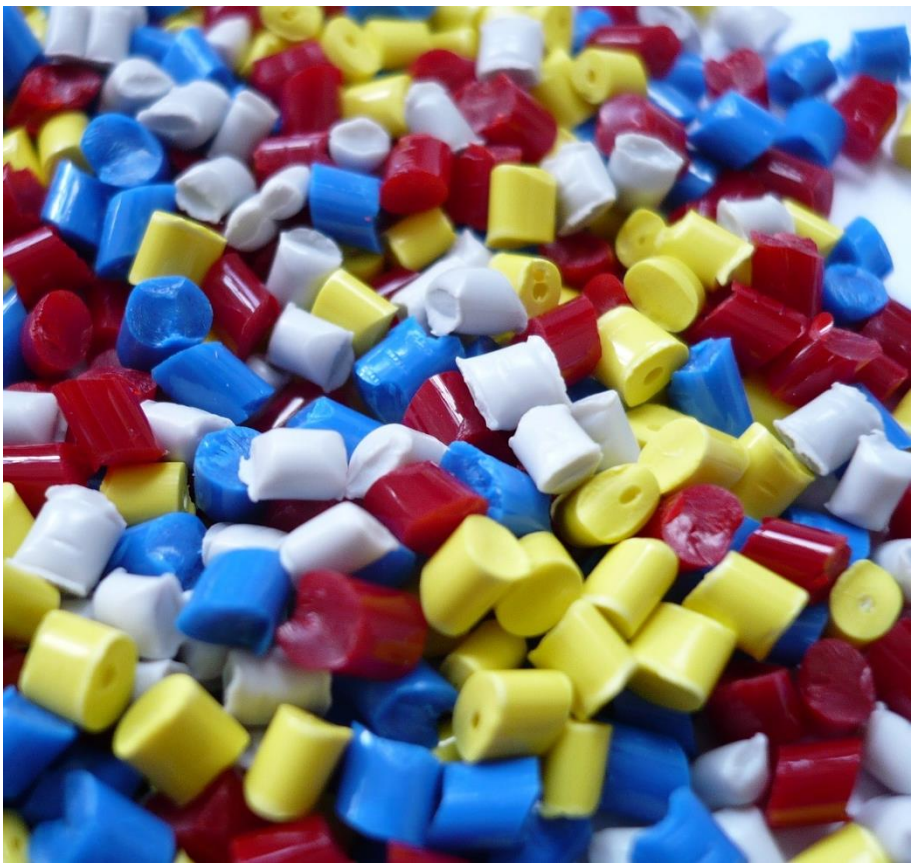

Plastics Topics – Plastics timeline

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Introduction

Whilst plastics are thought of as 'new' materials there is nothing further from the truth. Polymers have a long and full history and the following is simply a snapshot of some of the important events. Many of the discoveries were accidental but it took great men to turn from accident to reality.

If there are any events that you would like recorded on the Timeline then please let me know - amusing stories are always welcome but serious ones have to be really interesting!

c.1000 BC	• Lacquer work - A resin from a lacquer tree (Rhus vernicflua) this has been used by the Chinese since 1000 BC to form waterproof and durable coatings and until the 1950s used to coat domestic tableware.
c.23-79	• Amber - Amber is a thermoplastic resin from fossilized trees and is found mainly on the Baltic Coast. The material can be mixed into lacquers or small pieces pressed into compression moulds to produce small articles. Amber is described by Pliny the Elder (23 - 79) in the work Natural History.
c.0	• Horn - This behaves like a typical thermoplastic sheet and can be split and moulded into shape after heating in hot water. Layers can also be laminated together to build thicker products or pressed into wooden moulds to form snuff boxes or buttons. The raw material can also be ground up and mixed with a binder (such as blood) before being compression moulded for buttons and other products.
c.400	• Tortoiseshell - This is actually the shell of a turtle but it can be cut and shaped, similar to horn, to keep an attractive pattern for a variety of articles.
c.800	• Gutta percha - A natural resin from the bark of Malayan trees.
1284	• First recorded mention of the Worshipful Company of Horners. The Horners Company of London (one of the City of London Livery Companies) is regarded as the first plastics trade association and even today retains links with the British Plastics Federation via the annual Horners Awards.
c.1550	• Valdes describes first reference to natural rubber in reports of expeditions to Central America. The native Indians used the material for sports and waterproofing.
1596	• John Huyglen von Linschoeten, after visiting India, describes the use of shellac.
1638	• Horners Company receives Royal Charter.
c.1650	• John Tradescant introduces Gutta Percha to the West after his travels in the East collecting plants. Gutta percha was used to make products from garden hoses to furniture for many years after the introduction to the West and was only replaced for undersea cable insulation in the 1940's.
1725	• London is established as an important horn moulding centre with metal dies being manufactured for snuff boxes.

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1731	• Charles Marie de la Condamine reports natives in Amazon basin using rubber for waterproofing and flexible bottles. Rubber imported into Europe in 1736 but evidence suggests that it was in use by the natives for several thousand years. • la Condamine led an expedition to Peru (now part of Ecuador) to measure the size and shape of the Earth, he was scarred by smallpox and shy of women but led an expedition of French scientists into the jungles to 'advance the art of doing science' - in the process they introduced rubber to Europe, investigated the uses of quinine and discover platinum as well as advocating the standard measure that would lead to the metre - true heroes in the jungle.	 de la Condamine
1820	• Thomas Hancock (Britain) discovers that if strongly processed (masticated) then rubber became plastic and could be made to flow and develops the method of milling rubber.	
1823	• Scottish chemist Charles Macintosh begins using rubber to waterproof fabrics - the Macintosh is born!	
1835	• Regnault reports first production of vinyl chloride monomer.	
1831	• First description of styrene.	
1835	• Pelouze first produces cellulose nitrate.	
1839	• Charles Goodyear (USA) discovers the process of mixing natural rubber with sulphur to make a stronger and more resilient product, the process was later termed 'vulcanisation'. As with many discoveries in plastics this was an accident. Goodyear had been trying to find a method of preventing rubber from softening at high temperatures for many years and in 1839 he dropped accidentally dropped a mixture of rubber and sulphur onto a hot stove - a Eureka moment! • Payen (France) isolates cellulose as the principal constituent of wood.	 Charles Goodyear
1843	• Thomas Hancock (Britain) patents 'vulcanisation' process for rubber. • Dr W Montgomerie introduces Gutta Percha to the West (initially for cutlery handles).	
1844	• Charles Goodyear (USA) patents 'vulcanisation' process for rubber.	
1845	• Robert William Thompson invents the rubber tyre.	
1851	• Ebonite is patented and commercialised by Nelson Goodyear (USA). Charles Goodyear and Thomas Hancock both find that excess sulphur during vulcanisation leads to ebonite. Ebonite is a hard, dark and shiny material used for jewellery, fountain pens, pipe stems and is the basis for most dental plates (with pink colouring) for nearly 100 years. The material can also be inlaid with metals or painted to produce very decorative objects. • Ebonite is a milestone because it is the first thermosetting material and because it	

	involves modification of the natural material. • Gutta Percha used to insulate submarine cables between England and France.
1854	• Shellac (mixed with wood flour) patented as a moulding material by Samuel Peck (USA) for use in frames and carrying cases.
1855	• François Lepage patents an animal polymer composite based on albumen (from blood or egg white) with wood powder as filler. The material is known as Bois Durci and is used for moulding small items. • Soccer ball first produced by Charles Goodyear using vulcanised rubber panels.
1856	• First of many patents granted to Alexander Parkes (Britain) for nitrocellulose products. Parkes was to register over 20 patents on nitrocellulose products as the processes and products were developed. Cellulose nitrate is an explosive (guncotton), highly flammable and is brittle - but despite this it is a major development in plastics technology. The use of 'Parkesine' for the waterproofing of fabrics was patented in the same year by Parkes.
1859	• Butlerov describes formaldehyde polymers.
1861	• First of Parkes' patents for 'Parkesine' - a cellulose nitrate based product that forms a mouldable dough which looks like ivory or horn.
1862	• Parkes shows 'Parkesine' at the Great International Exhibition in London. The material was used to make household objects that looked like tortoiseshell and ivory.
1863	• Phelan and Collander, a billiard ball manufacturer, offers prize of $10,000 to anyone who can produce a substitute for ivory in billiard balls
1865	• Parkes obtains a major patent for 'Parkesine' that describes how the samples for the Great International Exhibition were made. • Cellulose acetate discovered.
1869	• John Wesley Hyatt and his brother Isaiah (USA) develop 'Celluloid' (a commercialised form of cellulose nitrate or nitrocellulose made less brittle by the addition of camphor) to try to win a prize of $10,000 in a competition to find a better billiard ball. They didn't win but Celluloid went on to replace Parkesine in many applications and was used to make spectacle frames, knife handles and photographic film.  John Wesley Hyatt
1870	• Hyatt brothers patent (US Patent 105,338) the use of cellulose nitrate and camphor to form a horn-like material (Celluloid).
1872	• Adolph Bayer (Germany) reports reactions of phenols and aldehydes to give resinous substances. • Hyatt brothers patent the first injection moulding machine.

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	• Celluloid registered as trademark by Hyatt. • Baumann successfully polymerises vinyl chloride into poly(vinyl chloride).
1876-77	• Seeds of Brazilian rubber trees smuggled out of Brazil by Sir Henry Wickham and later sent to Asia where they form the basis of the worlds rubber industry.
1877-84	• Series of legal cases between Hyatt and Spill (a collaborator of Parkes) over the invention of 'Celluloid'. The eventual result is that Parkes had mentioned the use of both camphor and alcohol in his patents and was therefore the true inventor - the result is that there was no restriction on the use of the processes.
1879	• Carbon fibres first used by Edison as filaments in electric light bulbs. • Gray obtains patent for first screw extruder.
1880	• Shellac used by the Berliner label to produce phonograph records because of the ability to reproduce fine detail - shellac was used until 1952 when PVC was first introduced for this purpose.
1884	• Louis Bernigaud (Count of Chardonnet) produces 'artificial silk' fibres from cellulose (later to be termed Rayon).
1885	• George Eastman patents machine for producing continuous photographic film and will become renowned for photographic products.  **George Eastman**
1887	• Goodwin invents celluloid photographic film and production process.
1890	• Thermoforming introduced to make babies' rattles from cellulose nitrate.
1894	• Cross and Bevan develop industrial process for cellulose acetate after research into cellulose esters to avoid flammability concerns with 'Celluloid' (cellulose nitrate).
1897	• Kritsche and Spitteler (Bavaria) discover casein plastics. It is rumoured that the discovery involved an accident with a cat, a saucer of milk and a bottle of formaldehyde because casein is made from skimmed milk curdled with rennet which is cured by immersion in formaldehyde.
1898	• Start of mass production of gramophone records using shellac.
1899	• Kritsche and Spitteler (Bavaria) patent casein plastics. Casein plastics later become available as 'Galalith' (1904 - Germany), 'Lactoid (1904 - UK) and 'Alladinite (1919 - USA). • Arthur Smith (Britain) patents phenol-formaldehyde resins to replace ebonite as electrical insulation.

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1903	• Stern and Charles Topham develop method for producing artificial silk (viscose). • Eichengrun and Becker (Germany) develop plastic form of cellulose acetate.
1905	• J. Edwin Brandenberger invents 'Cellophane' after dining at a restaurant and noticing that tablecloths absorbed moisture. He set about producing a waterproof material by applying a flexible film to the cloth to prevent soiling of materials.
1907	• Leo Baekeland (USA) mixes phenol and formaldehyde to produce phenol formaldehyde resins and obtains the first of 117 patents on phenol-formaldehyde resin systems.  **Leo Baekeland**
1908	• Charles Frederick Cross invents 'Cellophane' (cellulose acetate and viscose rayon).
1909	• Leo Baekeland (USA) patents Bakelite, the first widely used thermoset to replace traditional materials such as wood, ivory and ebonite. The trade name 'Bakelite' will later become synonymous with the materials.
1910	• Rayon stockings for women are first manufactured in Germany. • 'Formica' first produced by Herbert Faber and Daniel O'Connor (American researchers) as an electrical insulator. Formica is layers of paper impregnated with phenolic and melamine resins and pressed into sheets.
1912	• I. Ostromislensky (Russia) patents polymerisation of vinyl chloride to give PVC but decomposition during processing prevents commercial development.
1915	• First production of synthetic methyl rubber at Leverkusen.
1918	• Hans John prepares resins by reacting urea with formaldehyde and patents the urea-formaldehyde resin systems.
1920	• Fashion for long hair with women leads to Celluloid replacing horn as the material of preference for hair combs. Fashions change but even in 1944 most toilet goods are still made from Celluloid.

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1922	• Hermann Staudinger (Germany) synthesises rubber.	 **Hermann Staudinger**
1924	Edmund Rossiter (Britain) develops urea thiourea formaldehyde for the British Cyanides Co. to give the first water-white transparent thermosetting moulding powder. Marketed from 1928 onwards as 'Beetle'. Discovery of polyvinyl alcohol.	
1926	Hermann Staudinger (Germany) starts work on 'macromolecules' that will eventually show that polymers are long chains of monomers joined together (polymerised). Previously it was widely believed that plastics were composed of rings of linked molecules. Eckert and Ziegler patent first commercial injection machine in Germany but automatic production was not possible until 1937. Alkyd material first introduced for electrical applications.	
1927	Discovery of suitable plasticisers for cellulose acetate leads to rise of the material as a replacement for the more flammable celluloid. Otto Rohm (Germany) develops poly(methyl methacrylate) and limited production begins at Darmstadt (the aptly named Intestine Town). PVC first introduced for coating applications but processing is difficult.	
1928	• Ziegler becomes interested in organo-metallic chemistry and starts to lay the foundations for polyethylenes and polypropylenes. • Wallace Hume Carothers (1896 - 1937) starts work on polymers and polymerisation as head of a research group at DuPont - this was to be one of the most successful groups in the history of polymer science.	 Wallace Carothers
1929	• Dunlop Rubber Co. (Britain) produces the first foam rubber.	
1930	• BASF / I.G.Farben (Germany) develop polystyrene and Dow Chemical Co. (USA) starts to develop polystyrene but commercial production takes another 7 years. • W.L. Semon of B.F.Goodrich (USA) modifies PVC to improve processing and give more commercially processable material.	

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1931	• Carothers develops Neoprene. • Imperial Chemical Industries - ICI (Britain) develops polyethylene almost by accident when E.W. Fawcett and R.O. Gibson notice a small amount of a waxy solid produced during experiments with ethylene. This was later isolated to produce polyethylene which had excellent chemical resistance and insulation properties.
1932	• Improvements to urea thiourea formaldehyde products at British Cyanides Co. give urea formaldehyde resins.
1933	• ICI workers (R. Hill and J.W.C. Crawford) start to develop commercial synthesis of poly(methyl methacrylate) or PMMA - later to be commercialised under the names 'Perspex', 'Lucite', 'Plexiglas' and many others. • Ralph Wiley (Dow Chemical) accidentally discovers polyvinylidene chloride (Saran). Wiley was a college student cleaning glassware in the Dow labs when he found some glassware that he couldn't clean. The result was the discovery of polyvinylidene chloride or Saran. • First injection moulded polystyrene articles produced. • British Plastics Federation established making it the oldest national plastics organisation in the world.
1934	• Wallace Hume Carothers at DuPont (USA) develops nylon, originally as a fibre. • First commercial production of Perspex (PMMA).
1935	• Carothers and DuPont patent nylon. • Henkel patent the production of resins based on melamine.
1936	• ICI patents polymerisation of ethylene to give polyethylene and develop large volume compressor to commercially produce polyethylene. • PMMA used for cockpit canopies in the Spitfire, by 1940 it was used for almost all aircraft glazing.
1937	• Wallace Carothers commits suicide only three weeks after applying for a patent for nylon and before nylon is released to the public (1938/9) as 'Exton'. Unfortunately, he never has a chance to see how much he did for mankind. The frightening thing is that Carothers committed suicide because he felt that he was a failure - would that we could all fail as brilliantly as Carothers. • Otto Bayer starts development of polyurethanes at I.G.Farben. • Polystyrene first commercially produced. • Germany starts to commercially produce synthetic rubbers, styrene-butadiene (called Buna S) and butadiene-acrylonitrile (called Buna N).
1938	• Roy Plunkett (DuPont) accidentally discovers PTFE whilst looking for a reason that a cylinder of TFE was empty. Allegedly, Plunkett was working with tetrafluoroethylene when he found that a full cylinder of the gas had nothing in it - when the cylinder was cut up a white residue (polytetrafluoroethylene) was found on the inside of the cylinder and PTFE was born. • P Schlack develops 'perlon'. • First nylon bristle toothbrush (using DuPont materials) goes on sale. • Introduction of plastic contact lenses from PMMA.

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1939	• ICI patents chlorination of polyethylene to give PE-C. • ICI (Britain) commercialises production of polyethylene and opens first production site. • Plastics magazine complains of 'cheap, low-grade moulding powders, skimped designs and faulty moulding techniques' and of the 'wild scramble to exploit every available, and sometimes unsuitable market'. It is good to see that nothing has changed.
1940	• PMMA becomes widely used for aircraft glazing. • First production of PVC in the UK.
1941	• I.G.Farbenindustrie (Germany) starts to produce polyurethanes. • PTFE patented by Kinetic Chemical Ltd. • First commercial PET polymer announced. The work of Wallace Carothers on aliphatic polyesters is extended to cover aromatic polyesters by J.R. Whinfield and J.T. Dickson at the Calico Printers Association in Britain and poly(ethylene terephthalate) is developed. PET is initially used as a fibre (Terylene and Dacron - shirt makers of the world rejoiced) and later as a film (Melinex - ICI and Mylar - DuPont).
1942	• 'Super Glue' (methyl cyanoacrylate) first discovered by Dr Harry Coover (working for Eastman Kodak) during research into transparent materials for use as gun sights. The material polymerises and acts as an adhesive by extracting water vapour from the surfaces and the air. The potential adhesive qualities were not realised until 1951 and it was not until 1958 that the product was actually marketed as an adhesive. After accidentally sticking lots of fingers together one of the first applications was as a wound dressing in the Vietnam War.
1943	• First pilot plant for PTFE, later to be marketed under the name 'Teflon' comes on stream. Commercial production takes another 7 years until 1950. • Investigations into using woven glass fibres as reinforcement begins. A large quantity of woven glass fibre went missing at the Royal Aircraft Establishment in Farnborough in the early stages. It is thought that the soft 'feel' lead the thief to think that it was the new material 'nylon', then in great demand for ladies' underwear. It is amusing to think of what happened to any ladies wearing glass fibre underwear as the glass fibres tend to get into the skin and cause great irritation. Glad it wasn't me!
1947	• Formica first introduced to the British market. • Acrylic paint (PMMA in turpentine) available and used by artists such as Roy Lichtenstein.
1948	• George de Mestral (Switzerland) invents Velcro after seeing burrs in his socks and dog's hair after a walk in the Swiss woods. Velcro is later patented in 1955. • Tupperware (polyethylene), developed by Earl Tupper in 1942, launched.
1949	• 'Silly Putty' invented by James Wright (GE engineer) after mixing silicone oil with boric acid. 'Silly Putty' acts like a rubber but can also be stretched and formed but will revert to a 'blob' after a short period of time. Launched in 1950. • 'Lycra' invented by Joe Shivers (a chemist) working for DuPont. Shivers was looking for a material to improve girdles and came up with the polyurethane based 'Lycra'. This changed the shape (literally and pun intended) of fashion wear throughout the world. • Airfix releases first model from polystyrene.
c.1950	• High impact polystyrene introduced as commercial plastic.

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1952	• First long-playing records and singles manufactured from PVC appear - replacing shellacs and phenolics previously used.	
1953	• High density polyethylene (DuPont trade name of 'Polythene') first produced. • Karl Ziegler (Germany) develops metal ion catalysts for regular polymerisation of polyethylene. Giulio Natta (Italy) who had worked independently but also with Ziegler develops metal ion catalysts for production of isotactic polymers such as polypropylene. Ziegler and Natta had collaborated for some time before Natta filed a patent on polypropylene before informing Ziegler of its existence. Ziegler felt this breached their agreement to share their research and the partnership split in anger. Reconciliation was only achieved in 1963 in Stockholm when they received a joint Nobel prize. • Hermann Staudinger wins Nobel Prize for Chemistry for the study of polymers. • Herman Schnell at Bayer first synthesises polycarbonate at Bayer Uerdingen plant. The initial discovery attracted little attention because carbonates were thought to be thermally unstable - how wrong they were! • Commercial launch of polyester fibres - the start of 'wash and wear'.	 Giulio Natta
1955	• High density polyethylene (manufactured using the Phillips - metal oxide catalysts - or Zeigler - aluminium alkyl catalysts - processes) produced and marketed.	
1956	• Patent filed by DuPont for first acetals (POM).	
1957	• Polypropylene commercially produced and marketed by Montecatini as 'Moplen' using Zeigler-Natta catalysts to control the structure of the polymer and to polymerise products that had previously been impossible. • Chavannes and Fielding invent 'bubble wrap' and later form the Sealed Air company to take the product to market. Everybody loves popping the bubbles - go on, admit it!	
1958	• Commercial production of polycarbonate resins produced from bis-phenol A in both Germany (Bayer) and USA (General Electric Co.). • Acetals (POM) introduced by DuPont (USA) under the trade name 'Delrin™' for conveyor applications. • First nylon cable ties introduced by Thomas and Betts in the US under the name Ty-Rap. • Lego moves totally from wooden toys to plastic bricks (made from ABS since 1963).	
1962	• Polyimides introduced by DuPont (USA).	
1963	• Ziegler and Natta share Nobel Prize for Chemistry for the synthesis of polymers.	
1965	• Polysulphones introduced by Union Carbide (USA). • PPO introduced by General Electric Co. (USA) and Aku (Holland). • Aromatic polyesters, ionomers introduced.	

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	• First glass-filled grades of acetals (Delrin™) introduced by DuPont. • Stephanie Kwolek discovers Kevlar whilst working for Dupont in Wilmington Delaware and researching alternative materials for tyre reinforcements. Kevlar is later used for body armour, fire-fighter suits and other critical applications.
1969	• Nylon flag left on the moon by Neil Armstrong.
1974	• Oil crisis strikes! Crude oil prices increase by 300%, ethylene prices increase by 200% and most other petrochemical based polymers increase by between 50% and 100%. Strangely enough interest in reprocessing waste and reducing materials use also grows! Prior to this it was normal to have processors pay for scrap to be taken away. After 1974 they wanted money for it.
1976	• DuPont releases Zytel ST (PA 6,6). • Montedison patents on PP (see Zeigler and Natta above) are about to run out and plant is being built throughout Europe to produce PP (later to be called 'the new mild steel').
1977	• PEEK first prepared by ICI (UK). • PET bottles first introduced.
1980	• PE-LLD introduced.
1983	• ICI and Bayer launch PEEK, PES and PPS as the new engineering thermoplastics. The costs are enormous but specialist applications create a lasting market even after ICI leaves the plastics market.
1990	• Warner Lambert develops Novon - a starch which is also an injection mouldable plastic, ICI launches Biopol. Both are bio-degradable plastics.
2000	• New commercially important polymers are unlikely to be developed from scratch and the emphasis is now on compounding existing polymers to create composites with improved properties. Some of the most exciting developments are in the use of cellulose fillers (wood flour, flax and many others) to extend and improve the plastics properties. • Polypropylene described as 'the new mild steel' by Alan Griffiths.
2002	• 'Formica' company seeks Chapter 11 protection in USA. The end of an era?

Acknowledgments: We would like to thank Colin Williamson of the Plastics Historical Society for permission to use some key dates for this timeline. All Trade Marks and Copyrights are acknowledged.

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