuPont Corporation in the 1960s, Kapton remains stable (in isolation) across a wide range of temperatures, from 4 to 673 K (−269 to +400 °C).

Spacecraft

Aluminized Kapton thermal cover was used on the Ultra Heavy Cosmic Ray Experiment

The descent stage of the Apollo Lunar Module, and the bottom of the ascent stage surrounding the ascent engine, were covered in blankets of aluminized Kapton foil to provide thermal insulation. During the return journey from the Moon, Apollo 11 astronaut Neil Armstrong commented that during the launch of the Lunar Module ascent stage, he could see "Kapton and other parts on the LM staging scattering all around the area for great distances."[9]

The NASA Jet Propulsion Laboratory has considered Kapton as a good plastic support for solar sails because of its durability in the space environment.[10]

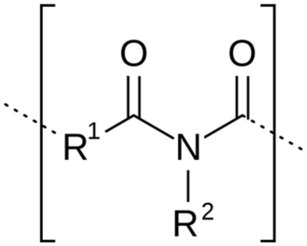
NASA's New Horizons spacecraft used Kapton in an innovative "Thermos bottle" insulation design to keep the craft operating between 283 and 303 K (10 and 30 °C) throughout its more than nine-year, 5-terametre (33-astronomical-unit) journey to rendezvous with the dwarf planet Pluto on 14 July 2015.[11] The main body is covered in lightweight, gold-colored, multilayered thermal insulation which holds in heat from operating electronics to keep the spacecraft warm. The thermal blanketing of 18 layers of Dacron mesh cloth sandwiched between aluminized Mylar and Kapton film also helped to protect the craft from micrometeorites.[12]

The James Webb Space Telescope sunshield is made of five Kapton E sheets coated with aluminum and doped silicon to reflect heat away from the spacecraft body.[13]

The crew aboard the International Space Station used Kapton tape to temporarily repair a slow leak in a Soyuz spacecraft attached to the Russian segment of the orbital complex in August 2018.[14] It was used again in October 2020 to temporarily seal a leak in the transfer chamber of the Zvezda Service Module of the ISS.[15]

https://en.wikipedia.org/wiki/Kapton

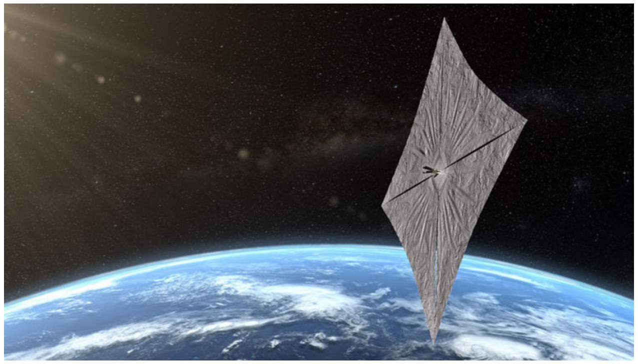
Polyimide



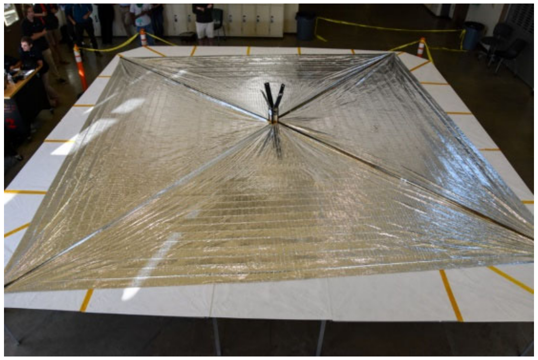
Test unit of the James Webb Space Telescope sunshield, made of aluminized Kapton

Space: How does solar sailing work?

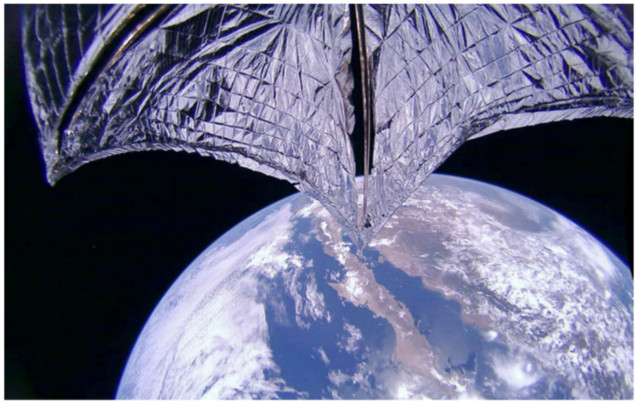
Time magazine recognizes LightSail 2 among year's top inventions
WEST LAFAYETTE, Ind. — A solar sail project led by Purdue University professor David Spencer was named as one of Time magazine's Best Inventions 2019. The LightSail 2 project launched into space during the summer, demonstrating the use of reflective sails to harness the momentum of sunlight for propulsion. Spencer, an associate professor in Purdue's School of Aeronautics and Astronautics, has been involved with the LightSail program since 2010 and serves as the project manager for LightSail 2. November 22, 2019
https://www.purdue.edu/newsroom/releases/2019/Q4/time-magazine-recognizes-lightsail-2-among-years-top-inventions.html



Josh Spradling / The Planetary Society
Artist's concept of LightSail 2 above Earth.



The Planetary Society's LightSail 2 spacecraft sits on its deployment table following a successful day-in-the-life test at Cal Poly San Luis Obispo on May 23, 2016.



LightSail 2 During Sail Deployment Sequence (Camera 2)
This image was taken during the LightSail 2 sail deployment sequence on 23 July 2019 at 11:48 PDT (18:48 UTC). Baja California and Mexico are visible in the background. LightSail 2's dual 185-degree fisheye camera lenses can each capture more than half of the sail. This image has been de-distorted and color corrected.

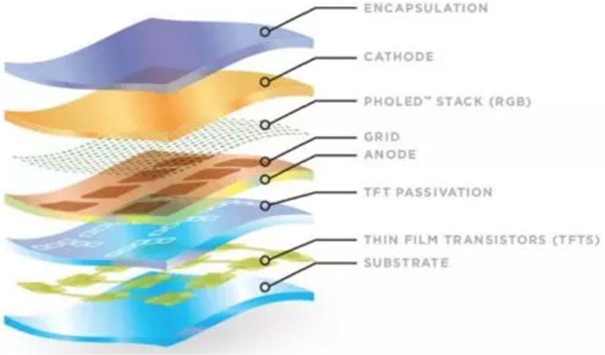
Light is made up of particles called photons. Photons don't have any mass, but as they travel through space they do have momentum. When light hits a solar sail—which has a bright, mirror-like surface—the photons in that light bounce off the sail (i.e, they reflect off it, just like a mirror). As the photons hit the sail their momentum is transferred to it, giving it a small push. As they bounce off the sail, the photons give it another small push. Both pushes are very slight, but in the vacuum of space where there is nothing to slow down the sail, each push changes the sail's speed.

What is a solar sail made of?
Current solar sails are made of lightweight materials such as Mylar or polyimide coated with a metallic reflective coating. LightSail 2 uses 4 triangular Mylar sails that are just 4.5 microns (1/5000th of an inch) thick. They unfold using 4 cobalt alloy booms that unwind like tape measures. The sails have a combined area of 32 square meters (344 square feet), about the size of a boxing ring.

How big does a solar sail have to be?
There is theoretically no minimum size for a solar sail, but for the same mass spacecraft, bigger sails will capture more sunlight and accelerate the spacecraft more quickly. A NASA team in the 1970s, headed by Planetary Society co-founder Louis Friedman, proposed a solar sail with a surface area of 600,000 square meters (6.5 million square feet), that would be used to send a spacecraft to rendezvous with Halley's comet. This is equivalent to a square of 800 meters (half-mile) by 800 meters – the size of 10 square blocks in New York City! Of course, the practicality of building and deploying such an enormous sail is questionable. But if such a sail could be successfully developed, amazing destinations could be reached.

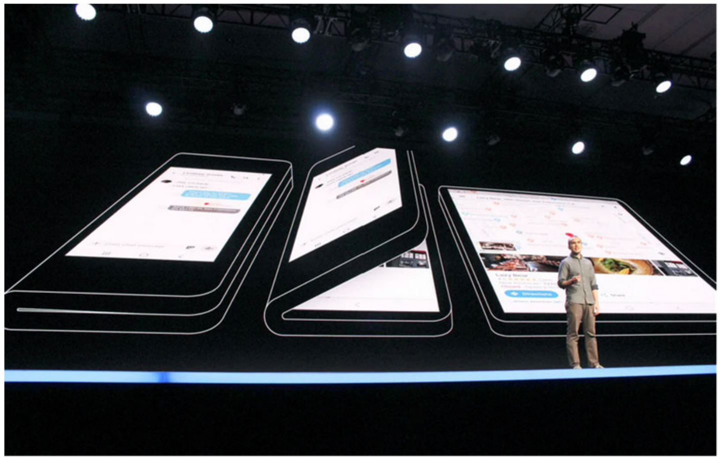
https://time.com/collection/best-inventions-2019/5733080/lightsail-2/
https://www.planetary.org/
https://www.planetary.org/explore/projects/lightsail-solar-sailing/what-is-solar-sailing.html

Foldable Screen

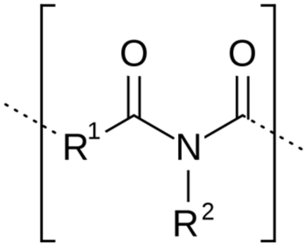


Cover layer — Also called the encapsulation layer, this is the layer that seals and protects the other layers. It's also the layer users touch when they interact with folding screens. In terms of materials, the cheaper option is polyimide (same as the substrate), while more recently, we've seen manufacturers adopt ultra-thin glass (UTG). UTG is tougher than plastic and feels more like regular glass, while still being able to bend. Samsung has been using UTG on the latest Z Flip and Z Fold.

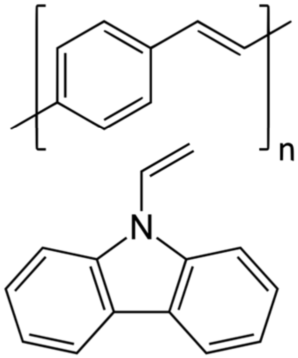
Substrate layer — Also called the board, this is the very base of the screen, which supports all the other layers. On a flexible display, the substrate is made of plastic or, less commonly, metal. Most flexible screen devices today use a substrate made of a polymer plastic called polyimide (PI). In addition to being flexible and insulating, polyimide features high mechanical strength and thermal stability.



Polyimide



Poly(p-phenylene vinylene)

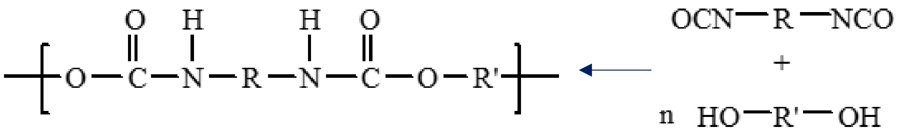


https://www.androidauthority.com/how-do-folding-screens-actually-work-3164822/
https://en.wikipedia.org/wiki/OLED

https://www.wired.com/story/foldable-phones-brief-history-and-uncertain-future/
https://www.zdnet.com/article/are-foldable-phones-the-next-big-thing/

Polyurethane

1941

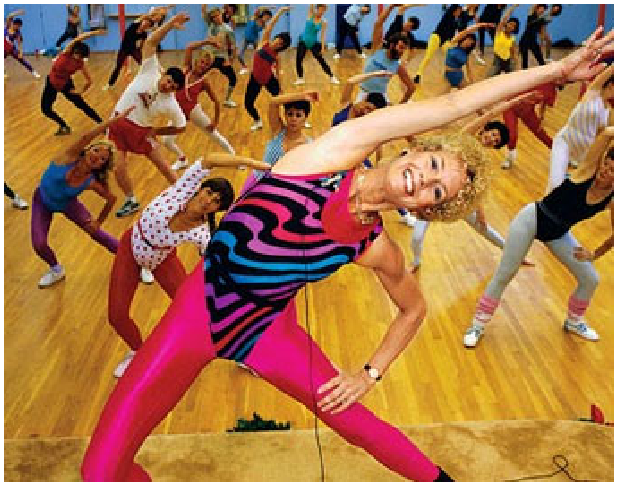


$$\left[O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R' \right] \longleftarrow \begin{array}{c} OCN-R-NCO \\ + \\ n\ HO-R'-OH \end{array}$$

Polyurethanes first used commercially in Germany in 1941. They can be both rigid and flexible, allowing may applications.

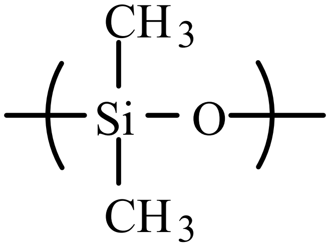
Properties: Rigid or flexible, soft, elastic.

Used in bathing suits, mattresses, under garments, automotive coatings, furniture.



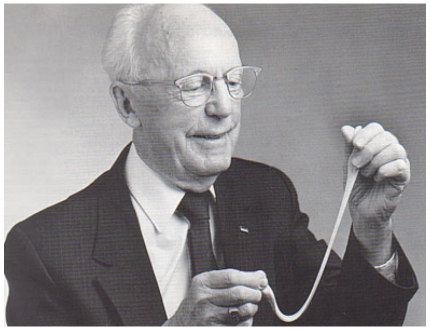
Poly(dimethylsiloxane) (PDMS)

1943

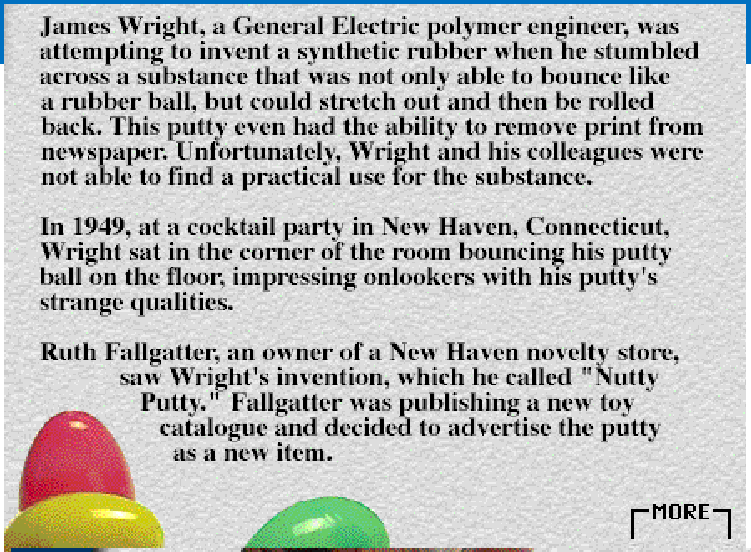


$$-\!\left(\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right)\!-$$

Silicone Rubber



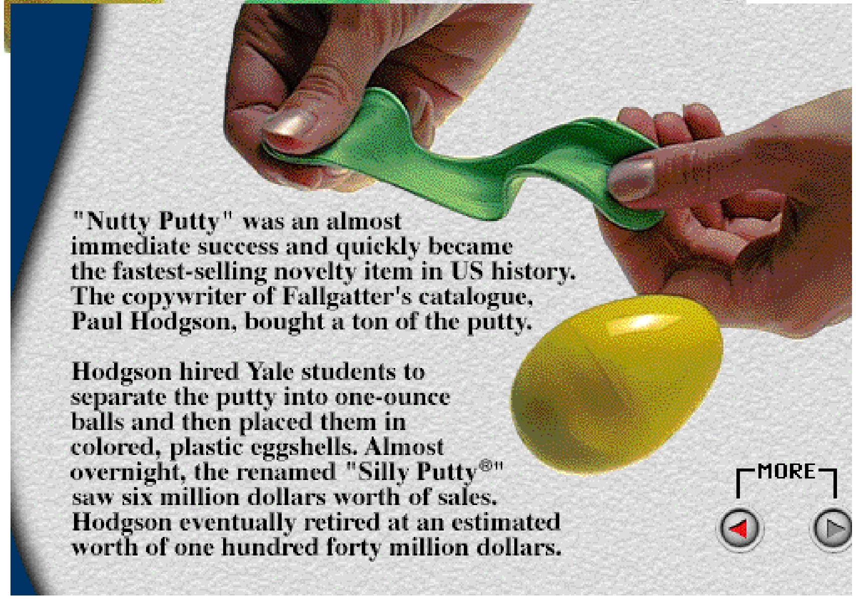
Dr. Earl Warrick (picture) and Dr. Rob Roy McGregor invented dilatant silicone compounds (such as bouncing putty) at Mellon Institute in 1943. A US. Patent resulted in 1947. Dr. McGregor later founded Dow Corning's Center for Aid to Medical Research. Dr. Warrick's career in research and management spanned 40 years at Mellon and Dow Corning. He invented the first silicone rubber that had sufficient strength and elasticity for commercial use.



James Wright, a General Electric polymer engineer, was attempting to invent a synthetic rubber when he stumbled across a substance that was not only able to bounce like a rubber ball, but could stretch out and then be rolled back. This putty even had the ability to remove print from newspaper. Unfortunately, Wright and his colleagues were not able to find a practical use for the substance.

In 1949, at a cocktail party in New Haven, Connecticut, Wright sat in the corner of the room bouncing his putty ball on the floor, impressing onlookers with his putty's strange qualities.

Ruth Fallgatter, an owner of a New Haven novelty store, saw Wright's invention, which he called "Nutty Putty." Fallgatter was publishing a new toy catalogue and decided to advertise the putty as a new item.



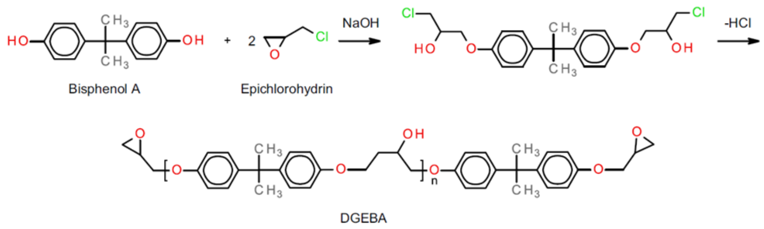
"Nutty Putty" was an almost immediate success and quickly became the fastest-selling novelty item in US history. The copywriter of Fallgatter's catalogue, Paul Hodgson, bought a ton of the putty.

Hodgson hired Yale students to separate the putty into one-ounce balls and then placed them in colored, plastic eggshells. Almost overnight, the renamed "Silly Putty®" saw six million dollars worth of sales. Hodgson eventually retired at an estimated worth of one hundred forty million dollars.

Epoxies

1947

Synthesis of diglycidyl ether of bisphenol A (DGEBA)



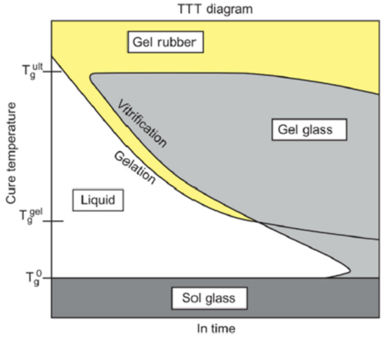
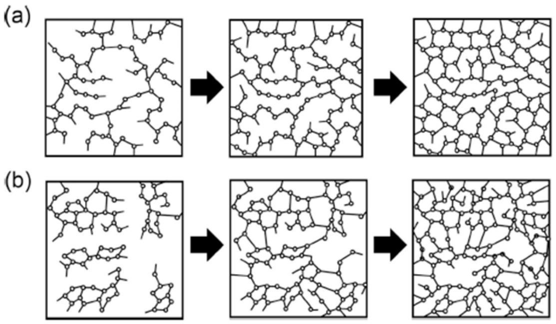


FIGURE 8.52 A typical time-temperature-transformation (TTT) diagram showing gelation and vitrification curves.

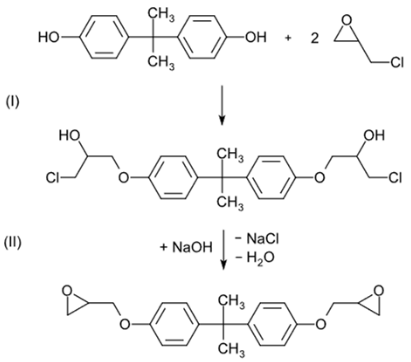


Network formation

Curing at lower temperatures

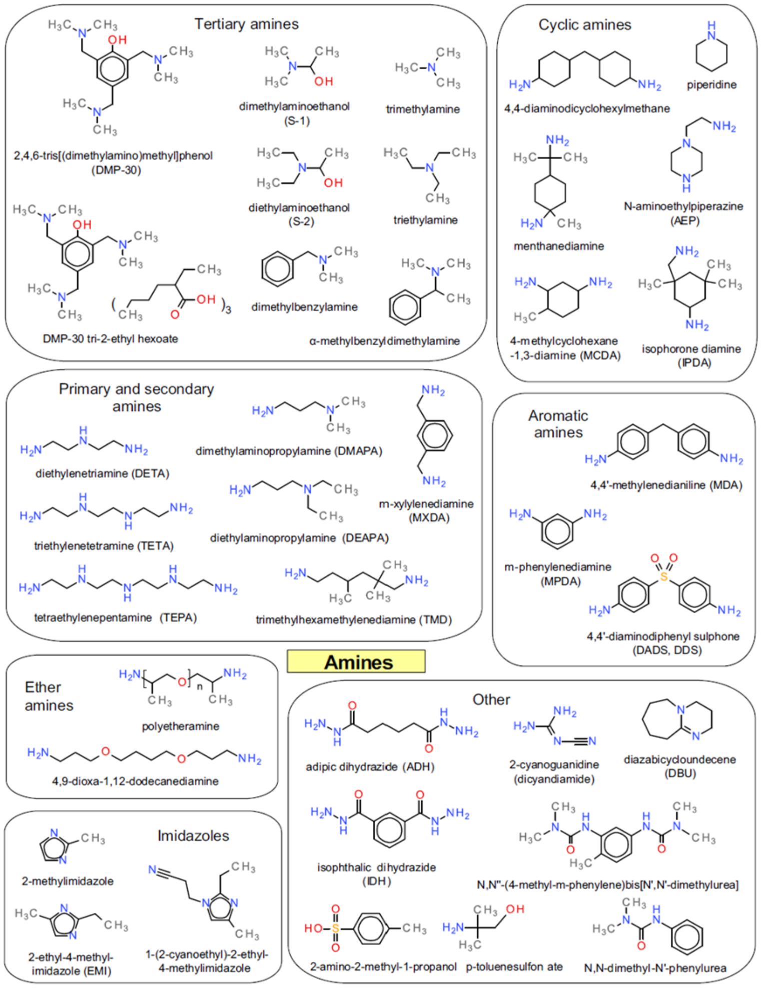
Curing at higher temperatures

Shundo 2022, Network formation and physical properties of epoxy resins for future practical applications



History

The historical development of epoxy compounds dates back to the late 19th century with initial accounts found as early as from 1863 [5]. However, only in the mid-20th century the commercial developments were realized [2]. In the late 1930s and early 1940s, two researchers independently synthesized the first epoxy resins from the reaction of bisphenol A with epichlorohydrin. The resulting diglycidyl ether of bisphenol A then became the first commercially available epoxy resin. Dr. Pierre Castan developed this material in 1938 while working at the De Trey Frères company in Zurich [6]. The resin was a thermoset obtained by reaction with phthalic anhydride (PA). Castan developed dental fixtures and casings [7]. In the United States, Dr. Sylvan O. Greenlee discovered the same material as Castan, but with a higher molecular weight. While working at Devoe and Raynolds, Greenlee's intention in synthesizing diglycidal ethers of bisphenol A resins was obtaining surface coatings. His first patent appeared in 1943 [8], followed by several more. Also in the early 1940s, Daniel Swern developed an alternate route to epoxy formation by formulating resins through the reaction of peroxy acids with olefins. This development is in close resemblance to the current commercial processes used in the creation of epoxy compounds with plasticizers and stabilizers. In the decades that followed, a proliferation of new epoxies took place. Industrial usage of epoxies also became widespread with the first commercial production beginning in 1947. Since that time, the market for epoxy resins has continued its growth due to additional applications—worth $7.2 billion in 2018. Projections show further growth up to 6% annually [9].



Structures of some representative compounds belonging to different groups of amine epoxy-curing agents.

Faltynowicz 2022, Epoxies

Epoxy

Epoxy is the family of basic components or cured end products of epoxy resins. Epoxy resins, also known as polyepoxides, are a class of reactive prepolymers and polymers which contain epoxide groups. The epoxide functional group is also collectively called epoxy.[1] The IUPAC name for an epoxide group is an oxirane.

Epoxy resins may be reacted (cross-linked) either with themselves through catalytic homopolymerisation, or with a wide range of co-reactants including polyfunctional amines, acids (and acid anhydrides), phenols, alcohols and thiols (usually called mercaptans). These co-reactants are often referred to as hardeners or curatives, and the cross-linking reaction is commonly referred to as curing.

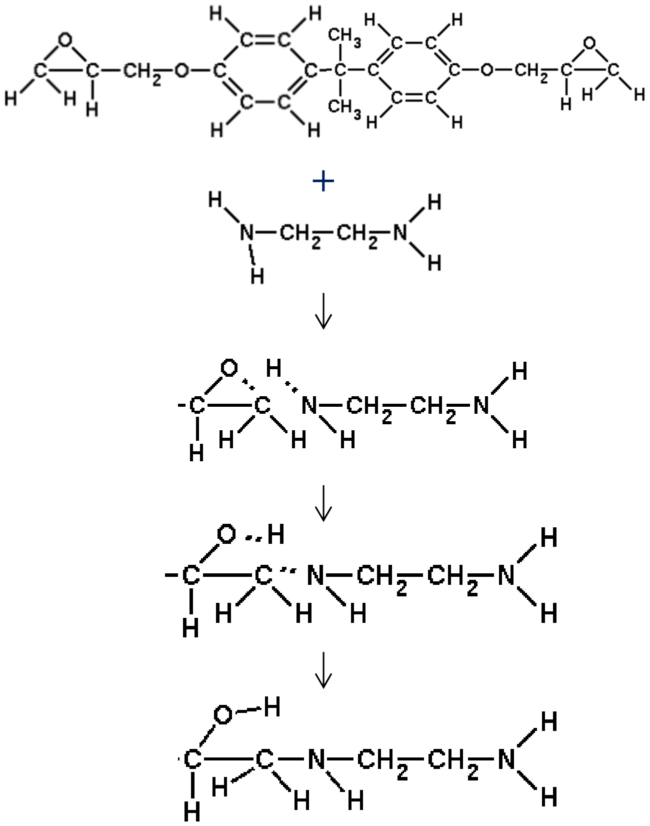
Reaction of polyepoxides with themselves or with polyfunctional hardeners forms a thermosetting polymer, often with favorable mechanical properties and high thermal and chemical resistance. Epoxy has a wide range of applications, including metal coatings, composites,[2] use in electronics, electrical components (e.g. for chips on board), LEDs, high-tension electrical insulators, paint brush manufacturing, fiber-reinforced plastic materials, and adhesives for structural[3] and other purposes.[4][5]

The health risks associated with exposure to epoxy resin compounds include contact dermatitis and allergic reactions, as well as respiratory problems from breathing vapor and sanding dust, especially when not fully cured.[6][7][8]

Condensation of epoxides and amines was first reported and patented by Paul Schlack of Germany in 1934.[9] Claims of discovery of bisphenol-A-based epoxy resins include Pierre Castan[10] in 1943. Castan's work was licensed by Ciba, Ltd. of Switzerland, which went on to become one of the three major epoxy resin producers worldwide. Ciba's epoxy business was spun off as Vantico in the late 1990s, which was subsequently sold in 2003 and became the Advanced Materials business unit of Huntsman Corporation of the United States. In 1946, Sylvan Greenlee, working for the Devoe & Raynolds Company, patented resin derived from bisphenol-A and epichlorohydrin.[11] Devoe & Raynolds, which was active in the early days of the epoxy resin industry, was sold to Shell Chemical; the division involved in this work was eventually sold, and via a series of other corporate transactions is now part of Hexion Inc.[12]

https://en.wikipedia.org/wiki/Epoxy#History

Epoxy resins are thermosetting resins that emerged in the world market in 1946.
The resins are useful when combined with fibrose reinforcements, providing mechanical strength.
Used in glue, circuit boards, switch coils, insulators for power transmission systems, socket motors coatings.



There’s a Plastic Film in Every Can

https://bioplasticsnews.com/2019/07/12/theres-a-plastic-film-in-every-can/

Bisphenol A - Toxic Plastics Chemical in Canned Food

Independent laboratory tests found a toxic food-can lining ingredient associated with birth defects of the male and female reproductive systems in over half of 97 cans of name-brand fruit, vegetables, soda, and other commonly eaten canned goods. The study was spearheaded by the Environmental Working Group (EWG) and targeted the chemical bisphenol A (BPA), a plastic and resin ingredient used to line metal food and drink cans. There are no government safety standards limiting the amount of BPA in canned food.

https://www.ewg.org/research/bisphenol-toxic-plastics-chemical-canned-food

Coatings

There’s always a thin plastic layer (coating) inside drink cans to protect the food or liquid and to protect the cans from corrosion. Every soda contains phosphoric and citric acid and it’s thus necessary to add a hidden liner inside the can to prevent the beverage from reacting with the metal.

Coatings contain different additives, e.g. agents to increase surface slipping as well as abrasion and scratch resistance of can coatings, lubricants, anti-foaming agents, adhesives, scavengers for hydrochloric acids, and pigments.

Epoxy-based coatings have the highest market share (>90%). The problem is that epoxy contains **bisphenol A (BPA)** and leaching of BPA into the can’s contents has been recognised as a potential health hazard

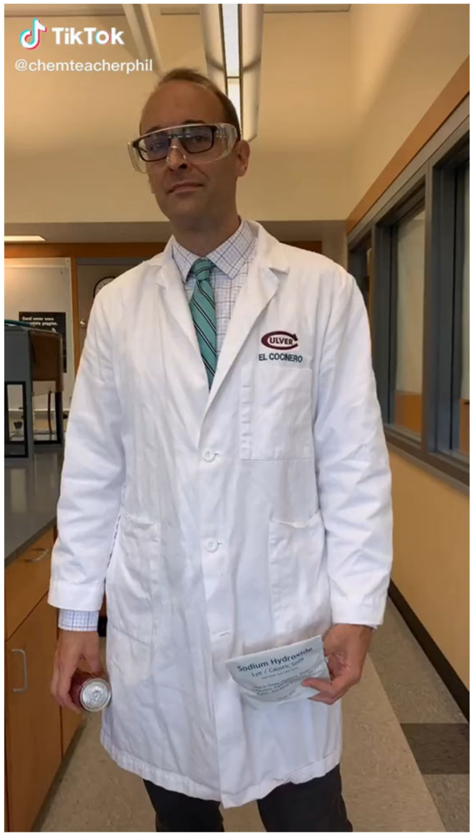
Epoxy Alternatives

Acrylic and polyester coatings are currently used as first generation alternatives to epoxy coatings and, more recently, polyolefin and non-BPA epoxy coatings were developed.

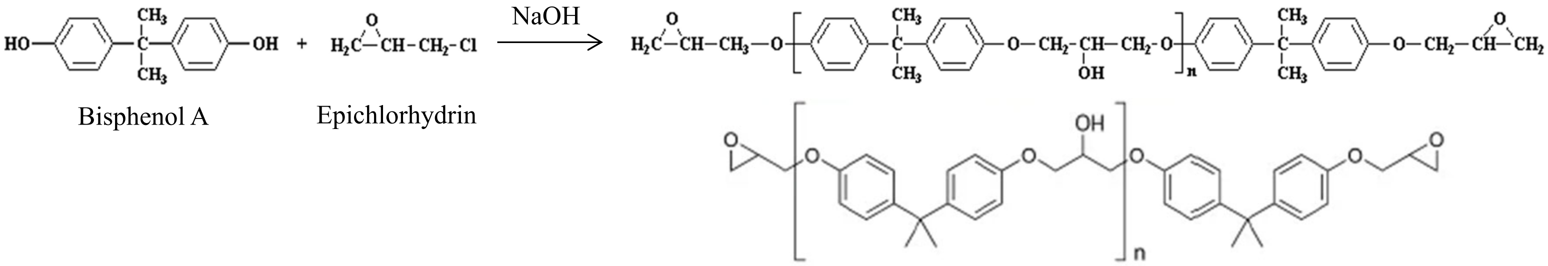
Further inventions include BPA capturing systems and top coatings. Most of these alternative coatings are more expensive than epoxy coatings and may not display the same array of characteristics with respect to their stability and universal applicability yet.

https://bioplasticsnews.com/2020/07/22/cans-sustainable-plastic-bottles/

Plastic Liners



https://www.pslc.ws/mactest/eposyn.htm
https://www.azom.com/article.aspx?ArticleID=23002



To line the hundred billion beverage cans we Americans gobble up every year takes about twenty million gallons of epoxy coatings. Creating those coatings takes a cross-linking resin, curing catalysts, and some additives to give it color or clarity, lubrication, antioxidative properties, flow, stability, plasticity, and a smooth surface. The resin is usually epoxy, but it may also be vinyl, acrylic, polyester, or oleoresin, and could even be styrene, polyethylene, or polypropylene. The mixture also requires either a solvent, so that the epoxy can cure when baked, or a photo-initiator, so that the epoxy can cure when exposed briefly to ultraviolet (UV) light. The cross-linking agent of choice for the most tenacious epoxy coating is bisphenol-A, or BPA. According to coatings specialists, roughly 80 percent of that epoxy is BPA.

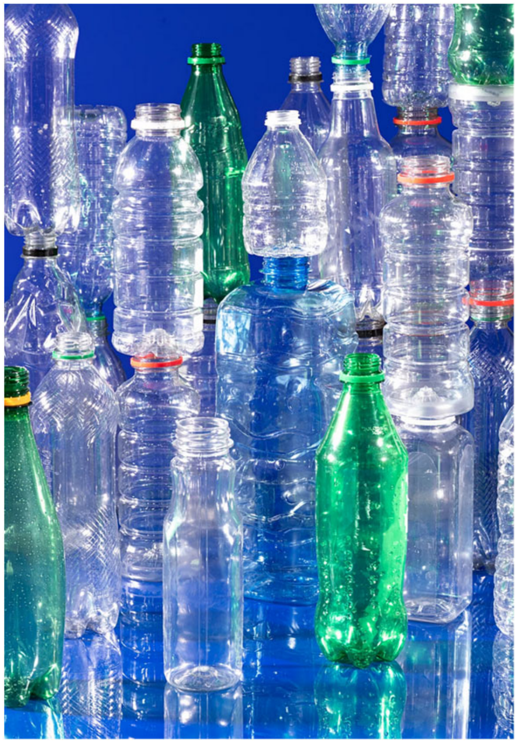
https://www.wired.com/2015/03/secret-life-aluminum-can-true-modern-marvel/

About BPA: Epoxy Resins

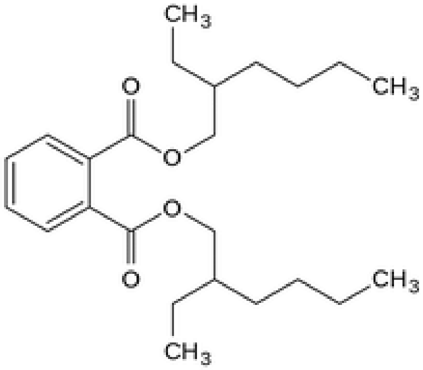
Epoxy resins, most of which are made from bisphenol A (BPA), are essential to modern life, public health, efficient manufacturing, and food safety. They are used in a wide array of consumer and industrial applications because of their toughness, strong adhesion, chemical resistance, and other specialized properties. Used in products we rely on every day, epoxy resins are found in cars, boats, and planes, and as components in fiber optics and electrical circuit boards. Epoxy linings create a protective barrier in metal containers to prevent canned foods from becoming spoiled or contaminated with bacteria or rust. Wind turbines, surfboards, composite materials holding up your house, even the frets on a guitar — all benefit from the durability of epoxies.

https://www.factsaboutbpa.org/wp-content/uploads/2020/08/About-BPA-Epoxy-Resins.pdf

Bisphenol A (BPA) & Phthalates



The plastics used to create these water bottles contain hormone disrupting chemicals including phthalates, which can leach into the water.



DEHP

How phthalates enter our body

Called "everywhere chemicals," phthalates are a family of chemical compounds that are manmade and often used as plasticizers to lend softness, flexibility, and durability to materials like polyvinyl chloride or PVC—one of the most widely used plastics—and synthetic rubber. They are present in many household items ranging from food packaging and processing equipment to shower curtains, building materials, and car interiors. Phthalates are also used as solvents in cosmetics and other personal care products and to coat or encapsulate certain pharmaceutical pills and dietary supplements.

How 'everywhere chemicals' help uterine fibroids grow

Scientists are just beginning to learn how these common tumors in women are linked to phthalates—chemicals found in hundreds of everyday household items and cosmetics.

By Priyanka Runwal

https://www.nationalgeographic.com/magazine/article/how-everywhere-chemicals-help-uterine-fibroids-grow-phthalates

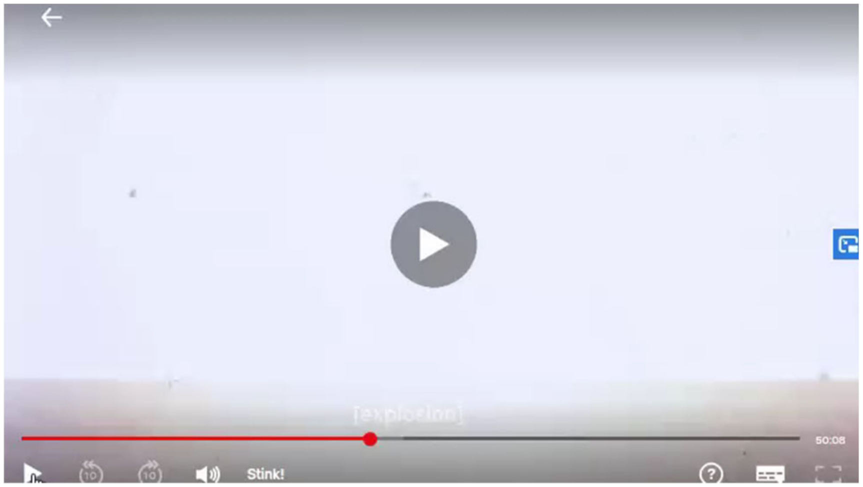
Plasticizers: Stink!

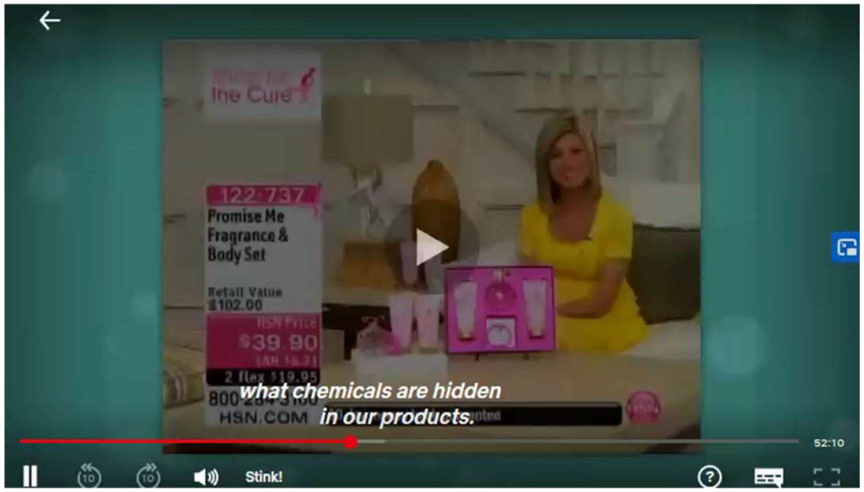
Plastics may contain toxic chemicals

Stink! (https://stinkmovie.com/)

https://en.wikipedia.org/wiki/Stink!

Stink! is a 2015 American documentary film directed by Jon J. Whelan. The film explores why there are toxins and carcinogens legally hidden in American consumer products. The film received multiple positive reviews. *Stink!* has appeared in 25 film festivals globally, and won multiple awards including Best Documentary Feature, at several film festivals. It premiered on Netflix on November 1, 2018.[1]





Bisphenol A (BPA): ≤0.018 ng/pound of body weight /day

European regulators propose ‘dramatic’ new regulation for BPA: Their new recommendation would slash daily exposure limits by a factor of 100,000.
Joseph Winters (News & Politics Fellow) Dec 21, 2021 (https://grist.org/regulation/europe-proposes-dramatic-new-regulation-for-bpa/)

Scientists have known for decades that bisphenol A, or BPA, a plastic additive used in products like food storage containers and food can liners, is harmful to human health. And the mountain of science on the chemical is finally spurring tighter regulations in Europe.

The European Food Safety Authority, or EFSA, proposed new safety standards for BPA last week, radically scaling down the recommended exposure limit by a factor of 100,000, to just 0.018 nanograms per pound of body weight per day. The new standard, based on years of scientific evidence of BPA’s harms to people’s immune systems and bodily development, is so low that it would all but bar BPA from use in any products that come into contact with food. “In effect it’s a ban,” Terry Collins, a green chemist at Carnegie Mellon University, told me. “It’s an incredibly dramatic number.”

The chemical industry first began using BPA for plastics in the 1940s, when they started using it to make a hard plastic material called polycarbonate, as well as durable epoxy resins. BPA became prevalent in all sorts of everyday plastic products like water bottles and dishware. It also made its way into food packaging such as plastic leftover containers and **the lining on the inside of cans of food, where it helps prevent the food from corroding the inside of the can**.

Although there are no restrictions on BPA use in the U.S. except for baby bottles and infant formula packaging, many manufacturers say they have phased it out. The Can Manufacturers Institute claims that more than 95 percent of canned food contains BPA-free lining. But other research suggests it was still widespread as recently as 2016, detected by infrared spectrometer in as many as 67 percent of cans.

According to Collins, the problem with BPA is that it messes with people’s hormones. It mimics estrogen, causing endocrine disorders in both men and women and potentially contributing to male infertility by decimating sperm counts. Other research has linked BPA to increased blood pressure, type 2 diabetes, heart problems, and problems with brain and prostate development in young children. Public health and environmental advocates have long advocated for it to be much more strongly regulated, if not phased out altogether. “BPA is a toxic chemical that has no place in our food supply,” said Sarah Janssen, a senior scientist in the Natural Resource Defense Council’s public health program, in a 2012 statement responding to the U.S. Food and Drug Administration’s declination to ban BPA.

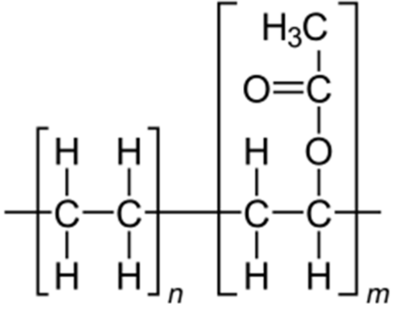
If approved following a public comment period that lasts until early February, the EFSA’s guidelines for BPA will be some of the strictest in the world — far more stringent than in the U.S., where the Environmental Protection Agency’s daily recommended exposure threshold of 22.7 micrograms per pound of body weight has not been updated since 1988. Even before the EFSA’s proposal last week, the U.S. recommendation was already more than 12 times higher than the European standard. Other countries like Denmark and Belgium have an outright ban on BPA in food contact materials for children. France has forbidden it in all nonindustrial uses since 2015.

Although scientists have framed the EFSA’s proposed rule as a necessary step toward protecting public health, many have also raised concerns that it does not apply to paper products like receipts, which are often lined with a BPA coating. It also fails to regulate potentially dangerous replacement chemicals. “The industry will likely comply by shifting to other chemicals with concerning health profiles,” Laura Vandenberg, a professor at University of Massachusetts Amherst School of Public Health and Health Sciences, told Grist.

However, Vandenberg and others said the new guideline highlights a growing recognition of the need for more stringent regulation, and the fact that BPA is unsafe even in tiny doses. “We can no longer accept the industry’s statement that ‘exposures are too low to hurt,’” Vandenberg said.

Poly(ethylene-co-vinyl acetate) (PEVA)

1956



Laminated, shatter proof glass

DuPont filed a patent in 1956 and introduced the Elvax range of materials in 1960. This is based on copolymerization products of ethylene with vinyl acetate and are normally produced either from bulk continuous polymerization or solution polymerization. The former produces low molecular weight copolymers useful for coatings, hot melt adhesives, etc., whilst the latter yields high molecular weight products for tougher applications.

As the level of vinyl acetate in the copolymer increases, the level of crystallinity found in polythene alone reduces from about 60% to 10%. This yields products ranging from materials similar to low density polythene to flexible rubbers. Common grades can contain from 2% to 50% vinyl acetate. Clarity, flexibility, toughness and solvent solubility increase with increasing vinyl acetate content. Of particular note is the retention of flexibility of EVA rubber grades down to (-70 °C) and because they are copolymers, problems due to plasticizer migration are not experienced.

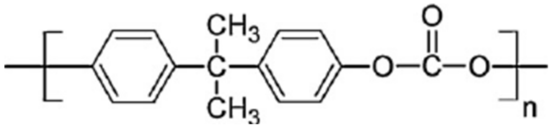
Good resistance to water, salt and other environments can be obtained but solvent resistance decreases with increasing vinyl acetate content. The copolymers can accept high filler and pigment loadings. Being thermoplastic EVA can be molded by extrusion, injection, blow molding, calendaring and rotational molding. Crosslinking with peroxides can produce thermoset products.

Applications are diverse, such as flexible shrink wrap, footware soles, hot melt and heat seal adhesives, flexible toys, tubing, wire coatings, medical gloves, masks, babies' dummies and bottle teats. Crosslinked foamed tires have been used for tough service. Many grades and modifications now exist to meet modern demands from these versatile EVA copolymer types.

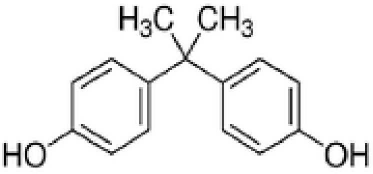
http://plastiquarian.com/?page_id=14280

Polycarbonate

1957



i use to do this when i was younger 💿



BPA

C&EN

news of the week

APRIL 28, 2008 EDITED BY WILLIAM G. SCHULZ & KENNETH J. MOORE

MOMENTUM BUILDS AGAINST BISPHENOL A

TOXICOLOGY: Move to eliminate chemical from some products begins

CANADA MOVED last week to become the world's first country to set exposure limits on bisphenol A (BPA), a high-volume chemical used to make polycarbonate and epoxy resins. U.S. politicians proposed similar measures, and a leading supplier of plastic drinking bottles announced that it will stop manufacturing products that contain the chemical.

Bowing to public concern over the health effects of BPA, bottle maker Nalgene said it will drop the use of polycarbonate. In addition, Wal-Mart, the world's largest retailer, announced it will stop stocking baby products containing the chemical immediately in Canada and early next year in the U.S. Toy store chain Toys 'R' Us has also announced a BPA phaseout for these products.

Scrutiny of BPA increased earlier this month with the release of a draft report by the U.S. National Toxicology Program (NTP) on the health effects of the chemical. The report concluded that although BPA is generally safe, there is "some concern" that it may cause neural and behavioral changes in infants and children at current exposure levels (C&EN, April 21, page 11).

The proposed ban in Canada targets polycarbonate baby bottles. Canadian Minister of Health Anthony P. Clement frames it as proactive. "Although our science tells us exposure levels to newborns and infants are below the levels that cause effects, it is better to be safe than sorry," he said, announcing the action. Barring any compelling information brought to light during a comment period that started on April 19, he added, the ban will take effect in mid-June.

Canada's decision is based on its risk assessment of the chemical. The study found that BPA is not a concern for adults but may pose a risk for newborns and infants.

Meanwhile, members of Congress are citing the NTP study in pushing for limits on BPA. Sen. Charles E. Schumer (D-N.Y.) announced plans to introduce legislation to ban BPA in all children's products and "food contact" containers, such as water bottles. On the House side, the Energy & Commerce Committee, led by Reps. John D. Dingell (D-Mich.) and Bart Stupak (D-Mich.), is investigating the safety of BPA in baby products as part of its oversight of FDA.

Manufacturers eliminating the chemical say they are taking action even in the absence of conclusive evidence of serious health risks. "Based on all the available scientific evidence, we continue to believe that Nalgene products containing BPA are safe for their intended use," says Steven Silverman, general manager of Nalgene's Outdoor line of polycarbonate containers. "However, our customers indicated they preferred BPA-free alternatives." Last week, a California mother filed a lawsuit against Nalgene claiming the company knew that BPA could leach from its bottles.

Nalgene recently introduced a new line of bottles manufactured with an Eastman Chemical copolyester called Tritan. CamelBak, another supplier of polycarbonate bottles, is also switching to the Tritan material. Last month, Eastman announced that it will expand capacity for the copolyester at its plant in Kingsport, Tenn.

In the infant care market, Playtex announced last week that it will phase out BPA-containing products by the end of the year. It is also distributing 1 million samples of a baby bottle product that employs disposable polyethylene bag inserts.

Polycarbonate resins account for roughly three-quarters of U.S. demand for BPA; epoxy resins for high-performance coatings make up nearly all the rest. Most uses of these products—including automotive parts, compact discs, flooring products, and electronics—are not affected by the BPA initiatives.

According to Mark Walton, communications leader for chemical and health issues at Dow Chemical, the number two U.S. producer of BPA, the impacted markets are "specialty" areas. "Our products tend not to be in the primary markets affected by the action in Canada," Walton says. "We are still trying to understand what kind of impacts current events could have on Dow's business."—RICK MULLIN AND SUSAN MORRISSEY

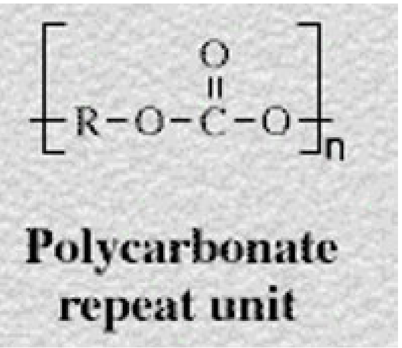
> **"Although our science tells us exposure levels [to bisphenol A by] newborns and infants are below the levels that cause effects, it is better to be safe than sorry."**
>
> —ANTHONY CLEMENT

Polycarbonate is being replaced in bottles by plastics such as Eastman Chemical's Tritan copolyester.

WWW.CEN-ONLINE.ORG 11 APRIL 28, 2008

Applications

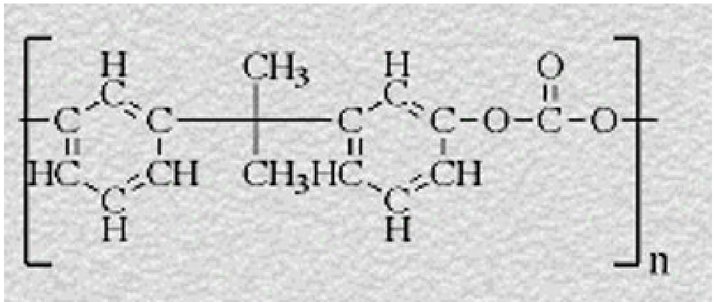
- **Clarity and Strength**
  Polycarbonate: Strong, light weight, UV resistant, scratch resistant. heat resistant, transparent.
  Used in safety glasses, airline windows, riot police shields, bullet-proof glass



Polycarbonate repeat unit

- **Lexan®**
  Made by GE. Tough, transparent, high tensile strength, temperature-resistant, light weight.

  Used in bicycle, motocycle, and football helmets, automobile and aircraft equipment, safety glass, unbreakable glass, signs, race car exterior.



Lexan® repeat unit

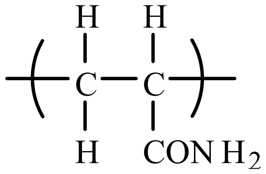
Polypropylene

1957

- **Greasy, Oily, and Fairly Stiff**
  Polypropylene: Hydrophobic, greasy, oily, fairly stiff, transparent. inexpensive
  Used in laminations, automobile interiors, automobile battery cases, textiles, toys, bottle caps, carpetting, street signs (STOP sign)

Polyacrylamide

1958



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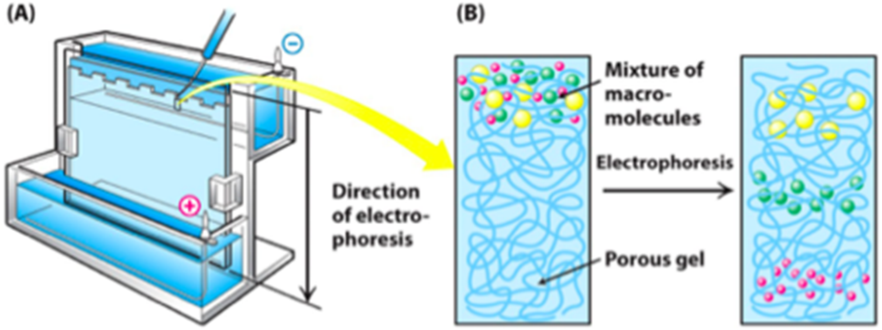
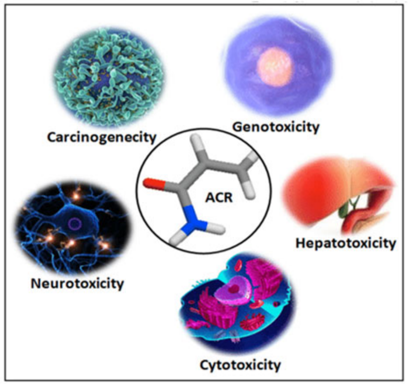


https://quizlet.com/435615222/bio-60-lab-5-sodium-dodecyl-sulfate-polyacrylamide-gel-electrophoresis-elisaantibodies-flash-cards/?src=search_page



Additional Evidence That Potato Chips Should Be Eaten Only In Moderation. ScienceDaily (Feb. 26, 2009) — A new study published in the March 2009 *American Journal of Clinical Nutrition* by Marek Naruszewicz and colleagues from Poland suggests that acrylamide from foods may increase the risk of heart disease. Acrylamide has been linked previously to nervous system disorders and possibly to cancer.

http://www.sciencedaily.com/releases/2009/02/090213161040.htm

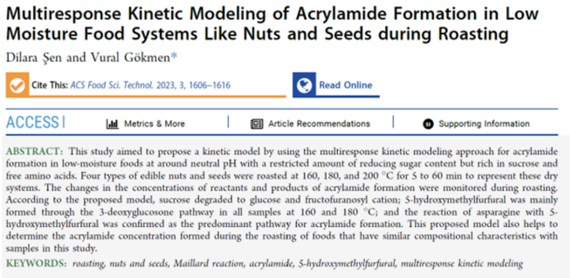
How to Make French Fries With Less Acrylamide (Feb. 26, 2010) — Researchers have developed a technique to to reduce acrylamide in French fries on an industrial scale. Acrylamide is a product that may cause cancer and was discovered in various ... > *read more*

Dietary Acrylamide Not Associated With Increased Lung Cancer Risk In Men (May 5, 2009) — Dietary acrylamide was not associated with an increased risk of lung cancer, according to data from a large prospective case-cohort ... > *read more*

Soaking Potatoes In Water Before Frying Reduces Acrylamide (Mar. 9, 2008) — Good news for chips lovers everywhere -- new research in the journal Science of Food and Agriculture shows that pre-soaking potatoes in water before frying can reduce levels of acrylamide. Acrylamide ... > *read more*

Acrylamide Not Linked To Breast Cancer, Study Finds (Aug. 24, 2007) — Foods that contain acrylamide are unlikely to cause breast cancer in women, according to preliminary results of a new study involving 100,000 US women. The finding is the largest epidemiological ... > *read more*

Polyacrylamide



Multiresponse Kinetic Modeling of Acrylamide Formation in Low Moisture Food Systems Like Nuts and Seeds during Roasting

Dilara Şen and Vural Gökmen*

Cite This: *ACS Food Sci. Technol.* 2023, 3, 1606−1616

ABSTRACT: This study aimed to propose a kinetic model by using the multiresponse kinetic modeling approach for acrylamide formation in low-moisture foods at around neutral pH with a restricted amount of reducing sugar content but rich in sucrose and free amino acids. Four types of edible nuts and seeds were roasted at 160, 180, and 200 °C for 5 to 60 min to represent these dry systems. The changes in the concentrations of reactants and products of acrylamide formation were monitored during roasting. According to the proposed model, sucrose degraded to glucose and fructofuranosyl cation; 5-hydroxymethylfurfural was mainly formed through the 3-deoxyglucosone pathway in all samples at 160 and 180 °C; and the reaction of asparagine with 5-hydroxymethylfurfural was confirmed as the predominant pathway for acrylamide formation. This proposed model also helps to determine the acrylamide concentration formed during the roasting of foods that have similar compositional characteristics with samples in this study.

KEYWORDS: *roasting, nuts and seeds, Maillard reaction, acrylamide, 5-hydroxymethylfurfural, multiresponse kinetic modeling*

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Sen 2023, Multiresponse kinetic modeling of acrylamide formation in low moisture food systems

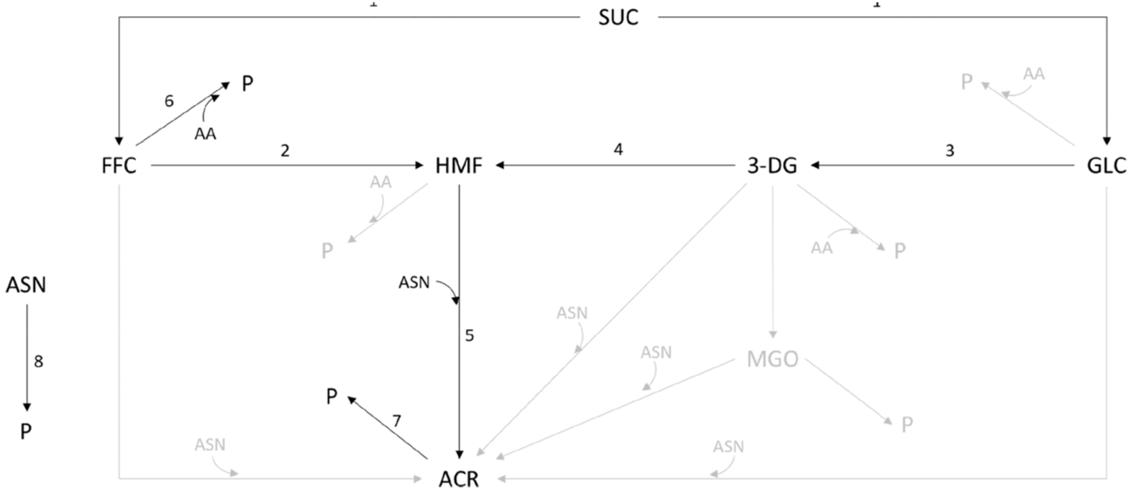
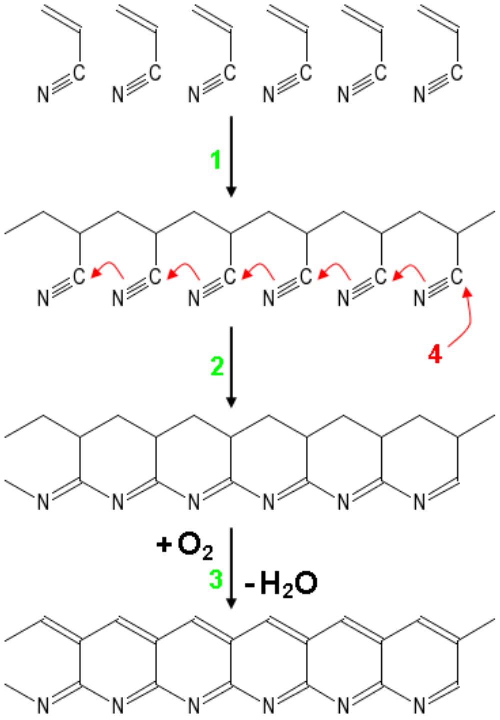


Figure 1. Comprehensive model for acrylamide formation in nuts and seeds during roasting. The gray steps are not included in the proposed kinetic model.

3-DG: 3-Deoxyglucosone;
AA: Total amino acids;
ACR: Acrylamide;
ASN: Asparagine;
FFC: Fructofuranosyl cation;
GLC: Glucose;
HMF: 5-Hydroxymethyl furfural;
MGO: Methylglyoxal;
P: Products;
SUC: Sucrose;

Carbon Fiber from Petroleum

1958



Polyacrylonitrile (PAN)

(1) Polymerization of acrylonitrile to PAN

(2) Cyclization during low temperature process

(3) High temperature oxidative treatment of carbonization
(hydrogen is removed)

(4) Process of graphitization: nitrogen is removed and chains are joined
into graphite planes

(http://en.wikipedia.org/wiki/Carbon_%28fiber%29)

A race car with a carbon fiber body. Rhots

Carbon Fiber from Plants

Scientists are making carbon fiber from plants instead of petroleum.
Cheaper, plant-based carbon fiber could be used to make lighter cars that consume less fuel. (By Jeremy Deaton Nexus Media January 12, 2018.)

Carbon fiber is the Superman of materials. Five times stronger than steel and a fraction of the weight, it is used in everything from tennis rackets to golf clubs to bicycles to wind turbine blades to passenger airplanes to Formula One race cars. There's just one catch: Carbon fiber is made from oil and other costly ingredients, making the end product exceptionally expensive. That's why carbon fiber shows up in race cars but rarely makes it into minivans. That could change. Scientists say it may soon be possible to make carbon fiber from plants instead of petroleum, driving down costs, making the material more widely available for use in cars, planes and other vehicles.

Carbon fiber is made from a chemical called acrylonitrile. Currently, producers make acrylonitrile from oil, ammonia, oxygen and an expensive catalyst. The process produces a lot of heat and yields a toxic byproduct. And, because acrylonitrile is made from petroleum, the cost of carbon fiber tends to rise and fall with the price of oil. "Acrylonitrile prices have witnessed large fluctuations in the past, which has in turn led to lower adoption rates for carbon fibers for making cars and planes lighter weight," said Gregg Beckham, a group leader at the National Renewable Energy Laboratory and coauthor of a recent paper detailing this research. "If you can stabilize the acrylonitrile price by providing a new feedstock from which to make acrylonitrile," he said, adding, "we might be able to make carbon fiber cheaper."

Beckham and a team of researchers at the National Renewable Energy Laboratory developed a new process for producing acrylonitrile that makes use of plants, namely the parts people can't eat, such as corn stalks and wheat straw. Scientists broke these materials down into sugars, which were converted into an acid and combined with an inexpensive catalyst to produce acrlyonitrile. The process generated no excess heat and returned no toxic byproducts.

Scientists believe the plant-based process could be scaled up and used in manufacturing. Researchers are now working with several firms to produce a large quantity of acrylonitrile that will be turned into carbon fiber and tested for use in automobiles. By making carbon fiber cheaper, scientists could help car owners save money in the long run. Cars made with carbon fiber are lighter than those made with steel. As a result, they need less fuel to cover the same distance, helping drivers save on gas while also cutting planet-warming carbon pollution.

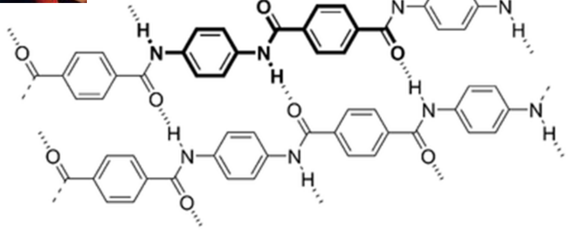
There's a trend underway of scientists making petroleum products from plants instead. Petroleum is, after all, made from prehistoric plants that were buried and subjected to intense heat and pressure for millions of years. Researchers are trying to cut out the middleman—deriving needed chemicals directly from plants, reducing our dependence on oil. "We'll be doing more fundamental research," Beckham said. "Beyond scaling acrylonitrile production, we are also excited about using this powerful, robust chemistry to make other everyday materials."

Jeremy Deaton writes for Nexus Media, a syndicated newswire covering climate, energy, policy, art and culture. You can follow him @deaton_jeremy.

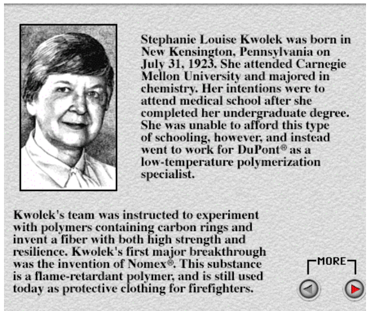
https://www.popsci.com/carbon-fiber-from-plants?CMPID=ene011418&spMailingID=32594080&spUserID=NTYxODU2MzAwMjg1S0&spJobID=1201594305&spReportId=MTIwMTU5NDMwNQS2#page-2

Polyaramide: Poly(*p*-phenylene terephthalamide) (Kevlar)

1964 Stephanie Kwolek

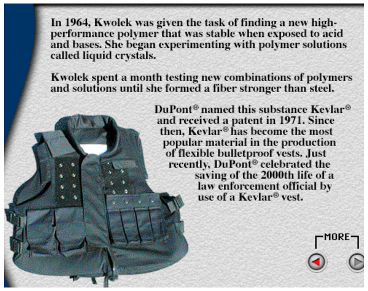


https://www.sciencehistory.org/historical-profile/stephanie-l-kwolek



Stephanie Louise Kwolek was born in New Kensington, Pennsylvania on July 31, 1923. She attended Carnegie Mellon University and majored in chemistry. Her intentions were to attend medical school after she completed her undergraduate degree. She was unable to afford this type of schooling, however, and instead went to work for DuPont® as a low-temperature polymerization specialist.

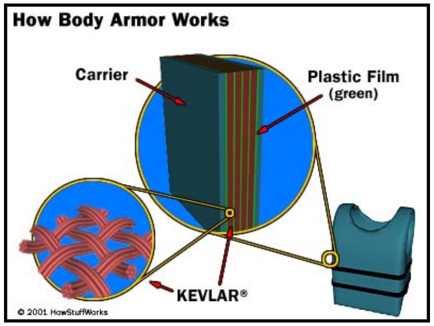
Kwolek's team was instructed to experiment with polymers containing carbon rings and invent a fiber with both high strength and resilience. Kwolek's first major breakthrough was the invention of Nomex®. This substance is a flame-retardant polymer, and is still used today as protective clothing for firefighters.

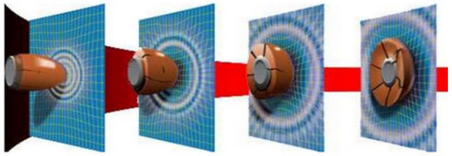


In 1964, Kwolek was given the task of finding a new high-performance polymer that was stable when exposed to acid and bases. She began experimenting with polymer solutions called liquid crystals.

Kwolek spent a month testing new combinations of polymers and solutions until she formed a fiber stronger than steel.

DuPont® named this substance Kevlar® and received a patent in 1971. Since then, Kevlar® has become the most popular material in the production of flexible bulletproof vests. Just recently, DuPont® celebrated the saving of the 2000th life of a law enforcement official by use of a Kevlar® vest.





Polyaramides, such as Kevlar, are known for their incredible strength and durability. Polyaramides are a type of polyamide which contain an aromatic ring.

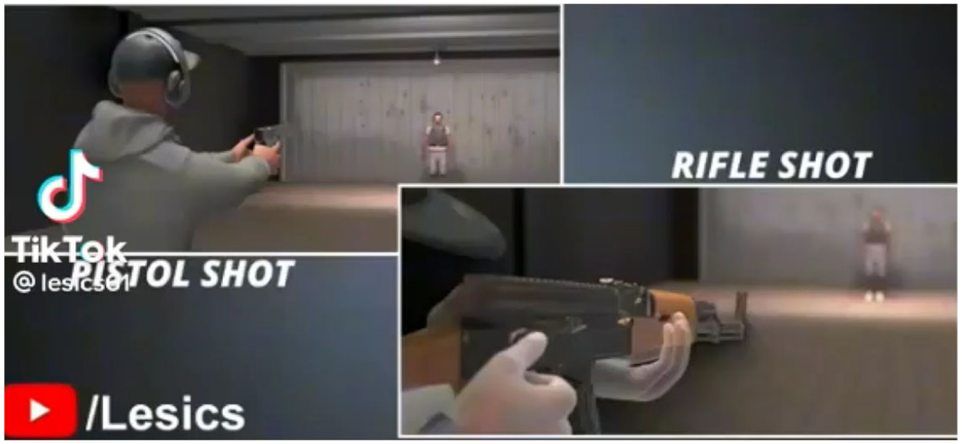
Properties: Fire resistant, durable, strong, virtually impenetrable.

Used in bulletproof vests, underwater cables, reinforcement fibers for automobile tires, canoes, jackets, rain coats, aviation.

How It Works?

When a handgun bullet strikes body armor, it is caught in a "web" of very strong fibers. These fibers absorb and disperse the impact energy that is transmitted to the bullet proof vest from the bullet, causing the bullet to deform of "mushroom." Additional energy is absorbed by each successive layer of material in bullet proof vests, until such time as the bullet has been stopped.

https://www.bodyarmour.shop/blogs/body-armor-wiki/how-does-armor-work



Reconstructing Ancient Linen Body Armor Unraveling the Linothorax Mystery (Gregory S. Aldrete, Scott Bartell, and Alicia Aldrete)

Laminated Linen Protected Alexander the Great

This mosaic of Alexander the Great shows the king wearing linothorax - an armor made from laminated linen.

Reconstructing Ancient Linen Body Armor Unraveling the Linothorax Mystery (Gregory S. Aldrete, Scott Bartell, and Alicia Aldrete)

Alexander and his soldiers protected themselves with linothorax, a type of body armor made by laminating together layers of linen. The main visual evidence for Alexander wearing linothorax is the famous "Alexander Mosaic" from Pompeii, in which the Macedonian king is depicted with this sort of armor.
Indeed, in his "Life of Alexander," the Greek historian Plutarch states that Alexander wore "a breastplate of folded (or doubled) linen" at the Battle of Gaugamela in 331 B.C. This battle a was a huge victory for the Greeks and led to the fall of the Achaemenid Empire. According to the researchers, there is further evidence that linen breastplates were standard equipment in the Macedonian army.

"The hardest part of the project was finding truly authentic linen. It had to be made from flax plants that were grown, harvested and processed, spun and woven by hand," Aldrete said. The other key ingredient was glue, which was placed over various layers of linen. The researchers chose to work with two simpler glues that would have been available everywhere: a glue made from the skins of rabbits and another from flax seeds.
Tests included shooting the resulting patches with arrows and hitting them with a variety of weapons including swords, axes and spears.
"Our controlled experiments basically dispelled the myth that armor made out of cloth must have been inferior to other available types. Indeed, the laminated layers function like an ancient version of modern Kevlar armor, using the flexibility of the fabric to disperse the force of the incoming arrow," Aldrete said.

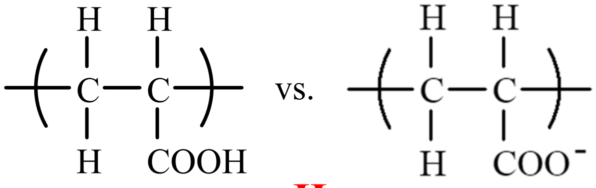
Jan 10, 2010 by Rossella Lorenzi. http://news.discovery.com/history/ancient-egypt/linothorax-alexander-great-armor.htm

Poly(acrylic acid)

Poly(acrylic acid) as a super-absorbent (SAP) was patented in 1966 by Gene Harper of Dow Chemical and Carlyle Harmon of Johnson & Johnson. It was first used in diapers in 1982 in Japan.

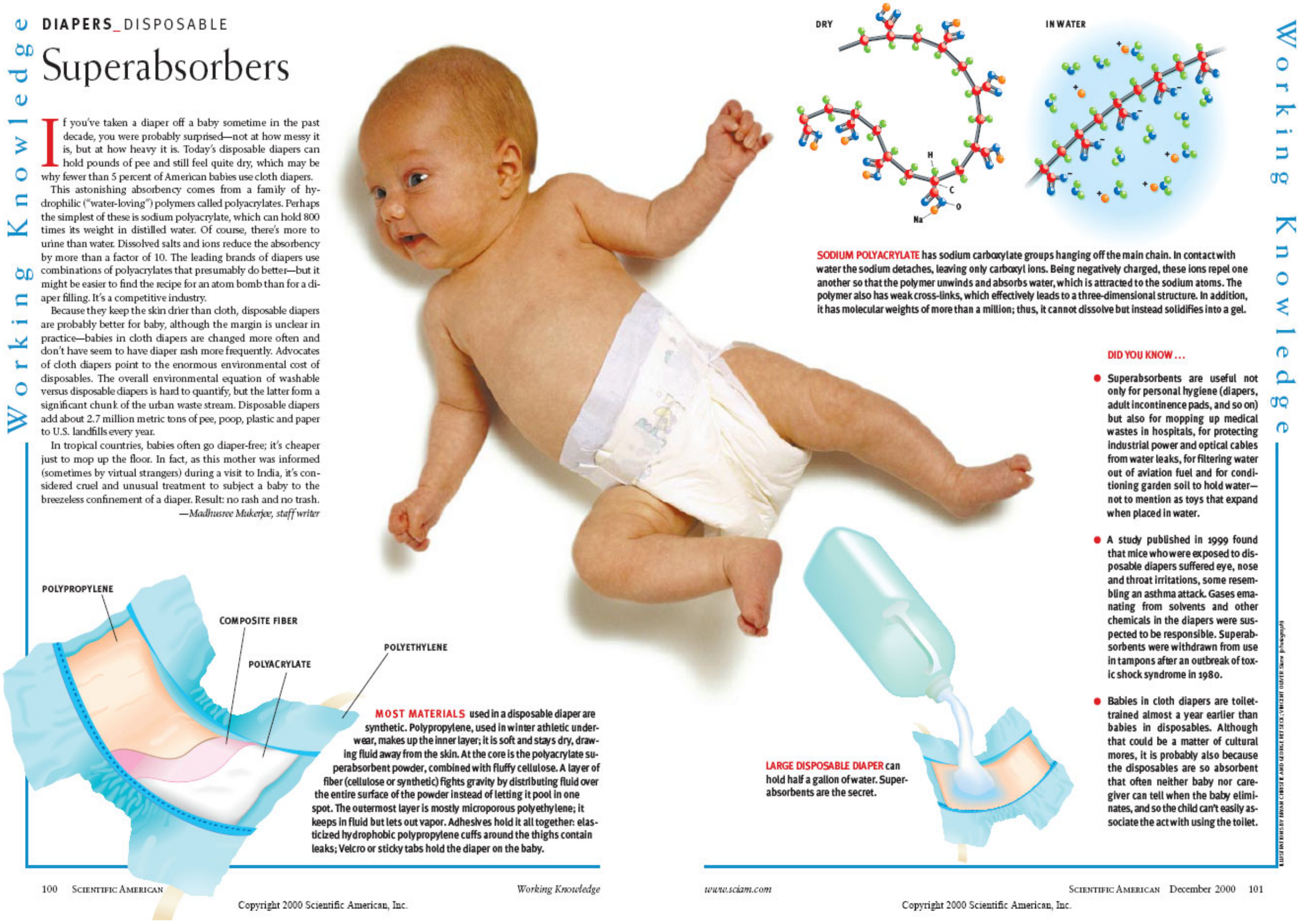
http://toxipedia.org/display/toxipedia/Polyacrylic+Acid

Patented in 1966



$-\!\left[\mathrm{CH_2-CH(COOH)}\right]\!-$ vs. $-\!\left[\mathrm{CH_2-CH(COO^-)}\right]\!-$

pH



Working Knowledge

DIAPERS_DISPOSABLE

Superabsorbers

If you've taken a diaper off a baby sometime in the past decade, you were probably surprised—not at how messy it is, but at how heavy it is. Today's disposable diapers can hold pounds of pee and still feel quite dry, which may be why fewer than 5 percent of American babies use cloth diapers.

This astonishing absorbency comes from a family of hydrophilic ("water-loving") polymers called polyacrylates. Perhaps the simplest of these is sodium polyacrylate, which can hold 800 times its weight in distilled water. Of course, there's more to urine than water. Dissolved salts and ions reduce the absorbency by more than a factor of 10. The leading brands of diapers use combinations of polyacrylates that presumably do better—but it might be easier to find the recipe for an atom bomb than for a diaper filling. It's a competitive industry.

Because they keep the skin drier than cloth, disposable diapers are probably better for baby, although the margin is unclear in practice—babies in cloth diapers are changed more often and don't have seem to have diaper rash more frequently. Advocates of cloth diapers point to the enormous environmental cost of disposables. The overall environmental equation of washable versus disposable diapers is hard to quantify, but the latter form a significant chunk of the urban waste stream. Disposable diapers add about 2.7 million metric tons of pee, poop, plastic and paper to U.S. landfills every year.

In tropical countries, babies often go diaper-free; it's cheaper just to mop up the floor. In fact, as this mother was informed (sometimes by virtual strangers) during a visit to India, it's considered cruel and unusual treatment to subject a baby to the breezeless confinement of a diaper. Result: no rash and no trash.

—*Madhusree Mukerjee, staff writer*

MOST MATERIALS used in a disposable diaper are synthetic. Polypropylene, used in winter athletic underwear, makes up the inner layer; it is soft and stays dry, drawing fluid away from the skin. At the core is the polyacrylate superabsorbent powder, combined with fluffy cellulose. A layer of fiber (cellulose or synthetic) fights gravity by distributing fluid over the entire surface of the powder instead of letting it pool in one spot. The outermost layer is mostly microporous polyethylene; it keeps in fluid but lets out vapor. Adhesives hold it all together: elasticized hydrophobic polypropylene cuffs around the thighs contain leaks; Velcro or sticky tabs hold the diaper on the baby.

SODIUM POLYACRYLATE has sodium carboxylate groups hanging off the main chain. In contact with water the sodium detaches, leaving only carboxyl ions. Being negatively charged, these ions repel one another so that the polymer unwinds and absorbs water, which is attracted to the sodium atoms. The polymer also has weak cross-links, which effectively leads to a three-dimensional structure. In addition, it has molecular weights of more than a million; thus, it cannot dissolve but instead solidifies into a gel.

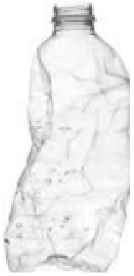
DID YOU KNOW . . .

- Superabsorbents are useful not only for personal hygiene (diapers, adult incontinence pads, and so on) but also for mopping up medical wastes in hospitals, for protecting industrial power and optical cables from water leaks, for filtering water out of aviation fuel and for conditioning garden soil to hold water—not to mention as toys that expand when placed in water.
- A study published in 1999 found that mice who were exposed to disposable diapers suffered eye, nose and throat irritations, some resembling an asthma attack. Gases emanating from solvents and other chemicals in the diapers were suspected to be responsible. Superabsorbents were withdrawn from use in tampons after an outbreak of toxic shock syndrome in 1980.
- Babies in cloth diapers are toilet-trained almost a year earlier than babies in disposables. Although that could be a matter of cultural mores, it is probably also because the disposables are so absorbent that often neither baby nor caregiver can tell when the baby eliminates, and so the child can't easily associate the act with using the toilet.

LARGE DISPOSABLE DIAPER can hold half a gallon of water. Superabsorbents are the secret.

ILLUSTRATIONS BY BRYAN CHRISTIE AND GEORGE RETSECK; VINCENT OLIVER Stone (photograph)

The Eleven Most Important Types of Plastic



1. Poly(ethylene terephthalate) (PETE or PET):
PET is the most widely produced plastic in the world. It is used predominantly as a fiber (known by the trade name "polyester") and for bottling or packaging. For example, PET is the plastic used for bottled water and is highly recyclable.
Wide applications as a fiber ("polyester"), Extremely effective moisture barrier, Shatterproof

2. Polyethylene (PE):
There are a number of different variants of polyethylene. Low and high density polyethylene (LDPE and HDPE respectively) are the two most common and the material properties vary across the different variants.
LDPE: LDPE is the plastic used for plastic bags in grocery stores.
HDPE: A stiff plastic used for more robust plastic packaging.
UHMW: Extremely strong plastic that can rival or even exceed steel in strength and is used is for applications like medical devices (e.g. artificial hips).

3. Poly(vinyl Chloride) (PVC):
PVC is perhaps most well known for its use in residential and commercial property construction applications. Different types of PVC are used for plumbing, insulation of electrical wires, and "vinyl" siding. In the construction business PVC pipe is often referred to by the term "schedule 40" which indicates the thickness of the pipe relative to its length.
Brittle, Rigid (although different PVC variants are actually designed to be very flexible), Strong

https://www.creativemechanisms.com/blog/eleven-most-important-plastics

The Eleven Most Important Types of Plastic

4. Polypropylene (PP):
Polypropylene is used in a variety of applications to include packaging for consumer products, plastic parts for the automotive industry, special devices like living hinges, and textiles. It is semi-transparent, has a low-friction surface, doesn't react well with liquids, is easily repaired from damage and has good electrical resistance (i.e. it is a good electrical insulator). Perhaps most importantly, polypropylene is adaptable to a variety of manufacturing techniques which makes it one of the most commonly produced and highly demanded plastics on the market.

5. Polystyrene (PS):
Polystyrene is used widely in packaging under the trade name "styrofoam." It is also available as a naturally transparent solid commonly used for consumer products like soft drink lids or medical devices like test tubes or petri dishes. Foam applications.

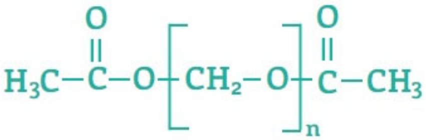
6. Poly(lactic Acid) (PLA):
Polylactic Acid is unique in relation to the other plastics on this list in that it is derived from biomass rather than petroleum. Accordingly it biodegrades much quicker than traditional plastic materials.

7. Polycarbonate (PC):
Polycarbonate is a transparent material known for its particularly high impact strength relative to other plastics. It is used in greenhouses where high transmissivity and high strength are both required or in riot gear for police.
Transparent, high strength

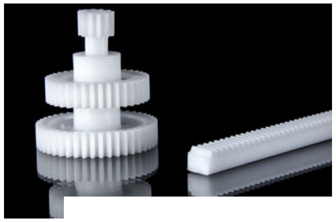
https://www.creativemechanisms.com/blog/eleven-most-important-plastics

The Eleven Most Important Types of Plastic

8. Acrylic (PMMA):
Acrylic is best known for its use in optical devices. It is extremely transparent, scratch resistant, and much less susceptible to damaging human skin or eye tissue if it fails (e.g. shatters) in close proximity to sensitive tissue.
Transparent, Scratch resistant


$$H_3C-\overset{O}{\overset{\|}{C}}-O-\left[CH_2-O\right]_n-\overset{O}{\overset{\|}{C}}-CH_3$$

9. Acetal (Polyoxymethylene, POM):
Acetal is a very high tensile strength plastic with significant creep resistant properties that bridge the material properties gap between most plastics and metals. High resistance to heat, abrasion, water, and chemical compounds. Acetal has a particularly low coefficient of friction which makes it very useful for applications that utilize gears. Low friction (Acetal gears and rack).



10. Nylon (Polyamide):
Nylon is used for a variety of applications to include clothing, reinforcement in rubber material like car tires, for use as a rope or thread, and for a number of injection molded parts for vehicles and mechanical equipment. It is often used as a substitute for low strength metals in applications like car engines because of its high strength (relative to other plastics), high temperature resilience, and high chemical compatibility. High strength, temperature resistant.

11. ABS (Acrylonitrile Butadiene Styrene):
ABS has a strong resistance to corrosive chemicals and physical impacts. It is very easy to machine, is readily available and has a low melting temperature making it particularly simple to use in injection molding manufacturing processes or 3D printing.
Impact resistant, readily available, simple to manufacture. #1 material for 3D printing.

https://www.creativemechanisms.com/blog/eleven-most-important-plastics

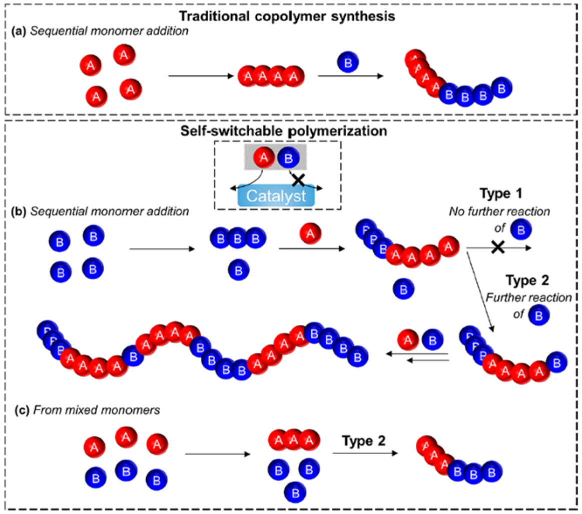
Emergence of Synthetic Polymers

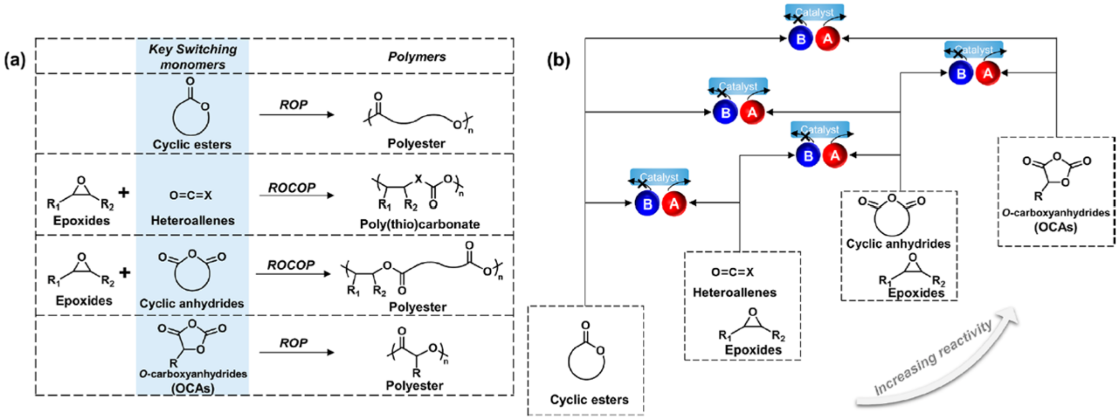
Year 1960 - present

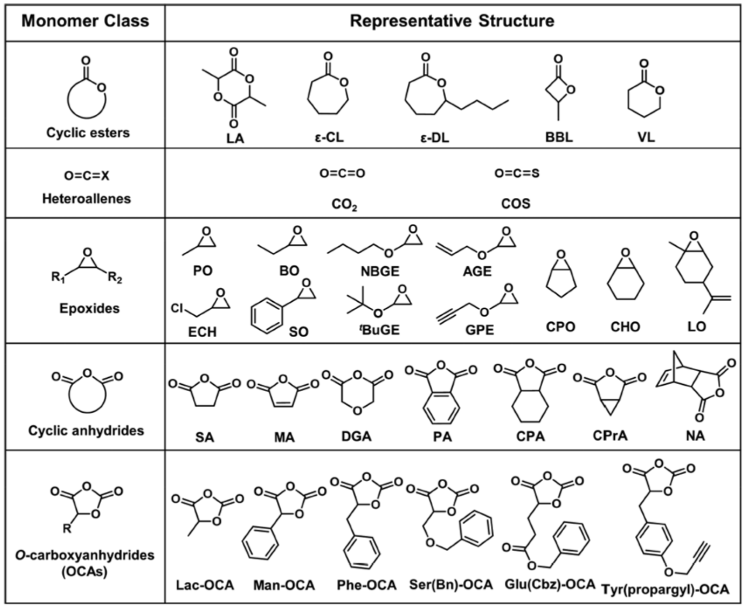
1. **Large scale operations**
2. **Applications in daily lives, transportation, communications, education, & leisure**
3. **Polymer composites**
4. **Polymers as biomaterials**
5. **Functional polymers: Polymers with bioactivity**
6. **Smart polymers and hydrogels**
7. **Biodegradable polymers**
8. **Polymers for solar cells**

Kataria 2022, Y-Series-based polymer acceptors for high-performance
all-polymer solar cells in binary and non-binary systems

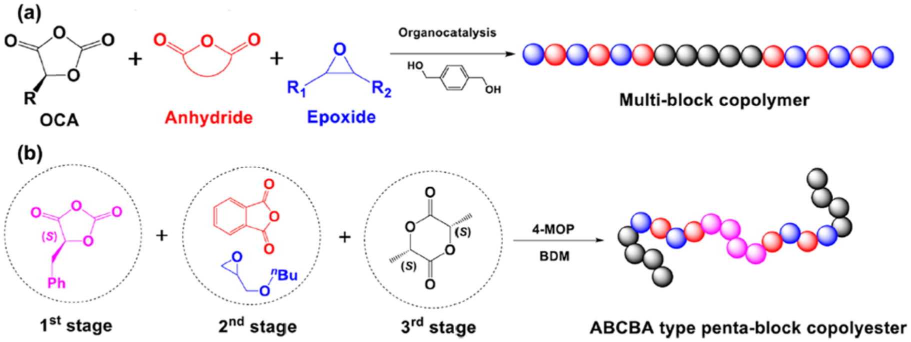
Sequence-Controlled Degradable Copolymers





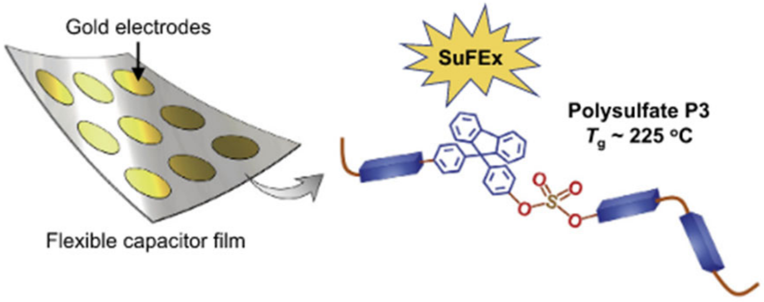


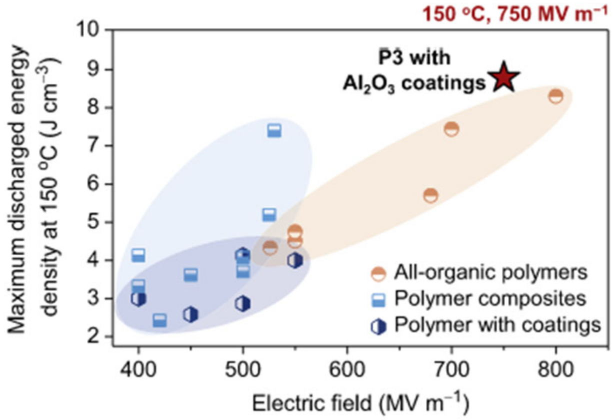
Monomer Class	Representative Structure
Cyclic esters	LA ε-CL ε-DL BBL VL
O=C=X Heteroallenes	O=C=O CO_2 O=C=S COS
Epoxides	PO BO NBGE AGE ECH SO ᵗBuGE GPE CPO CHO LO
Cyclic anhydrides	SA MA DGA PA CPA CPrA NA
O-carboxyanhydrides (OCAs)	Lac-OCA Man-OCA Phe-OCA Ser(Bn)-OCA Glu(Cbz)-OCA Tyr(propargyl)-OCA

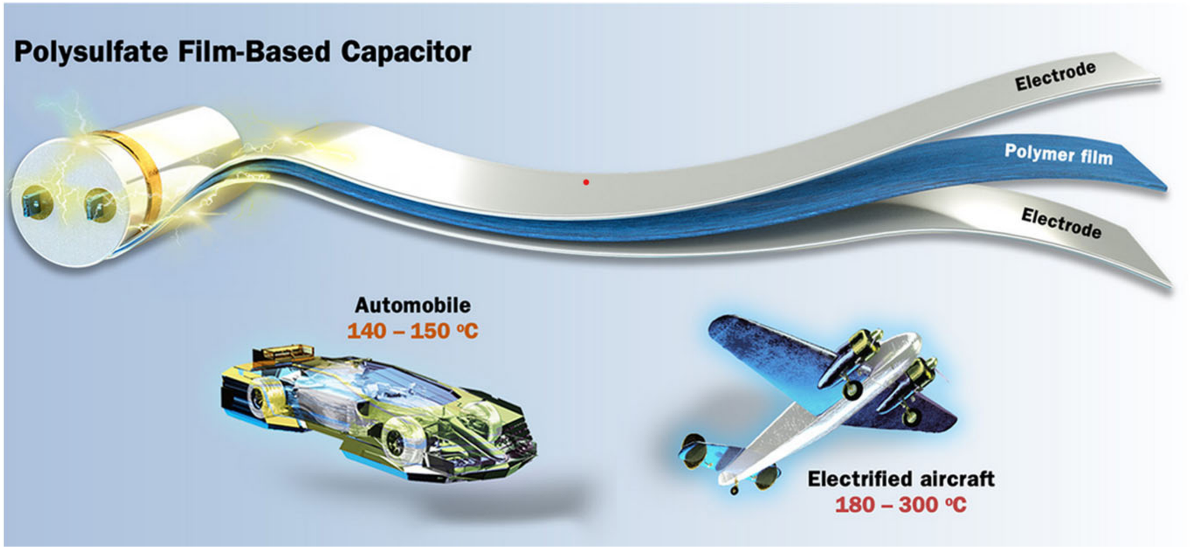


Hu 2022, Self-switchable polymerization- A smart approach to sequence-controlled degradable copolymers

Polymers for Energy Storage

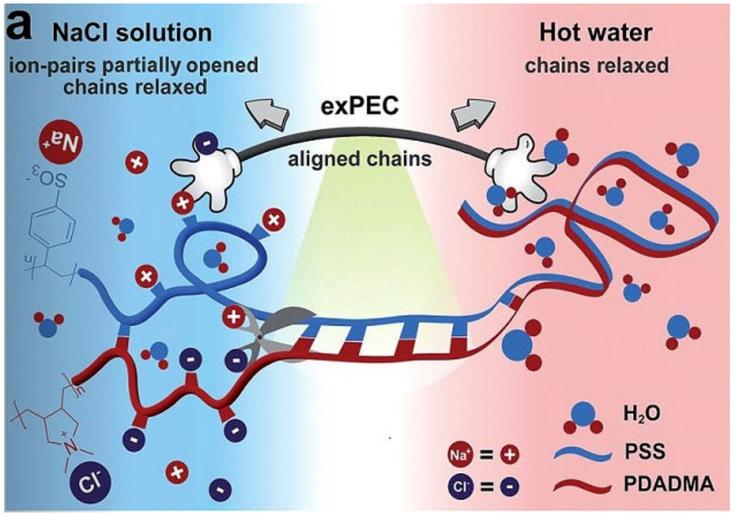






Li 2023, High-performing polysulfate dielectrics for electrostatic energy storage under harsh conditions
https://newscenter.lbl.gov/2023/02/15/new-compound-could-lead-to-next-generation-energy-storage-devices/

Saloplastics



https://www.chem.fsu.edu/~schlen/Saloplastics.html

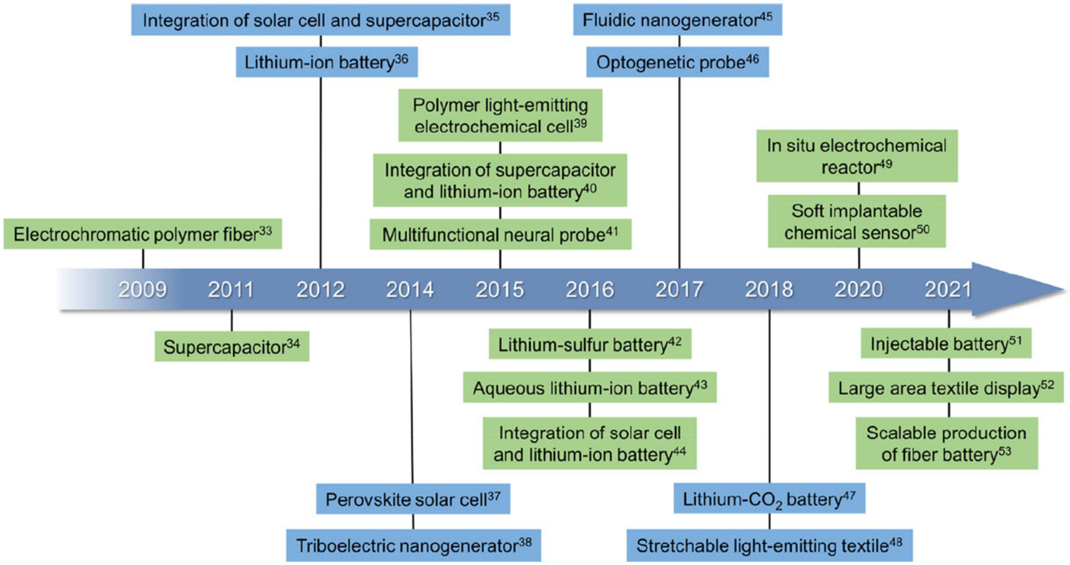
Polyelectrolyte complexes are made by mixing solutions of charged polymers (polyelectrolytes). (e.g., poly(diallyldimethyl ammonium) (PDADMA) and poly(styrene sulfonate) (PSS)). Because they are brittle and salt-like when dry, polyelectrolyte complexes were thought to be unprocessible for decades. But we recently found that if enough salt is added to break the ion pairs between polyelectrolytes, they can be processed with a regular extruder. The two photos on the left show salt-plasticized complexes extruded into tapes, rods and tubes. Note that the tube has the dimensions of a blood vessel.

These extruded polyelectrolyte complexes offer a wide range of applications. Adding other materials to the bulk complex before extruding it results in (nano)composites held together by a polymer matrix. We recently mixed iron oxide nanoparticles with PDADMA/PSS and extruded tough, dense fibers which can be heated remotely by applying radiofrequency fields.

One of our main interests is the effect of salt on these polyelectrolyte complexes. Observing how they go from being glassy to rubbery to a liquid solution with increasing salt concentrations gives a deeper understanding of the conditions under which these materials are molded and offers new ways of manipulating their properties. The benefits of this area of research are countless as we explore complexes in their solid, liquid and coacervate states.

- J. Fu, Q. Wang, J.B. Schlenoff*; ACS Applied Materials and Interfaces, 7, 895-901 (2015), Extruded Superparamagnetioc Saloplastic Polyelectrolyte Nanocomposites. DOI: 10.1021/am507469
- Q. Wang, J.B. Schlenoff*; RSC Advances, 4, 46675-46679 (2014), Tough Strained Fibers of Polyelectrolyte Complex: Pretensioned Polymers. DOI: 10.1039/c4ra08733j
- R.F. Shamoun, A. Reisch, J.B. Schlenoff*; Advanced Functional Materials, 22, 1923-1931 (2012), Extruded Saloplastic Polyelectrolyte Complexes. DOI: 10.1002/adfm.201102787

Smart Fiber Devices



Integration of solar cell and supercapacitor[35]

Lithium-ion battery[36]

Polymer light-emitting electrochemical cell[39]

Integration of supercapacitor and lithium-ion battery[40]

Multifunctional neural probe[41]

Electrochromatic polymer fiber[33]

Fluidic nanogenerator[45]

Optogenetic probe[46]

In situ electrochemical reactor[49]

Soft implantable chemical sensor[50]

2009 2011 2012 2014 2015 2016 2017 2018 2020 2021

Supercapacitor[34]

Lithium-sulfur battery[42]

Aqueous lithium-ion battery[43]

Integration of solar cell and lithium-ion battery[44]

Injectable battery[51]

Large area textile display[52]

Scalable production of fiber battery[53]

Perovskite solar cell[37]

Triboelectric nanogenerator[38]

Lithium-CO_2 battery[47]

Stretchable light-emitting textile[48]

Figure 1. Timeline of key developments in fiber devices in the recent decade, categorized mainly according to their functions.

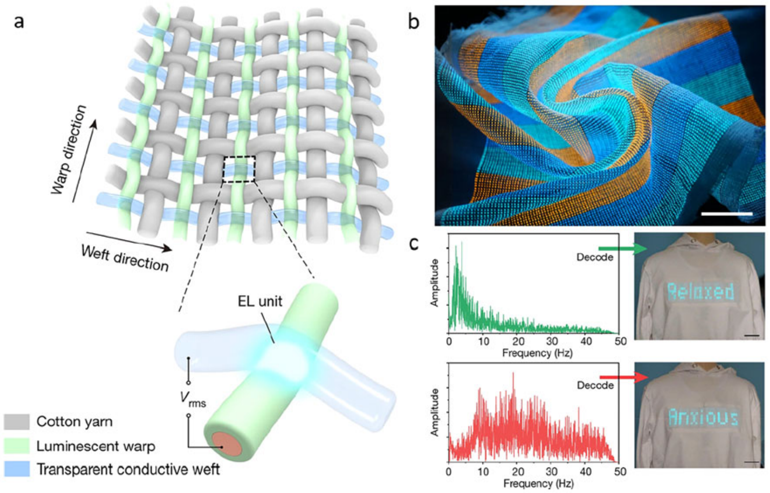


Figure 24. (a) Schematic showing the structure design and electroluminescence mechanism of the light-emitting textile, where the cross point emits light to function as a pixel. (b) Photograph of a three-color display textile under twisting. The blue and orange colors in the textile were achieved by doping ZnS with Cu and Mn, respectively. Scale bar, 2 cm. (c) Information related to brain wave being shown on the light-emitting textile.

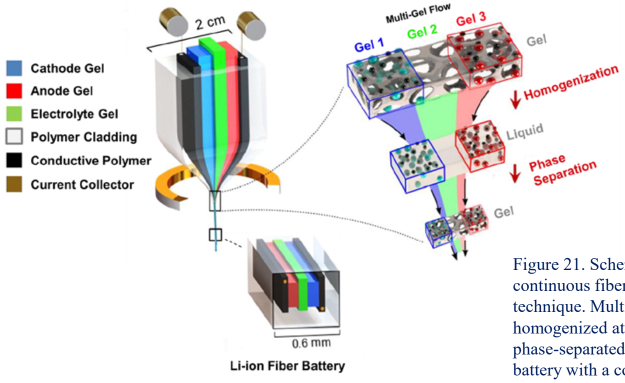


Figure 21. Schematic illustration of producing a continuous fiber battery using a thermal-drawing technique. Multiple components could be homogenized at the elevated temperature and then phase-separated at room temperature to form a fiber battery with a controllable configuration.

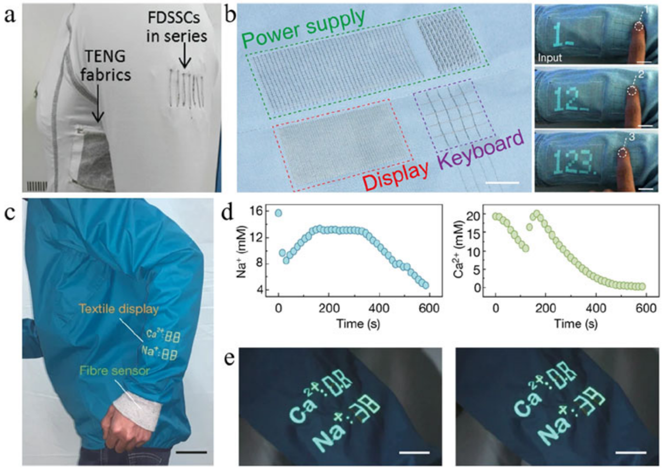


Figure 35. (a) Photograph of an integrated energy-harvesting textile with TENG fabrics underneath the arm and seven fiber DSSCs in series on the shoulder. Reprinted with permission from ref 558. Copyright 2016 Wiley-VCH. (b) Photograph of an integrated textile system consisting of display, power supply, and information input units. The inputted information via the keyboard could be displayed by the textile. Scale bars, 2 cm. (c) Photographs of an integrated textile system consisting of textile display and sensors, powered by a fiber Li-ion battery (not shown). Scale bar, 10 cm. (d, e) Fiber sensors detecting Ca^{2+} and Na^+ in sweat and displaying the results via the electroluminescent module, respectively. Scale bars, 2 cm.

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