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ARTICLE / ARTIGO

Plastics in fashion: a review of plastic materials in modern and contemporary costume collections and their conservation

Plásticos na moda: uma revisão dos materiais plásticos usados em coleções de moda moderna e contemporânea e a sua conservação

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Abstract

The conservation of plastics has become a real concern in fashion collections. The researches carried in the last years in institutions dedicated to preserve modern and contemporary clothing, show the existence of a surprising number of polymeric materials, natural based or chemically synthetized, as well as several emerging conservation problems related to them. Literature and publicity from the 19th and 20th centuries evidences that their introduction to fashion was possible thanks to scientific and technical discoveries focused in obtaining lower-budget alternatives to costly materials historically used in jewelry and dressmaking. These discoveries lead to the creation of a new range of materials that revolutionized fashion, from the earliest moldable materials to the first artificial plastics produced by chemical modification and finally, synthetic plastics. The present work aims to review the characteristics, applications and conservation of plastic materials within contemporary costume collections, which nowadays, represent a big challenge for the field.

KEYWORDS
Costume
Contemporary fashion collections
Plastics
Synthetic materials
Conservation

Resumo

A conservação dos plásticos tornou-se uma preocupação real nas coleções de moda. A investigação efetuada, nos últimos anos, em instituições dedicadas à preservação do vestuário moderno e contemporâneo, mostra a existência de um número surpreendente de materiais poliméricos, de base natural ou sintetizados, bem como vários problemas emergentes de conservação com eles relacionados. A literatura e a publicidade dos séculos XIX e XX mostram que a sua introdução na moda foi possível graças a descobertas científicas e técnicas centradas na obtenção de alternativas menos dispendiosas a materiais historicamente utilizados na joalharia e na confeção de vestuário. Essas descobertas levaram à criação de uma nova gama de materiais que revolucionaram a moda, desde os primeiros materiais moldáveis até aos primeiros plásticos artificiais produzidos por modificação química e, finalmente, os plásticos sintéticos. Este trabalho pretende fazer uma revisão das características, aplicações e conservação dos materiais plásticos nas coleções de trajes contemporâneos, que hoje em dia representam um grande desafio para a área.

PALAVRAS-CHAVE
Trajes
Coleções de moda contemporâneas
Plásticos
Materiais sintéticos
Conservação

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Introduction

Clothing accessories have been used to complement and enhance garments throughout history. These are fickle to changes in fashion, styles and other social circumstances [1] and the trends of each period have dictated the incorporation of new accessories and objects, as well as the materials and techniques used in their creation, becoming authentic "symbols of their time" [2]. Some examples of this representativeness are the large-format combs made of tortoiseshell and metallic applications popularized in the 1830s, the Victorian mourning jewelry (Figure 1) or the corsets, whose use began to decline as girdles and brassieres became popular and gradually disappeared from women's clothing during the twentieth century [3].

Fashion and costume making have used all kinds of materials carved and molded into small accessories, amulets or jewels, ranging from wood, metal, precious stones and ceramics to pastes and even breadcrumbs or wax. However, the development of what we today know as plastics or moldable materials begins in the second half of the nineteenth century.

By the end of 1800s, materials obtained from different animal and vegetal sources along with new modified products based on resins or rubbers have been developed in order to replace natural materials that were beginning to be scarce [4]. These shortages inspired the research for substitutes and simulants, and different attempts were made to obtain more affordable materials for the production of jewelry and decorative accessories traditionally made of precious stones, metals and expensive materials like ivory and tortoiseshell. Progressively, less costly alternatives were produced parting from natural polymers like cellulose or casein that fast popularized thank to their convincing aesthetic properties and especially due to the fact that only a mechanical shaping or a simple processing was needed for their transformation, leading to the creation of the first artificial plastics.

During the last decades of the century, different noble materials such as marble, ebony or jet coexisted with the new products introduced to the market like casein-formaldehyde, gutta percha or vulcanized rubber. Not many samples of these early plastics have arrived to date due to their instability and fragile conservation [5].

Plastic materials are organic polymeric compounds that can be shaped or molded into different forms under pressure or heat and can be classified according to multiple aspects: the structure of the macromolecules that constitute them, their polymer base, applications or their manufacturing method [6]. Another general classification tends to divide polymers that soften with heat, called thermoplastics, and those that remain unchanged once molded, known as thermosets or thermosetting plastics [7].

Friederike Waentig, on her part, performs a chronological classification where she establishes four phases within the development of plastics [8]. Among the materials included in the first phase, "The origins, plastics and their predecessors", we find those derived from natural substances and used pre-1839 like horn, tortoiseshell or amber, rubber or even paper mache, considered as precedents of modern plastics.

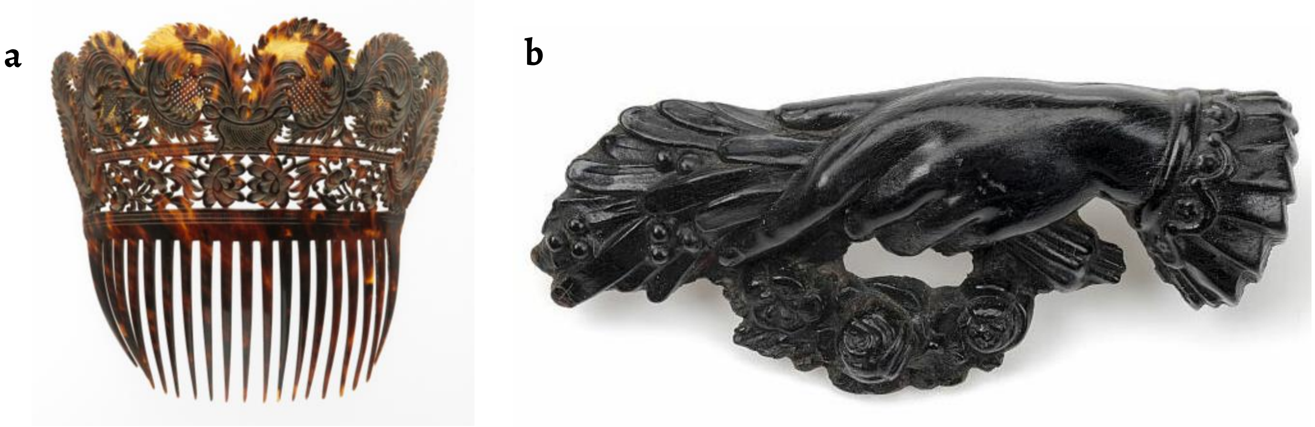

Figure 1. Jewelry: *a*) Tortoiseshell comb, late 18th century, Metropolitan Museum of New York; *b*) Victorian Mourning brooch, jet, 1850-1910, Museum of Rotterdam (photo: Europeana).

The second group, "The era of imitation materials", goes from 1839, when rubber vulcanization process was patented, to 1914 and enlists substances and mixtures that intended to simulate natural materials. Shellac, bois durci or the new chemically modified plastics such as Celluloid or Vulcanite are included here.

The following period from 1914 to 1950, entitled "The era of substitutes" will be characterized by the development of pure synthetic plastics still created as substitute materials like aminoplasts urea and melamine-formaldehyde.

The World War II definitively marked a turning point in the history of plastics. Many of them had been created in the 1930s, but it will be during the post-war years when new properties and qualities for the existing ones would be further investigated and developed. The "poly-era", as Waentig [8] named it, was constituted by synthetic plastics as polyesters, polyamides or polymethyl methacrylate that became regular in art and fashion collections from the 1960s.

Finally, according to their origin, another usual classification divides them into plastics based on natural polymers (animal or vegetable), semi-synthetics or modified natural polymers (casein, cellulose nitrate and cellulose acetate), early synthetics (phenol formaldehyde, amino formaldehyde) and those thermoplastics included in the "poly-era" or "poly-products" mentioned above [8-9]. Within the first ones, a subgroup called "mixed plastics" can be distinguished with materials such as bois durci or paper mache [10-11]. Those have in common the presence of a filler or stuffer (e.g. paper or sawdust) and a naturally occurring organic binder such as bitumen or albumen.

Currently, plastic materials can be found in museums, galleries and costume collections and it has been observed that many of them degrade far more faster than other traditional materials like stone or ceramics, glass or even wood [8]. These polymers shrink, discolor and turn yellow, distort, crack, become sticky, powdery and brittle to even disintegrate [12] depending on their composition and formulation and certainly due to the action of environmental conditions.

Even though research on the conservation of plastics has advanced significantly since its start in the 90s, the behavior of plastics is still hard to predict. Their chemical characterization and correct identification are essential in order to avoid or at least inhibit further deterioration and define safe preservation measures, intervention and display strategies [13].

However, for conservators, it is also necessary to understand their historical context and which technologies were available when the object was made because the history of plastics is of decisive importance when we are considering how to best to conserve and restore them [8]. A correct interpretation of the elements and objects present in modern and contemporary costume and fashion collections requires understanding their social and cultural framework, the qualities and functions that should be preserved and even the intend of their designer or creator [14].

Through the study of historical and scientific literature and advertisements available from the period, is visible that the introduction of plastics and synthetic materials to fashion was possible thanks to different discoveries and researches developed between the nineteenth and the twentieth centuries [10-11]. Many of the new materials and objects created then, are today studied and preserved in museums and institutions all over the world, and "collecting the various stories of plastic" [12] is necessary in order to conserve adequately these pieces, both from a material viewpoint as well as from a historical perspective.

Taking into account the different classifications mentioned, their chemical composition as well as their historical and technological background, the most important materials that are likely to be found in modern and contemporary costume collections and their main conservation problems are next reviewed.

Plastics in fashion

Within naturally occurring plastic materials that can be softened when heated and sculpted or formed in molds, we can distinguish a group of animal origin that include materials like horn, tortoiseshell or ivory and another group of vegetable origin materials such as rubber, gutta-percha or amber. Although many of those materials, especially those obtained from animals, are no longer used, for centuries they were very well considered in the fabrication of decorative artifacts, fashion accessories and jewelry.

Animal origin natural plastics

Horn and baleen

Horn is a protein-based material composed mostly of keratin, which can be considered the first material modeled on a commercial scale. The earliest written reference to the processing of this material is from 1284, but it was later in 1712 when John O' Brisset discovered that applying heat and pressure it was possible to obtain thin layers that could be shaped into molds [4, 8]. It could be colored to obtain tones ranging from black, used mainly to simulate ebony and jet, to almost translucent sheets that served as substitute for glass [8, 10].

The use of this material boomed when snuffboxes made to carry powdered tobacco became popular in London, and later in the nineteenth century, especially during the mourning period for Queen Victoria, due to the obligation to wear only black clothing and jewelry in public [15]. Horn was then molded into brooches, buckles, bracelets and also hairpins and combs [16-17]. Gradually they incorporated metallic elements such as screws (never present in real jet jewelry) (Figure 2a-b) or inlaid pearls to these brooches and other objects such as glasses.

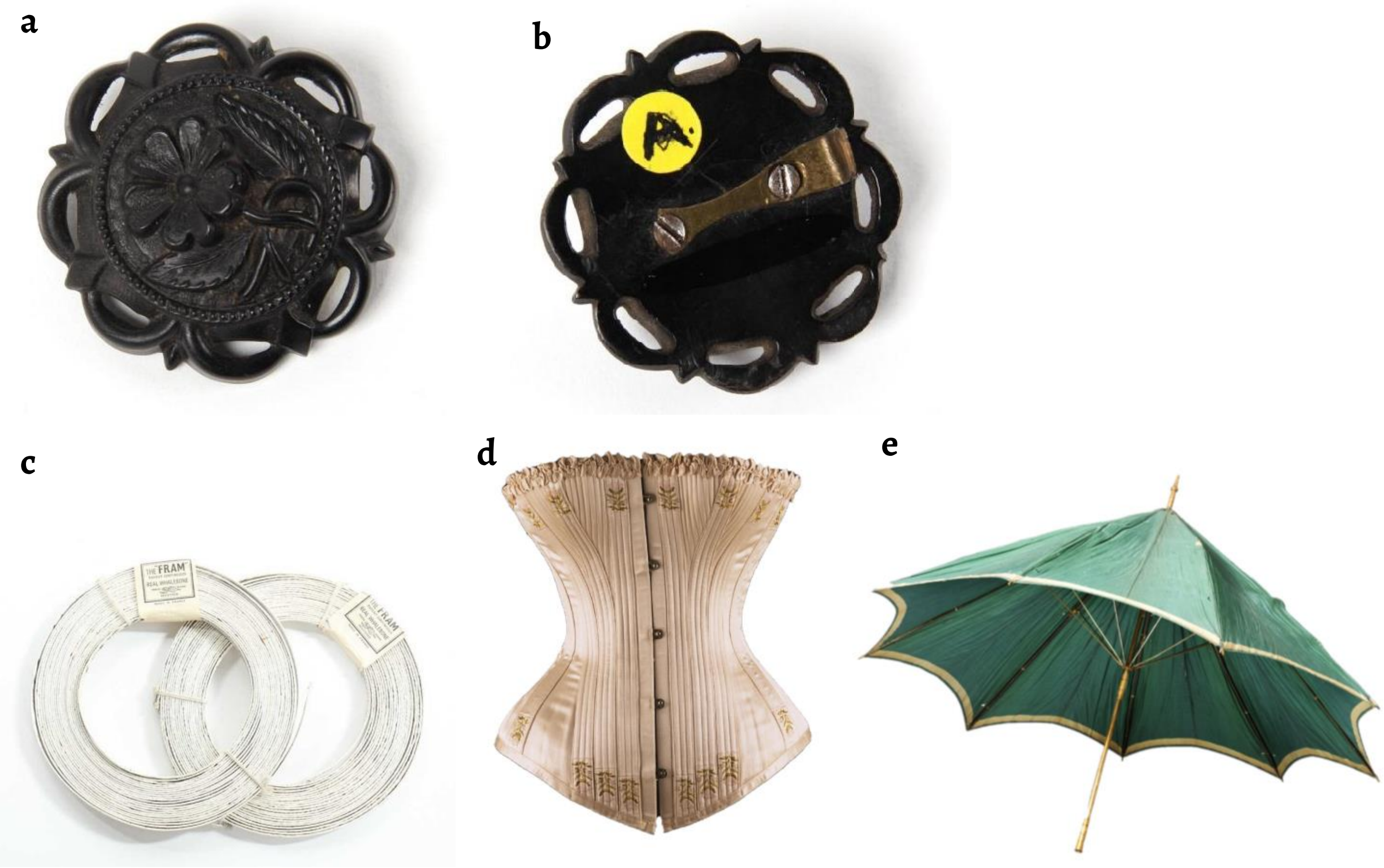

Figure 2. Pressed Horn Brooch, c.1850, Worshipful Company of Horners collection: *a)* front side and *b)* back side, Museum of Design in Plastics (MODIP), Arts University Bournemouth; And objects made with baleen: *c)* The Fram baleen rolls for corsets; *d)* Corset, ivory silk satin embroidered with silk, baleen, metal busk, c. 1900, Philadelphia Museum of Art; *e)* Parasol, silk, baleen, iron and cooper, 19th -20th century, Zuiderzeemuseum.

Horn objects conserved today are usually stable but the material has a tendency to delaminate due to its layered structure [16] and can present stress cracks, distortion and shrinkage in some cases [18] resulting sometimes in extreme fragility and break down of the material [19].

Baleen, usually miscalled whalebone**,** refers to the elastic bone plates that are located in the upper part of the jaws of the whale consisting of keratin. They are firm yet flexible and do not break easily. These properties made this material especially suitable for skirt and corset structures [20] and even umbrella bars (Figure 2c-e) but, while these garments and accessories were built to be sturdy, they can present specific damages in the boning and busks that tend to snap or slip respectively affecting their conservation [21].

Obviously, this material was neither easy to obtain or cheap, so corset makers began to use more economic substitutes as flexible woods like hazelnut or willow, spiral and flat steel or featherbones to be later substituted by artificial plastics such as Celluloid [4, 22].

Authentic whalebone was also used to make carved umbrella and cane handles, delicate jewelry and fans that usually contain metallic elements that can stain and affect it due to corrosion processes as it is been observed with other polymeric materials [23].

Tortoiseshell

Tortoiseshell is a thermoplastic material composed of β-keratin obtained from the back shells of the Hawksbill sea turtles (*Eretmochelys imbricata*). It was processed in much the same way as horn, retaining its natural pattern. By applying heat, the shell material could be divided into layers to get one of the most popular materials historically used for costume accessories, woodworking and other applied arts, and especially for toilet articles, i.e. combs, brushes, mirrors and costume jewelry [24].

It was difficult and expensive to obtain, so first horn was colored in red-brown to resemble tortoiseshell combs and inlaid work [25] and later on cellulose nitrate and cellulose acetate were used to replace it [4, 26].

This keratinous material is porous and even if it is not soluble in water, high relative humidity can cause swelling, warping and dimensional changes [27]. On the contrary, low relative humidity can bring desiccation and shrinkage producing hardly visible separations between layers resulting in a loss of translucency [28-29]. Besides tortoiseshell becomes grey and cloudy under UV light exposure [30].

It is of special importance to identify tortoiseshell and its imitations within fashion collections because even simple treatments with solvents like acetone that are innocuous for tortoiseshell pieces [31-32], could be fatal in the case of imitation materials like cellulose acetate [33].

Mother-of-pearl and ivory

Materials such as nacre, also known as mother of pearl, or ivory should also be mentioned despite not being fully organic polymer based, but organic-inorganic or biomineral composites since they have been historically shaped and manipulated into objects and elements in dressmaking. Besides, they both have been extensively imitated materials by the artificial plastics so it is of great importance to identify the most usual conservation problems affecting them.

Nacre is a material obtained from the inside of the shell of many mollusks and has a white color with a characteristic iridescent shine [34]. Considered as a precious material, it appears in jewelry, combs (Figure 3), buttons, fans and other clothing accessories and objects. Mother of pearl buttons and small accessories like buckles, can be dyed in different colors and decorated with engravings. These small nacre objects are generally quite stable to environmental conditions but large size objects can brittle and become fragile [35].

Figure 3. Combs: *a)* Nacre comb, 19th century, Hormiman Museum and Gardens' Collections; *b)* Ivory comb, 1907, MAK collection – Museum of Applied Arts of Vienna.

Several materials have been used through history to simulate nacre including iridescent coated wax or glass, and during the twentieth century, both cellulose nitrate and cellulose acetate and even polyester [4, 36] were used to manufacture fashion accessories and fake pearl and beads under trade names like Pearloid.

Ivory, obtained mainly from elephant tusks has also been used since prehistoric times to make artifacts, sculptures and decorative elements. Until the arrival of synthetic substitutes such as cellulose nitrate or casein, it was the main material used to make billiard balls, piano keys and different decorative elements in costume accessories such as fans, umbrella handles or modernist jewelry and hair combs [4].

As tortoiseshell, ivory is not soluble in water but can swell and deform in high humidity conditions [27] and desiccate when relative humidity is too low bringing cracking and splitting producing microscopic separations between its layers [28-29]. Ivory gets darken due to natural aging developing a yellow-brown patina [28] and it bleaches when exposed to light [37].

Vegetal origin natural plastics

Vegetable kingdom is also a rich source for moldable materials. Especially important are natural rubber and gutta-percha, very similar and chemically related substances. Rubber needs technical intervention to stabilize so it is often listed as a modified natural substance, thus, as a semisynthetic plastic. Resins like amber or shellac are usually included within this group along with other mixed plastics based on wood and cellulose like bois durci or paper mache.

Natural rubber

Rubber is an elastic hydrocarbon obtained as a milky emulsion (latex) from the exudation of trees of the Ephorbiacea family, primarily the *Hevea Brasiliensis* or Pará rubber tree. It is a material long known and used by ancient cultures (e.g. Mayans or Aztecs) because of its qualities of elasticity and impermeability for what it was first marketed as India Rubber [4].

After being introduced in Europe in the eighteenth century, the first investigations were conducted during the next century to achieve waterproof fabrics to obtain coated tissues, protective films and water-repellent textiles [38]. It is widely known that Scottish chemist Charles Macintosh patented in 1823 one of the first waterproof fabrics originally designed for awnings, combining rubber dissolved in naphtha with cotton.

No doubt, this material would later revolutionize fashion and clothing for its usefulness, but its early versions were not very successful. Untreated natural rubber is not stable in its solid form, oxidizes easily and it is very sensitive to temperature changes [8]. The rapid deterioration of early rubberized clothing was reported by the press of the time mentioning its "odious smell of sweat and the occasional melt down of the garments" [39]. Indeed, it became tacky and sticky when exposed to heat and brittle at low temperatures [40]. These problems were avoided with the discovery of the vulcanizing process.

Natural rubber

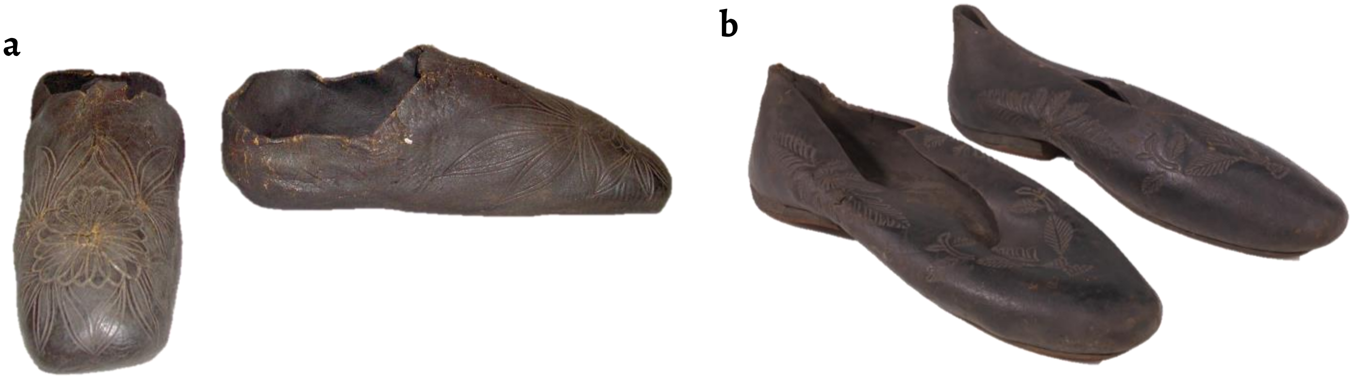

Figure 4. Shoes: *a*) Gutta percha overshoes, 1830, Metropolitan Museum of New York; *b*) Rubber galoshes, 1820-1839, Metropolitan Museum of New York.

The other version of rubber existing in nature is gutta-percha, a very similar material with a slight variation in the structural unit. It is also obtained from the solid latex of some Asian trees like *Palaquium Gutta*, *Palaquium Obloginfolia* or *Palaquium supfianum* [8]. Unlike rubber, it is hard but flexible and softens in hot water at a temperature of 100 °C becoming malleable, allowing molding and getting hardened when cooled [41].

John Tradescant, an English traveler and gardener, introduced the material in Europe, in 1656, but the discovery was at first considered just a botanical curiosity. It was during the nineteenth century when the first objects made with this material were exhibited in Europe after the Gutta Percha Company was founded in London in 1845 [4, 42].

Gradually it acquired interest as a material for medical devices, golf balls, dolls and small fashion accessories and shoes (Figure 4) as well as jewelry pieces, cameos and medals. It also became the favorite material for coating submarine telegraph cables with such a success that it would not be replaced by a synthetic material until 1940 [4, 43].

Gutta-percha oxidizes quite easily and it becomes brittle when exposed to air. It crumbles and tears relatively quickly, so very few examples have been preserved until today [5].

Amber

Alike nacre, amber it is considered a precious material and one of the most popular materials used along the history for jewelry making, amulets, buttons or cigarrete holders [4].

It is a fossilized tree resin (coming from conifers) that can be found in colors from pale yellow to black, always translucent and several factors including environmental conditions can affect it. Amber artifacts can suffer deterioration due to chemical alteration resulting in fragility and subsequently physical damage [44].

Being expensive and hard to work, plastic manufacture companies such as Celluloid Company during the nineteenth century or Pyralyn from DuPont around 1910, tried different substitutes to replace it [26]. Later on, one of the first uses of Bakelite, the first synthetic plastic, was precisely to imitate it [45].

Shellac

Shellac is an organic substance result of a parasitic relationship between the insect *Laccifer Lacca* and a tree species from Southeast Asia (*Butea frondosa*). It is a resin-like secretion than can be found in different colors from pale yellow to red and to be molded it was mixed with wood dust and subjected to heat and pressure [8].

It was manufactured in USA as molding material for making "union cases", protective frames for daguerreotypes and ambrotypes fabricated by companies like Peck, Halvorson or Critchlow. Later on new mixtures with mineral fillers were created and patented, both in United States (US) and in the United Kingdom (UK) [11]. It was also used to make brooches, decorated objects and cosmetic items such as toiletries under the name Diatite (Figure 5) [4-5, 46]. Not many of this objects can be found today in good conditions, because they tend to crack and chip over time.

Traditionally, shellac has been used as a protective and decorative lacquer applied in solution similar to Chinese lacquerwork [5]. Dissolved in alcohol, provides a bright and adhesive mixture used in "French polish" technique [10-11] and employed as a shiny coating for wood and metals. Shellac coatings have also been detected in metallic and gelatin sequins of several twentieth century dresses and accessories [47].

In addition, headgear and fashion manuals from the twentieth century mention a material used to obtain a glossy finish and give hardness to natural fabrics like raffia under the name "Shellac for headgear" that could be purchased in different colors. This coating was applied during the shaping of the hat and later to regain the luster that may have lost during this process, and was presumably pretty resistant to water [48].

According to García Fernández-Villa and San Andrés Moya, shellac varnishes show worse behavior against humidity than molded objects but both can be affected by high temperatures and strong lighting, producing softening and darkening. It generally does not suffer biological attack [10].

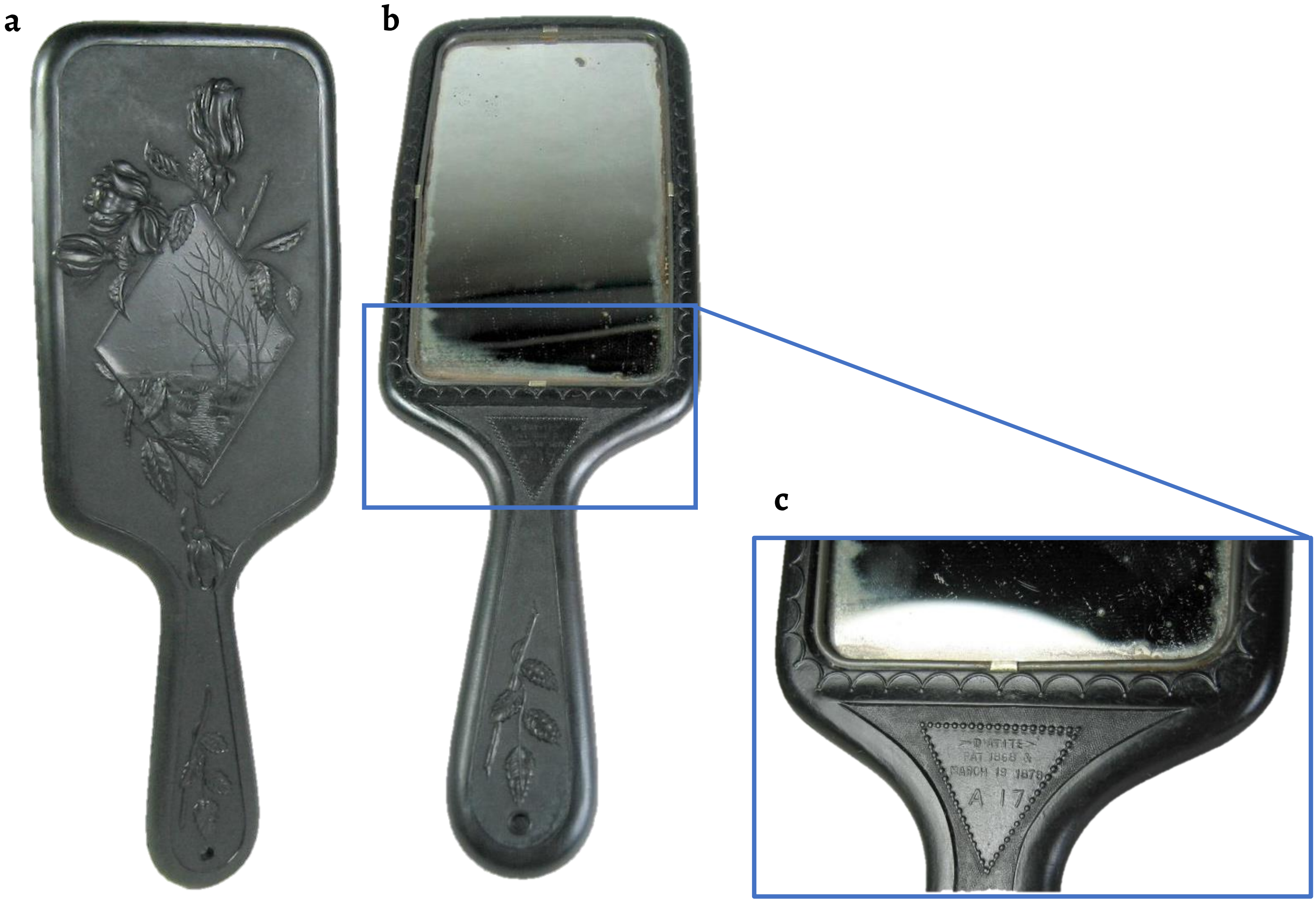

Figure 5. Diatite hand mirror, 19th century: a) back side; b) front side; c) detail "Diatite" (photo: WorthPoint Corporation, 2022).

Bois durci

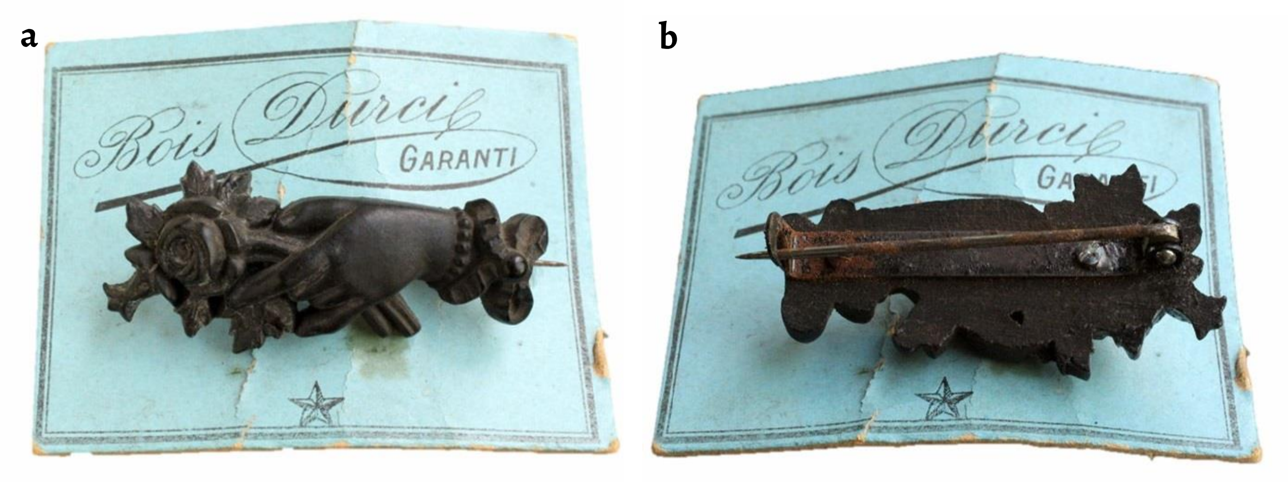

Figure 6. Victorian mourning brooch of hand clasping roses made of bois durci (photo: A. Kobensis).

In 1855, François C. Lepage patented a mixture for molding and casting called bois durci (hardened wood in French) obtained by mixing sawdust and egg albumen or cow blood [17]. By subjecting it to temperatures between 150 and 200 °C and pressure, a hard mass could be obtained. This brown or black thermosetting material with a polished surface served mainly to replace ebony or rosewood, which were costly and valued materials at the time [8].

It was widely used to create small decorative objects such as hair combs, pipes, commemorative plaques, desktop objects and specially mourning brooches and jewelry during the nineteenth and early twentieth century (Figure 6).

Bois durci is quite stable and many of the objects conserved today show no signs of degradation and even keep their original shiny appearance [8]. In some cases, pieces were polished with waxes, which according to Morgan may have contributed to their conservation [9]. In the case of objects that have been exposed to excessive light, a slight discolouration and an increase in the dustiness of the surface has been observed [8].

Papier-mâché (Paper mache)

Although the French term *papier-mâché* or paper mache refers us inevitably to crafts, it has been since the eighteenth century, when it was first patented [43], a versatile material that served as a substitute for wood and even used for the fulfillment of architectural elements and furniture [8, 49]. It was first used as glued panels by applying heat used in construction, furniture and paintings [43, 50] and in paste form, consisting of paper pulp, wood fibers or rags bound with animal glue. Other version of these pastes were made of flour and arabic gum and even had fillings or loads of rice flour, rye or mashed potatoes [8]. This last mixture was directed mainly to the manufacture of dolls. Decorative and snuff boxes and imitation jewelry was made with this material.

Pulp ware is a more recent British variant that was bound with natural resins and linseed oil. Cleaned sawdust was used in addition to paper and the mass obtained was baked in a kiln and it was more waterproof than paper mache [8].

Thetford Pulp was another example of a patented waterproof material developed during the nineteenth century from jute sacking, wood pulp, vegetable fibers and linen rags used to produce decorative boxes, small pottery and crockery items and even helmets until the end of the 40s [43].

In Germany, a variant was also used to create an artificial leather named Presstoff that was manufactured using a layered and treated paper pulp directed to all kinds of costume accessories from belts to bags and cases. With time, it tended to delaminate and loose cohesion and it broke down when it became wet [51].

All the materials mentioned above, especially those using cellulosic fillers (paper or sawdust) in their mixture to obtain moldable objects, are highly reactive to high humidity conditions and their chemical behavior determines all possible conservation treatments [52-53].

Semi-synthetic plastics

Artificial or semi-synthetic plastics come from raw natural materials that have been altered or chemically modified. Treated rubber, cellulose esters like nitrate or acetate or milk protein based casein plastics were among the first artificially created materials that transformed clothing and accessories from the nineteenth century.

Vulcanized rubber

The vulcanization process, by which a resistant and stable material could be obtained from natural rubber, can be considered one of the technological discoveries of major repercussion in clothing and costume of the time [54]. The invention is attributed, on the one hand, to Charles N. Goodyear in the US and, on the other hand, to Thomas Hancock in England. Goodyear claimed to have discovered the sulfur-based vulcanization heating raw rubber with sulfur and white lead in 1839, but did not patent his invention until 1844 meanwhile Hancock patented it in 1843 [4, 8].

By the middle of the nineteenth century, many companies were legally manufacturing all kinds of rubber articles using Goodyear's and Hancock's patents in the US and the UK respectively. Hancock and Macintosh had formed a company in 1825 named "Charles Macintosh & Co." where from 1844 they produced durable soft-rubber products, such as shoes, collars, cuffs and rainwear. Even underwear, corsets and elastic girdles were made out or rubber (Figure 7a-c) as well as innumerable products for domestic and industrial use such as hose pipes, soccer balls or tires [8].

Besides Macintosh, Goodyear and Roxbury India Rubber in the US, Hutchinson and Rattier & Guibal in France were the major producers that commercialized rubber goods during that period [55]. Other manufacturers like Leverett Candee in the US acquired at the time licenses from Charles Goodyear for the production of rubber shoes and other garments with great success [56] and companies like Burberry or Bax & Company introduced impermeable clothes like the *Aquascutum* model (1851) that was made of wool treated and waterproofed with rubber [38]. Burberry also created and patented the water and wind proof fabric called gabardine in 1879 and patented it in 1907, producing one the most popular predecessors to the trench coat used years later by the soldiers during World War I [38, 57].

From the 1840s to 1890s rubber clothes were in high fashion but their use gradually declined [55]. During the twentieth century, the popularity of rubber coats began to give way to the new fashion of chemically treated rainproof coats [54] and many other different treatments and processes were investigated to create waterproof and resistant films using oil on cotton or silk fabrics. From the 40s lighter fabrics for clothing were used, popularizing polyvinyl chloride (PVC) and other plastic imitations [58].

Vulcanize rubber was also utilized to produce rigid elements such as dress buttons, jewelry or tobacco pipes under the name Ebonite or Vulcanite in Britain or "hard rubber" in the US, becoming an excellent synthetic substitute for expensive natural materials [4, 46].

The introduction of sulfur in the vulcanization process was used to generate many crosslinks between chains of polyisoprene creating a material that was no longer thermoplastic but thermoset. This way a more stable and harder rubber is obtained without losing its natural elasticity, resulting more resistant to chemical attack and temperature changes than natural rubber. Its mechanical properties can differ varying the amount of sulfur added during vulcanization getting a harder material the higher the proportion of sulfur is [59].

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Figure 7. Advertisements of rubber garments and objects: *a)* Medicated Rubber Undergarments, 1909 (https://bit.ly/3MORRvY); *b)* Ladies' silk Rubber Mackintosh garments (1890), The Miriam and Ira D. Wallach Division of Art (photo: Picture Collection, The New York Public Library, https://bit.ly/3WINnvg); *c)* Worcester Rubber Company, Bloss & Rousseau, 19th century, (https://bit.ly/3IPZwst); And vulcanite-ebonite items: *d)* Vulcanite Comb, c.1851, Metropolitan Museum of New York; *e)* Ebonite Brooch. c. 1875, The Cloth Museum, Madrid (photo: F. J. Maza Domingo).

It could be manufactured in various colors although black and brown were predominant and therefore it was mostly employed for imitations of jet, to produce mourning jewelry, brooches (Figure 7d-e), bracelets and necklaces but also buttons and decorative boxes [4, 8]. In its bleached state, it was used from about 1860 as a substitute for ivory and horn [60] and it mixed with white and red pigments a pink substance was produced and used to resemble gums for false dentures [46].

Vulcanite can become brittle and cannot be re-molded. The exposure to light and moisture can oxidize the surface and bring color changes to typical dark grey-green (in the case of brown objects) [5] and khaki brown in the black ones [16]. It can also carry chemical changes due to the oxides of sulfur and sulfuric acid formed during the degradation with the consequent migration to the surface. Copper or brass inserts or screws in jewels can accelerate degradation [61].

Casein plastic

After several attempts to obtain a moldable material from casein, German scientists Adolph Spitteler and Wilhem Krisched developed and patented in 1897 casein formaldehyde, an artificial polymer manufactured from milk fat and formaldehyde [8].

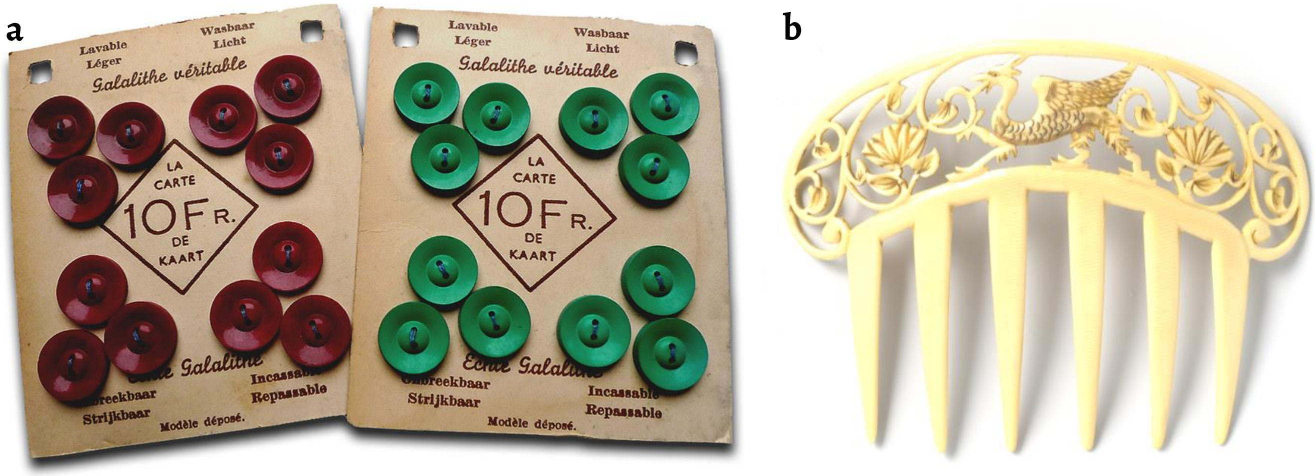


Figure 8. Casein products: *a*) Galalith buttons (photo: K. J. Cole); *b*) Hair comb imitating ivory, c.1925-1930, Rijksmuseum.

It was first marketed as Galalith and used to make imitations of tortoiseshell, horn, ivory and jade [2] and to simulate marble or stone objects. It was also known by trade names as Erinoid, Dorcasine or Lactoid in UK and Aladdinite or Amaroid in the US [4]. Casein was mainly used to make modernist jewelry and hair combs (Figure 8) by designers such as Auguste Bonaz as well as in the fabrication of buttons, buckles, corset clips or umbrella handles [4, 8].

Commercialized and labeled as "washable, light weighted, unbreakable and ironable", it has been considered as one of "the best of the early plastics" [62] since all kind of colors, finishes and effects could be achieved by an easy and cheap processing. Even more, unlike Celluloid, which was in trend at that time, it was non-flammable and burned very weakly [8].

However, the material had a few drawbacks from the beginning. Casein plastics were plasticized with water so they absorb and expel moisture expanding or shrinking depending on the surrounding environment. Being very reactive to fluctuations, the recommended relative humidity for this material is usually higher than for the rest of plastics, around 60 %. At low relative humidity (RH), eventually, dehydration causes shrinkage and consequent distortion resulting in brittle surfaces, cracks and crackles although it is unlikely to reach disintegration as happens to cellulose nitrate [4-5].

It is resistant to many solvents but acids or strong alkaline solutions cause degradation of the polymer and may cause crazing [63]. Casein objects are also susceptible to biological attack due to its protein base [64] and other usual problems is color fading from light exposure and failure of colorfastness of the dyes employed in its manufacture that is non-reversible [65].

Cellulose nitrate

When in 1845, German chemist Christian Friedrich Schönbein discovers nitrocellulose, also known as guncotton or pyroxylin gunpowder, the doors opened to the race for new materials and plastics. In 1846, after applying for a patent for cotton gunpowder, he obtains a cellulose nitrate with a lower degree of nitration, soluble in a mixture of ether and alcohol that formed a clear and gelatinous solution known as collodion. With the evaporation of the solvent a transparent film was formed that was initially used to heal wounds and in photography [8].

It was not until the mid 50s of the nineteenth century when the first attempts to obtain a marketable cellulose nitrate succeeded in the hands of British Alexander Parkes, who achieved to produce cellulose nitrate from nitric acid, sulfuric acid and cellulose, derived from sources such as cotton. This was mixed with vegetable oils and organic solvents giving a moldable dough [4, 8].

The pyroxylin solutions had problems when molded since the high temperatures that were required caused its decomposition and eventually it became hard and brittle. In 1865, after obtaining several patents of collodion and modified pyroxylin, he introduced a new type of cellulose nitrate, to which camphor was added, under the name Parkesine. Later the production of cellulose nitrate objects continued under the name Xylonite. Other commercial brands were Viscoloid, Ivoride (imitation ivory), Cristaloid (glass imitations), Fiberloid, Coraline, Pulveroid, Pasbosene, Cellonite or Pyralin (Figure 9a-c) [4, 8].

Meanwhile in the US, John Wesley Hyatt also developed a type of cellulose nitrate using camphor as a plasticizer and he patented the product as Celluloid, which became the first commercial plastic in America [7]. Hair slides, glasses' frames, combs, buttons, fans and toiletries were manufactured with cellulose nitrate simulating the appearance of materials like amber, ivory or tortoiseshell and reproduced hardness, transparency, colors and designs of all kinds (Figure 9d-f). The use of hair combs and hatpins decreased in the 1920s with the coming of the short bobbed hairstyle, resulting in a much reduced market [4, 17, 66].

Little plastic elements such as corset clasps, bust bodice's bonings or zippers can be found in Cristobal Balenciaga or Elsa Schiaparelli's dresses from the 30s and 40s. They usually appear next to natural fabrics such as silk or cotton or semi-synthetic fabrics as viscose-rayon or triacetate, that can be affected by deterioration processes and products emitted by those plastics [67].

Figure 9. Advertisements of commercialized cellulose nitrate brands: *a*) Ivory Pyralin from Du Pont de Nemours Company, 1920 (https://bit.ly/3gSMhrP); *b*) Amber Pyralin from Dupont, c. 1921 (https://bit.ly/3oSGLrZ); *c*) Fiberloid Company, 1923 (https://bit.ly/2K9IPNB); Cellulose nitrate pieces: *d*) Celluloid comb simulating tortoiseshell, Metropolitan Museum of New York; *e*) Ivorine Comb, Gillian Horsup Online Catalogue; *e*) Celluloid fan imitation of mother in pearl, 1925, Museum of applied arts in The Hague (photo: Europeana).

Contemporaneous designs and dresses may also contain trimmings and decorations that can present important conservation issues due to their moisture sensitivity as in the case of gelatin sequins. They were cheap and versatile and often laminated with cellulose nitrate to obtain iridescent and other decorative finishes [47].

Among men's fashion, cellulose nitrate detachable collars, cuffs, and shirtfronts became a successful and economic alternative to textile ones in the late nineteenth and early twentieth century due to their alleged waterproof and perspiration-proof characteristics [4, 68].

Other uses included its application as a varnish or coating film in order to create a synthetic replacements for leather. Materials such as Fabrikoid from Dupont or Rexine by Rexine Ltd of Hyde company were created to resemble expensive skin and leather by applying layers of cellulose nitrate on cotton fabric [69-70] and for millinery purposes. Bags, shoes, belts, and all kind of accessories were fabricated with these new pleather materials until the 1940s when it was replaced by the new vinyl materials.

Cellulose nitrate's deterioration has been widely documented and it is considered one of the plastics with more conservation problems in collections nowadays. Due to its chemical composition, it can degrade to release nitrogen oxides (NOx), which reacts with the environment moisture to produce nitric acid that can damage contiguous materials and elements, especially those presenting tissues like clothing and metallic clasps commonly found in costume garments and accessories [71].

It is important to be aware that this chemical damage can be occurring even when the object may appear to be in good condition, especially during long storage periods. Once degradation is detected, it is recommended to isolate the deteriorated piece from the rest of damageable objects using barrier materials to avoid direct contact, such as plastics sheeting and films fit for conservation [72-73].

Cellulose acetate – CA

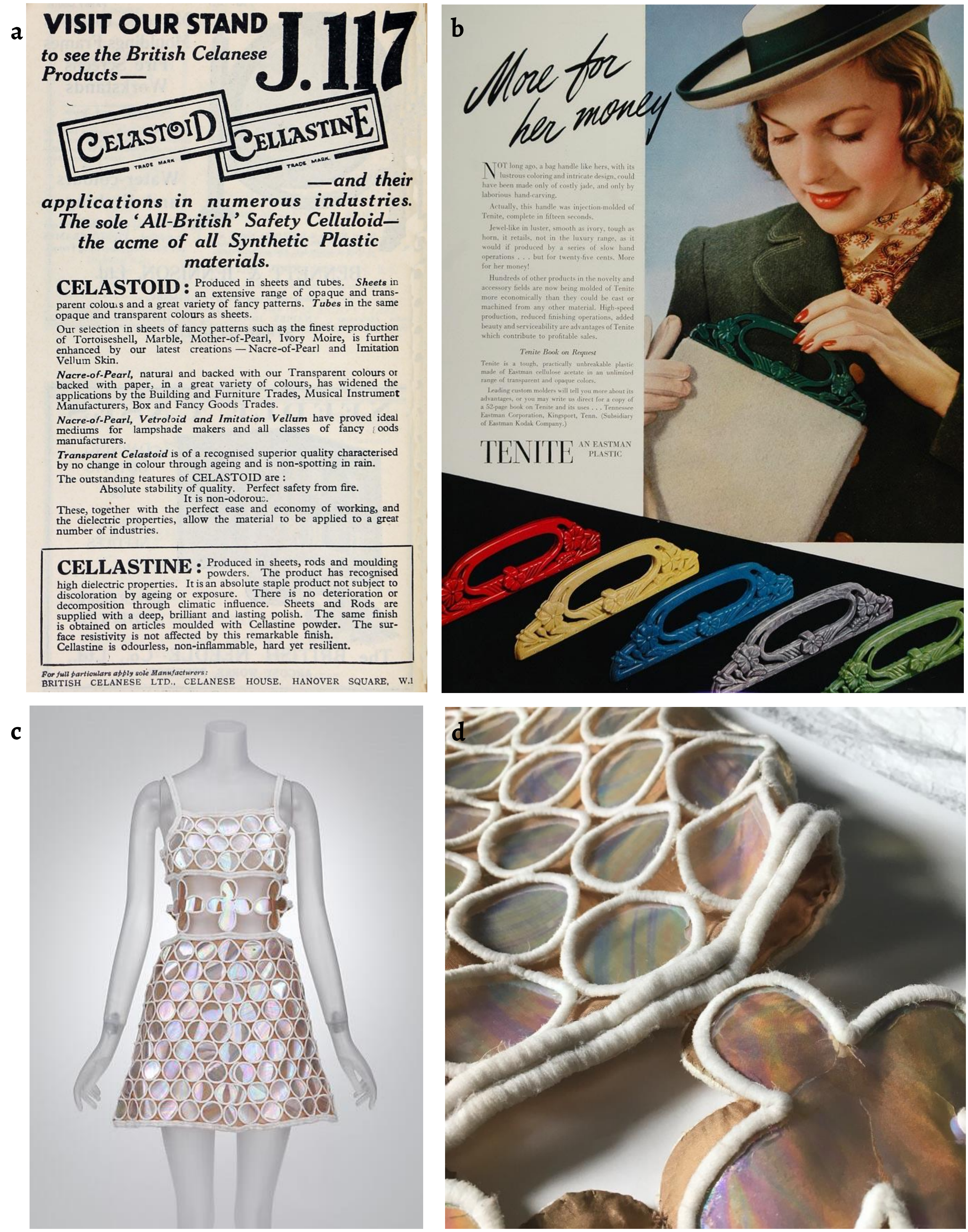
Cellulose nitrate caused problems since its start because of its high flammability, which boosted the search for other cellulose esters. In 1865, French chemist Paul Schutzenberger obtained the first cellulose acetate (CA) soluble in highly toxic chlorinated solvents and its processing was very costly. Cellulose triacetate was mainly used for the manufacture of textile fibers and gained commercial importance after World War II while the cellulose diacetate was also used to be molded [59].

In 1894, British scientists Charles Cross and Edward Bevan discovered and patented a process for the manufacture of a more stable CA, which had a similar structure to that of cellulose nitrate but it was not as flammable. Further investigations to find a common and inexpensive solvent to dissolve the polymer led the American chemist Georges Miles, in 1904, to discover that if the polymer was hydrolyzed it could be partially dissolved in acetone [8].

Following this new line, German researchers Arthur Eichengrün and Theodor Becker patented in 1909 the method for obtaining partially acetylated cellulose or cellulose diacetate that could be dissolved in acetone. During the World War I, it became popular for waterproofing fabrics of the airplanes' fuselages, promoting the interest in further research to improve the material [8].

Although it was marketed as "Safety Celluloid" [24], CA still presented some drawbacks: it suffered thermal degradation due to high temperatures that were required to be molded. The use of plasticizers (e.g. phosphoric acid esters) improved the elasticity and pliability of the polymer [8, 11].

Among the trade names under which CA was sold (including manufactured fibers and fabrics) were Celanese, Celastoid, Clarifoil and Cinemoid of Celanese Corporation or Tenite, Plastecele, Fibestos, Tortoloid and Viscoloid from DuPont, among others [4, 8].



VISIT OUR STAND J.117

to see the British Celanese Products—

CELASTOID TRADE MARK

CELLASTINE TRADE MARK.

—and their applications in numerous industries. The sole 'All-British' Safety Celluloid— the acme of all Synthetic Plastic materials.

CELASTOID: Produced in sheets and tubes. ***Sheets*** in an extensive range of opaque and transparent colours and a great variety of fancy patterns. ***Tubes*** in the same opaque and transparent colours as sheets.

Our selection in sheets of fancy patterns such as the finest reproduction of Tortoiseshell, Marble, Mother-of-Pearl, Ivory Moire, is further enhanced by our latest creations — Nacre-of-Pearl and Imitation Vellum Skin.

Nacre-of-Pearl, natural and backed with our Transparent colours or backed with paper, in a great variety of colours, has widened the applications by the Building and Furniture Trades, Musical Instrument Manufacturers, Box and Fancy Goods Trades.

Nacre-of-Pearl, Vetroloid and Imitation Vellum have proved ideal mediums for lampshade makers and all classes of fancy goods manufacturers.

Transparent Celastoid is of a recognised superior quality characterised by no change in colour through ageing and is non-spotting in rain.

The outstanding features of CELASTOID are:
Absolute stability of quality. Perfect safety from fire.
It is non-odorous.

These, together with the perfect ease and economy of working, and the dielectric properties, allow the material to be applied to a great number of industries.

CELLASTINE: Produced in sheets, rods and moulding powders. The product has recognised high dielectric properties. It is an absolute staple product not subject to discoloration by ageing or exposure. There is no deterioration or decomposition through climatic influence. Sheets and Rods are supplied with a deep, brilliant and lasting polish. The same finish is obtained on articles moulded with Cellastine powder. The surface resistivity is not affected by this remarkable finish. Cellastine is odourless, non-inflammable, hard yet resilient.

For full particulars apply sole Manufacturers:
BRITISH CELANESE LTD., CELANESE HOUSE, HANOVER SQUARE, W.1

More for her money

NOT long ago, a bag handle like hers, with its lustrous coloring and intricate design, could have been made only of costly jade, and only by laborious hand-carving.

Actually, this handle was injection-molded of Tenite, complete in fifteen seconds.

Jewel-like in luster, smooth as ivory, tough as horn, it retails, not in the luxury range, as it would if produced by a series of slow hand operations . . . but for twenty-five cents. More for her money!

Hundreds of other products in the novelty and accessory fields are now being molded of Tenite more economically than they could be cast or machined from any other material. High-speed production, reduced finishing operations, added beauty and serviceability are advantages of Tenite which contribute to profitable sales.

Tenite Book on Request

Tenite is a tough, practically unbreakable plastic made of Eastman cellulose acetate in an unlimited range of transparent and opaque colors.

Leading custom molders will tell you more about its advantages, or you may write us direct for a copy of a 52-page book on Tenite and its uses . . . Tennessee Eastman Corporation, Kingsport, Tenn. (Subsidiary of Eastman Kodak Company.)

TENITE AN EASTMAN PLASTIC

Figure 10. Cellulose acetate advertisements for: *a*) British Celanese's Cellastine and Celastoid, 1929 (https://bit.ly/3n7YcUS); *b*) Tenite from Eastman, 1938 (https://bit.ly/37OPmoR); and cellulose acetate used in fashion: *c*) André Courrèges dress (1968), made of cellulose acetate, silk and cotton, The Metropolitan Museum of Art; *d*) Detail of the deteriorated cellulose acetate film (photo: S. Scaturro).

It was used to make transparent movie negatives and photographic films and with the development, during the 30s, of the first injection molding machine invented by Eichengruen, making articles by pressure injection molds was enabled leading to the manufacture of all kind of objects as toys, toiletries, combs, necklaces or purse handles in different colors (Figure 10a-b). Popular plastic purses were made, like the "Shell bag" model (made of a mixed material named French Shell and Blonde) made of CA used during the 50s for hard bags alternating with Lucite (polymethyl methacrylate) [74].

In 1917, French chemical company Rhône – Poulenc invented another material based on CA that was called Rhodoid, from which plastic transparent sheets could be obtained and shaped to create accessories and jewelry. Rhodax, Rodhialine, Rodhophane were other commercial variants [75].

Different decorations, trimmings and elements like sequins were also fabricated with all variants of CA from flat sheets and films to moulded elements [47]. They can be found in the early works of artists and fashion designers as Schiaparelli or Balenciaga as well as in the futuristic designs by Paco Rabbane or André Courrèges [33, 76] (Figure 10c-d).

Both CA along with cellulose nitrate are inherently unstable due to their poorly stabilized and largely experimental formulations [77-80]. Cellulose acetate costume pieces in poor conservation state are not easy to treat and usually present irreversible damage, as is the case of pieces affected by chemical breakdown processes due to acid hydrolysis referred to as "vinegar syndrome" [8]. Besides moldable versions of CA also films and laminated fabrics found in hats and dresses present a real conservation challenge [33]. Nevertheless, still the best option to extend the lifetime and minimize damages of these works is the application of preventive measures [77, 81].

Synthetic plastics

Between the two World Wars, a breakthrough in the knowledge of plastic materials took place. The investigation was prompted to search for innovations in military material and many new plastics appeared during the period between 1935 and 1947. During the following decades, the production and consumption of plastics grew unstoppably.

In the late 20s and early 30s, plastics had stormed into fashion in the form of accessories, buttons, bracelets and jewelry imitating materials like ivory, jade or jet. After the Great Depression, plastic costume jewelry became very popular and became one of the favorite materials for Art Deco designs. Coco Chanel or Elsa Schiaparelli were among the first designers to include plastic jewelry and other elements in their fashion collections; soon many more would follow [82].

Phenol-formaldehyde resin (Bakelite)

At the time casein and CA were being introduced into the market, Leo Hendrick Baekeland, a Belgian American chemist, discovered the phenolic resin that patented in 1909 under the name Bakelite.

It was the first fully synthetic thermoset plastic that was obtained by condensation of phenol and formaldehyde with a catalyst. He first developed the resin in liquid form to be used as a lacquer to insulate electrical cables and waterproofing textiles. Then it was modified until a viscous resin could be poured into molds and completely polymerized at high temperatures to obtain a molded plastic [5], "perfectly insoluble, infusible and not sensitive to most chemical products; excellent as an insulator for heat and electricity" [83].

Figure 11. Different Bakelite jewelry pieces imitating: *a)* ivory and *b)* marble (photo: Chic Antique) (https://bit.ly/33heBBv); *c)* amber (photo: Collectorweekly); and Sample charts of: *d)* Marblette Corporation (photo: Meghan Weatherby, Art Deco Society of New York, Inc., 2020); *e)* Catalin Corporation (photo: Merrill Mabbs) (ClassicRadioGallery.com); *e)* Resinol fabric samples, Amsterdam Bakelite Collection, Reindert Groot.

Shortly, pieces of Bakelite appeared on the market imitating any possible material, from ivory to pearls and it was welcomed by fashion and haute couture designers of the time. "The material of the thousand uses" as it was advertised by the Bakelite Corporation, could be produced in any shape and color. There were transparent and translucent variations as the Applejuice version used to imitate amber, or opaque and mottled finishes simulating marble under brand name Marblette (Figure 11a-c)[45].

Accessories such as buttons, umbrella handles, jewelry and bangles, brooches or buckles were designed and molded with the new phenolic resin and sold under many different trademarks as Catalin, Herolite, Acrolite, Amberlite, Carvacraf, Erinite or Monolite [4, 8]. In addition, laminates and fabrics impregnated with phenolic resin were commercialized as Formica, Kellite, Resinox, Synthane, Resinol or Tufnol (Figure 11d-f) [2, 84].

Over time, colored Bakelite can be altered. It gradually develops a patina that can change the color of the surface; discolored and white versions turn yellow and other times blue colors may change to green [85]. It is one of the most collected plastics of the twentieth century and the conservation treatments as cleaning or volumetric reintegration are still a debate issue due to different criteria as it can be observed among collectors and conservators.

Formaldehyde urea and thiourea

The research to achieve an unbreakable glass led to the first experiments with amino resins combining urea and thiourea with formaldehyde. The aim was to obtain a molding plastic that allowed a wider range of colors in their production [8]. These investigations will culminate around 1920 when the Czechoslovakian Hans John achieved synthesizing a urea resin commercialized in 1924, a material that could stand the heat much better and would not get as dark as the existing phenolic resins. It was initially introduced as a material in the form of viscous solution for coating fabrics and adhesives [86].

After various researches carried out during the mid 20s, in 1928 the company British Cyanides introduced the urea/thiourea formaldehyde resin in powder with great advantages over phenol formaldehyde. In addition, other different resins, the amino formaldehyde resins, were also beginning to be used to create dishes, trays and other objects to mimic alabaster and marble [8, 17].

During the 20s and the 30s, the different formulas obtained were perfected and marketed: Kaurit or Aerolite for adhesives during the 30s and urea formaldehyde with loads of cellulose that was first introduced as Beetle to be later named as Beatl, to avoid the association between insects and kitchen items. Thiourea formaldehyde plastics were also sold under names like Bandalasta, Plaskon, Duraware, Hemocoware or Uralite from English and American companies of the British and American Cyanamid [8, 84].

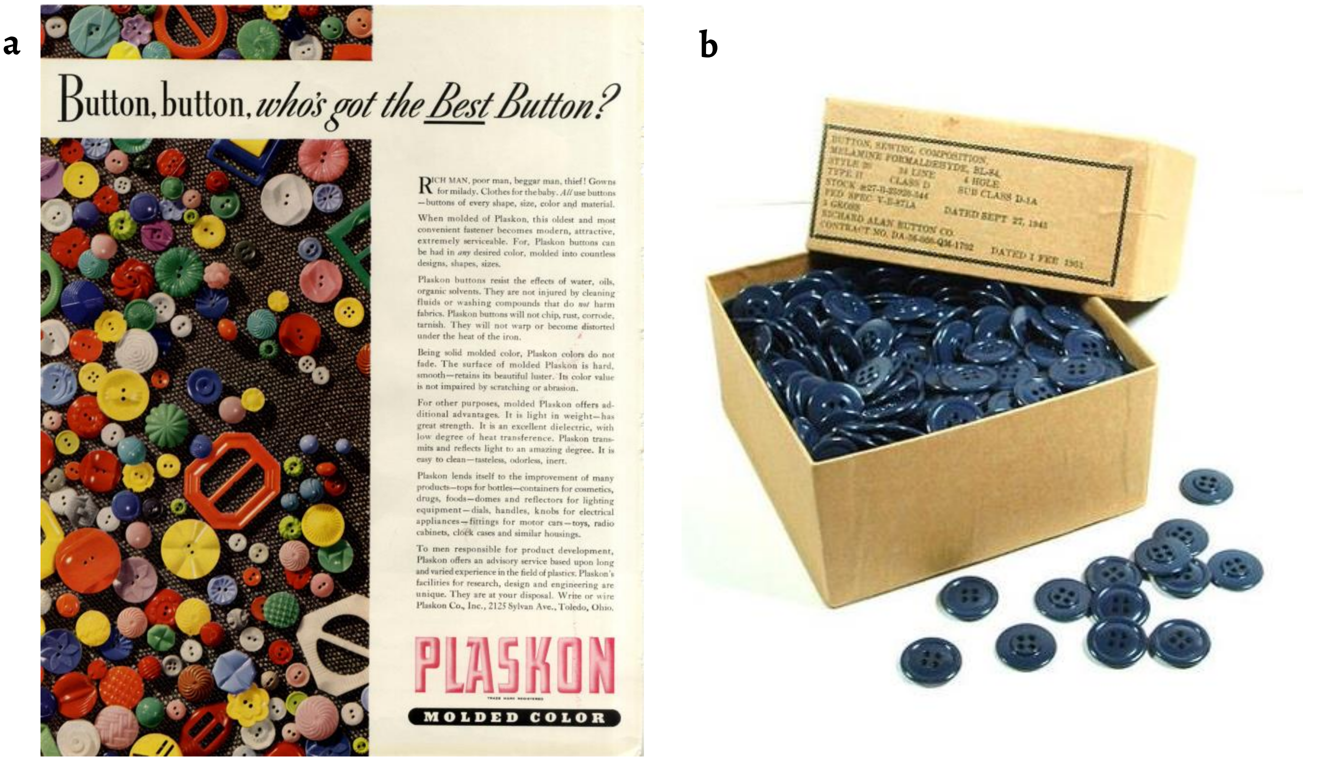
Although its processing was more expensive, urea formaldehyde plastics had some advantages over phenol-formaldehyde plastics. Besides being possible to get a wider range of colors, these resins were odorless and stable to light.

This type of plastics had, nevertheless, very limited uses because of the damages they tended to suffer from their early beginning. They had very little resistance to heat and humidity and many of the objects made for picnics in the 30s show nowadays a notable discoloration as they were used to serve hot tea [5]. Different accessories like snuff boxes and brushes were made with these plastics but a new and more successful melamine material soon replaced them.

Melamine formaldehyde

During the 30s, melamine formaldehyde is introduced to the market by big companies as American Cyanamid, Ciba or Henkel, that would eventually replace all other ureas for their better resistance to high temperatures and water. Melmac, Formica (Formica Corporation) or Melaware were some of the trade names used to name it [5, 84].

It was first used for impregnating textiles to avoid wrinkles and also as an adhesive, but its real development happened in the form of pieces created by a molding powder mixed with sawdust, cellulosic fibers, pigments or other mineral fillers and loads [8, 11]. It was widely used to make buttons, mainly for military clothing (Figure 12).



RICH MAN, poor man, beggar man, thief! Gowns for milady. Clothes for the baby. *All* use buttons—buttons of every shape, size, color and material.

When molded of Plaskon, this oldest and most convenient fastener becomes modern, attractive, extremely serviceable. For, Plaskon buttons can be had in *any* desired color, molded into countless designs, shapes, sizes.

Plaskon buttons resist the effects of water, oils, organic solvents. They are not injured by cleaning fluids or washing compounds that do *not* harm fabrics. Plaskon buttons will not chip, rust, corrode, tarnish. They will not warp or become distorted under the heat of the iron.

Being solid molded color, Plaskon colors do not fade. The surface of molded Plaskon is hard, smooth—retains its beautiful luster. Its color value is not impaired by scratching or abrasion.

For other purposes, molded Plaskon offers additional advantages. It is light in weight—has great strength. It is an excellent dielectric, with low degree of heat transference. Plaskon transmits and reflects light to an amazing degree. It is easy to clean—tasteless, odorless, inert.

Plaskon lends itself to the improvement of many products—tops for bottles—containers for cosmetics, drugs, foods—domes and reflectors for lighting equipment—dials, handles, knobs for electrical appliances—fittings for motor cars—toys, radio cabinets, clock cases and similar housings.

To men responsible for product development, Plaskon offers an advisory service based upon long and varied experience in the field of plastics. Plaskon's facilities for research, design and engineering are unique. They are at your disposal. Write or wire Plaskon Co., Inc., 2125 Sylvan Ave., Toledo, Ohio.

Figure 12. Buttons: *a*) Plaskon thiourea formaldehyde buttons advertisement, 1940 (https://bit.ly/2K95BoS); *b*) Melamine formaldehyde buttons, 1940s (https://bit.ly/37p8HxP).

According to Arthur Penfold (1956), director of the Museum of Applied Arts & Sciences of NSW in Sidney, it had advantage over other traditional button materials such as bone, ivory and horn [87]. It was durable, water resistant, did not burn or melt and could be easily manufactured in many colors. These plastics also have a good resistance to light (although they become matte sometimes), abrasion and the action of solvents and general recommendations are common museum conditions of around 40-60 % RH allowing seasonal fluctuations [63].

Poly methyl methacrylate - PMMA

During the 1930s, polymerized methyl methacrylate was developed, creating an unbreakable alternative to glass [8]. Indeed, the visual qualities of PMMA led to the creation of names like "acrylic glass" because the material had an exceptional optical clarity and transparency [76]. Plexigum and later Plexiglas were among the first trademarks under which the PMMA appeared in the market to introduce the material developed in 1928 by Otto Röhm and Walter Bauer from the German company Röhm & Haas when they were trying to develop a material for safety glasses [42, 88].

One of its most interesting applications was the design of jewelry. The first pieces were born at the hands of some British RAF pilots and war prisoners who carved in their free time recycled pieces of their planes [89]. From the 40s on, jewelry pieces were created using the same method as with phenolic resins obtaining a wide range of colors and designs with motifs of flowers, swans and boats, among many others (Figure 13a-c) [45].

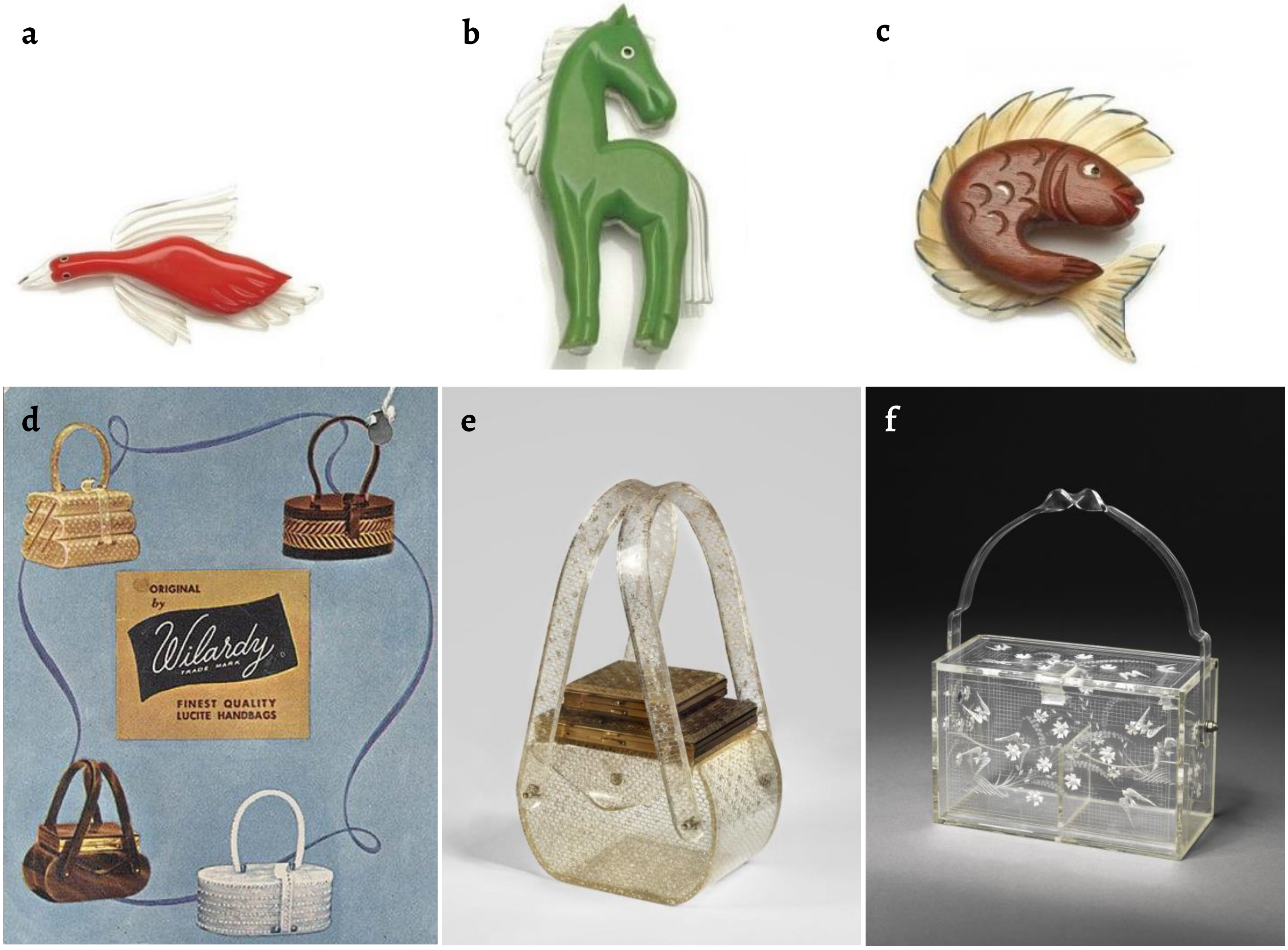


Figure 13. PMMA objects. Plastic jewelry: *a)* Swan made of Lucite and red Bakelite; *b)* Green Bakelite and Lucite horse; *c)* Fish-shaped brooch, Lucite and wood (photo: Leshner, 2005). Bags: *d)* Wilardy's original advertisement from the 1950s, *e)* "Stardust" Lucite evening bag, Wilardy Originals, 1950-1960; *f)* USA Engraved clear Perspex handbag, V &A Museum, London, 2021.

Perspex, another brand name patented in 1934 by Imperial Chemical Industries (ICI), was used to make design fashion objects such as heel shoes [90] during the war. Later, in the 50s, the name Lucite was given by the American company DuPont and it was used for molding square bags lavishly decorated and engraved (Figure 13d-f).

Perspex was also used in sheet or laminated form for performing flat elements such as sequins [70] by fashion designers like Paco Rabbane that had previously experimented with other plastics as acetate cellulose Rhodoid and other laminates in his famous haute couture designs. Several of the garments from his first collection of 1966, *12 Unwearable Dresses in Contemporary Materials*, are conserved today in museums like Philadelphia Museum of Art, the Metropolitan of New York or The Clothing Museum CIPE in Madrid.

Despite its hardness and toughness, the surface of PMMA has poor resistance to scratches and surface abrasion. Such defects tend to be obvious because, once cast or extruded, the material has usually a high surface gloss [76]. Another PMMA's specific degradation is the formation of small cracks and fractures on or below the surface, that can't be reversed [8].

The conservation of transparent acrylic plastics like PMMA entail a big challenge for art and fashion conservators and different researches [91-93] have been carried during the last years to find appropriate treatments directed to this delicate plastics in order to preserve them adequately.

Polyvinyl-chloride – PVC

After the investigations conducted during the nineteenth and in the early twentieth century by companies like B.F Goodrich, Union Carbide or Du Pont, finally, American Waldo L. Semon of Goodrich achieved to develop a method to plasticize PVC by blending it with various additives obtaining a rubbery solid [8]. Plasticized PVC could be achieved in many different types, with specific functional and aesthetic properties depending on the additives introduced during the processing (e.g. plasticizers, stabilizers, lubricants or fillers) [5, 84].

It was initially used for coating fabrics for raincoats, to waterproof shower curtains, watchbands or cables under the name Flamenol [26]. The first PVC moldable plastic was presented and marketed in 1931 as Koroseal and transparent garments and belts were fabricated [94] (Figure 14a).

It was one of the most used plastic materials in artistic production during the twentieth century so it is usual to find it in many contemporary collections. From Barbie dolls or LP discs previously made with shellac to different costume accessories were manufactured with PVC plastic under denominations like Vinylite, the brand name for products made of vinyl resins by Carbide and Carbon Chemicals Corporation and put on the market in the 1930s (Figure 14b) [8, 95]. One of the most interesting functions of PVC was to imitate leather (Leatherette), to make shoes, bags and raincoats during the 60s and 70s [2].

Fashion designers like Pierre Cardin, Andre Courregés, Mary Quant or Stephen Willats (Figure 14c-e) incorporated flexible PVC to their clothing designs during the 60s that are nowadays conserved in important design and fashion museums like the Victoria and Albert Museum in London or the Metropolitan Museum of New York.

PVC is one of the most adaptable synthetic plastics usually conformed by many different additives, especially stabilizers and plasticizers but, unfortunately, is not always stable. It can degrade chemically and physically [5, 84], getting tacky and brittle with time [26] becoming PVC objects' exhibition, handling and storage a challenge for costume and fashion conservators [96].

One of the biggest problems with PVC museum objects is that its plasticizer, typically di(2-ethylhexyl) phthalate (DEHP), easily migrates out. Some PVC objects, literally sweat and "weep plasticizer" [71], leaving the plastic vulnerable to cracking. Besides, the destabilization of the structure of PVC objects due to loss of the plasticizer leaves the objects' surfaces wet and sticky making them attractive to dust and grime. This problem can be found in contemporary collections with garments and coats made of PVC imitating leather (Figure 14c-e) [97].

Also stearic acid, which is a common additive used in many plastics as a lubricant to keep the object from sticking to its mold, tends to migrate out and harden in the case of deteriorate PVC, coating the surface of objects with a white powdery substance [71, 98].

Figure 14. Advertisements of PVC costumes: *a*) B.F Goodrich Koroseal Raincoats, 1947; *b*) Vinylite Plastics from Bakelite Corporation for handbags and shoes, 40s; and problems that can occur on the PVC costumes: *c*) Stephen Willats, "Variable Sheets/Optical Shift" mini dress (1965), dress with zipped panels of PVC presenting a sticky surface because plasticizer migration (photo: V&A Museum, London); *e*) Detail of a Paco Rabbane's raincoat from the 70s showing exudation of di(2-ethylhexyl) phthalate (DEHP) usually used as plasticizer for PVC, Museé Galliera, Paris [97, pp. 304-305]; *e*) Cleaning process of the weeping plasticizer of a PVC boot (photo: J. Hackett,V& A Museum, London).

Figure 15. Nylon ideas: *a)* First display of nylon stockings at the 1939 New York World's Fair, Hagley Museum And Archive, Science Photo Library Limited 2022; *b)* Advertisement from DuPont nylon combs and toothbrushes, Hagley Museum and Archive; *c)* Salvatore Ferragamo, invisible sandals, 1947, V&A Museum, London.

Polyamide – Nylon

Polyamide, commonly known as Nylon, was the first synthetic fiber introduced by DuPont in the New York Fair in 1939. Besides the popular nylon stockings that revolutionized fashion at the end of the 30s, fabrics, underwear, brush bristles and hair combs were produced with polyamide fibers (Figure 15a-b).

Polyamides also had their development in moldable shaped objects, which have very good result when mixed or reinforced with glass or other fillers [5] and as monofilament that appear in costume collections in jewelry pieces and other accessories like the iconic Salvatore Ferragamo's "invisible sandals" from 1947 [76, 99] (Figure 15c).

Nylon monofilament differs from other polyamide fibers for having a thicker diameter ranging from 0.1 to 1.8 mm. The numerous variations of nylon get different trade names corresponding to their molecular polymeric structure, and each type has different properties (e.g. nylon 6 (Celon, Danamid, Kapron, Nivion Dederon, Enalon, Perlon), nylon 6.6 (Blue C, ICI nylon, Perlon T, Ultron), nylon 6.10 (Decalon, Perfilon, Riplon, Tecron), nylon 7 (Enant, Onanth), nylon 11 (Rilsan, Undekalon), nylon bicomponent (Cancetrece), etc. [76, 100].

Nylon will darken when exposed to light and absorb moisture becoming subject to hydrolysis, especially in the presence of acidic pollutants [101].

Polyurethanes – PUR

Polyurethanes are one of the most versatile polymer groups being obtainable as rigid and flexible foams, fibers, as a coating material and can as well be molded [42]. They were first synthesized in 1937 by German chemist Otto Bayer [7] and began to be commercially available around the 1950s [8, 102].

Throughout his "brief museum history" it has been believed that its application in fashion collections was limited to fabrics made out of polyurethane elastomeric fibres knowns as Spandex or Lycra [100]. However, they are also present in coatings and in foam linings and interlinings [103] made out of the two chemical versions of PUR, polyurethane ethers and polyurethane esters.

PUR, along with PVC has been widely used to make artificial leather and during the twentieth century, different imitations made with both plastics would gradually enter in the market to replace natural leather in times of scarcity or simply because of their lower price [104].

Figure 16. Artificial leather: *a)* Naugahyde handbag, created in 1920 using leather fibers and rubber compounds first used for handbags (https://www.naugahyde.com/about/history.cfm); *b)* Corfam shoes designed by Mabel Julianelli (1964-1969), National Museum of American History, Behring Center, Smithsonian Institution (https://s.si.edu/3Nz8dZy).

Initially, the first leather substitutes were produced by soaking cotton in resins or waterproofing it with lacquers to be later fabricated in foils or PUR and plastic films. PUR synthetic leather is more flexible and has a higher resistance to extension, abrasion and other damage than PVC, so it was directed to the production of boots, costume accessories, belts or gloves as well as for upholstery for furniture and car seats.

This artificial leather popularly known as "pleather" was sold under names like Pantasote used for upholstery along with Fabrikoid, or Naugahyde [8] (Figure 16). Corfam, for instance, was a rubber based synthetic leather created by DUpont that produced handbags and shoes from 1958 until 1971 [8].

All forms of PUR are susceptible to chemical degradation by oxidation, resulting in discoloration and a loss of mechanical properties [5]. Polyurethane ether foam is more sensitive to oxidation meanwhile polyurethane esters are generally more sensitive to hydrolysis [102]. For instance, deteriorated Polyester polyurethane foam (PUR-ES) has been detected in some laminated dresses from the 60s in the costume collection of the Museum of London [105] showing a severe conservation state, with "brittle and weak foam that is being lost as dust", typical deterioration signs of polyurethane foams.

Polyester

Natural polyesters are known since 1840s, but the term polyester is used to refer to synthetic polymers derived from petroleum obtainable in sheets or molded, but especially important for the textile industry [8]. The main types that can be found in museums are divided into saturated and unsaturated polyesters. Polyethylene terephthalate (PET), for example, patented in 1941 by Jon Rex Whinfield and James Tennant Dickson, employees of the Calico Printer's Association of Manchester, is a saturated polyester type obtained by condensation [84].

Polyester and PET plastics had been used in fashion elements such as Lurex yarns. Lurex is the generic name given to imitation metallic threads since its introduction in the early 40s and later popularization in the 60s and was often used in fashion collections of the twentieth century (Figure 17) [106].

It has also been used for the creation of Melinex or Mylar films and the creation of plastic sequins in combination with acetate [107] along with other registered trademarks mainly used to commercialize fabrics like Cronar, Teijin, Teonex, Tetoron, Dacron or Terylene [84].

Even if polyesters are highly variable they all are generally quite stable to moisture and standard temperatures [8] but they suffer photo-oxidation causing discoloration and yellowing of the material [84].

LES NUITS PLUS BELLES QUE LES JOURS

De gauche à droite. Givenchy. Ce magnifique fourreau enroulé comme un arum est en crêpe rose Gauguin. Il est enrichi d'un boléro brodé, de forme asymétrique. Grès. Un empiècement, tout brodé par Mesrine, éclaire cette belle robe en mousseline de soie grise de Bianchini Férier. Coiffure Guillaume. Bijoux de Sterlé. Balenciaga. L'éclat d'un boléro givré de pierreries vert émeraude et piqué de plumes d'autruche légères, éclaire à *ravir* cette merveilleuse robe en satin jaune.

Figure 17. PET plastics used in fashion: *a)* Balenciaga's Bolero jacket advertised in 1966 (*L'officiel de la mode* n°537: 118-119); *b)* Balenciaga, Cristobal, Night Bolero with PET plastic strips and turquoise feathers, Balenciaga-Eisa, 1966, Cristobal Balenciaga Museum; *c)* Usual twisted ¨neck" deterioration present in PET strip simulating Lurex.

Other plastics present in costume and fashion collections

Although their presence might be rather punctual, other synthetic plastics should be mentioned and considered when it comes to characterizing contemporary costume collections. Polystyrene, for instance, is a hard and brittle material first commercialized in 1929 in Germany as a clear plastic. By 1933, it was marketed in the US as Victron without great success due to its high cost and limited color range, so it was replaced four years later by a new material called Styron of Dow Chemical (Figure 18). Other trademarks that are still in use today are Styrofoam, Luran, Lustrex, Fome-Cor, Algil, Shalon, Permene, Polyfil *or* Durastran [8]. It was used to make plastic jewelry, toiletries, decorative boxes and caskets [17, 71].

It is usually resistant to moisture but it yellows and brittles further due to photo- oxidation processes that turn the material stiffer [84].

Also polycarbonate, a plastic introduced around 1953 and marketed in 1959 under the name Makrolon [108] has occasionally been used in jewelry while polypropylene, commercialized around 1957, has been mainly applied in the fabrication of design objects [8] and specially for weaving techniques used in recent jewelry from the last decades [76].

You have a date with PLASTICS

It's a big and important date that America has with plastics. From Main Street to metropolis, Americans are familiar with durable plastic utensils in the kitchen, sparkling plastic jewel boxes in the boudoir. They know that plastics are warm and brilliant and give a welcome friendly touch to daily living. Yet better things in plastics are on the way. More and more these colorful and useful materials will contribute lasting satisfaction to America's life of the future—through new uses for plastics in automobiles and airplanes, tools and appliances, even in furniture-making and home-building. For better plastics, like Styron—developed through Dow's continuing research—are strong and enduring, as well as bright and beautiful. Styron and other plastics produced by Dow promise new luxury, new comfort, new scope—to everyday life and to "dress-up" occasions. They'll be within reach of everybody's pocketbook, too. And that's Dow's aim in striving for better plastics and hundreds of other useful products of chemistry.

STYRON
PLASTICS DIVISION

DOW
CHEMICALS
INDISPENSABLE TO INDUSTRY

Figure 18. Advertisement for Dow Styron, c.1950s, Dow Chemical Historical Collection, CHF Archives.

The first one is physically stable, resistant to moisture and oxidation under ambient conditions but transparent versions can become yellow if impurities were added to the plastic during the fabrication process. Polypropylene on the other side, discolors and becomes brittle due to photo-oxidations and thermal damage [84].

Synthetic rubbers like neoprene (based on polychloroprene) had also interesting applications in clothing and fashion collections during the twentieth century. DuPont marketed it for the first time in 1931 as a cheaper alternative to substitute natural rubber under the trade name Duprene but the early material had poor colour, a strong smell and was not very stable even if these defects were cured later [109].

Like its predecessor, the natural rubber, it was used to create water-resistant coatings for clothes and coats. Even if neoprene resists degradation more than natural rubber, currently presents considerable problems of deterioration within contemporary costume collections [110-111] as well as happens to most of the plastic materials mentioned along the text.

Considerations on the conservation of plastics

A surprising number of materials, natural based or chemically synthetized, have been used through the history to create fashion accessories and decorative objects that today form part of contemporary costume collections.

The second half of the nineteenth century represented a decisive period in the research and development of plastics and essential discoveries lead to the creation of a completely new range of materials that revolutionized clothing and fashion.

The struggle in order to obtain simulants and lower-budget alternatives to expensive and costly materials historically used in jewelry and dressmaking, and the demand for rubber and waterproof garments increased toward the end of the century thank to improvements such as vulcanization or the creation of artificial plastics like Celluloid. By the twentieth century, most plastic products moved away from natural raw materials to synthetically produced ones.

Relating to their conservation, the research carried in the last years in museums and institutions concerning the care of costume and contemporary fashion, has confirmed the wide presence of the mentioned materials and the number of emerging conservation problems related to them that need to be tackled.

Early detection of plastic components and accessories inside costume collections is the key to define proper conservation needs and treatments, but due to their original function as substitutes of other costly materials, they often camouflage among many other elements and materials within the contemporary "multimedia" clothing [103]. A significant fact is that curators and conservators sometimes are not even aware that plastics might be part of their collections until is too late to stop deterioration processes [112] what, according to contemporary fashion conservators makes them authentic “hidden time bombs" [99].

Back in 2008, Friederike Waentig [8] stated in his extensive investigation over plastics in art, that scientific concern with the restoration and conservation of synthetic materials was still in infancy. While important research results are available nowadays for some polymeric materials and their conservation [5, 84], others have hardly been investigated and, as pointed in the introduction, the behavior and deterioration of plastic materials is not easy to predict nor easy to detect.

Plastics preserved in contemporary costume collections often show problems during exhibition periods and storage. Although it is known that cellulose acetate, cellulose nitrate, PVC, polyurethane and synthetic rubber are currently considered the most problematic plastics [84, 113], museum objects made from polyester and polypropylene are also beginning to show problems [71]. The deterioration of natural rubber is still another of the biggest challenges that appear in particular costume accessories such as shoes’ soles [70].

Besides molded plastic accessories and clothing elements, also laminated and coated fabrics imitating leather have been detected in recent designs and works showing deterioration signs and conservation problems [113-115] that need to be addressed immediately.

As it is well known, degradation of plastic materials can be accelerated by exposure to factors like ultraviolet and visible light, heat, humidity, solvents and chemicals or pollutants as well as by other components and additives usually present in their formulation.

Identification of the polymeric structure of these materials is important to understand how these chains may be affected by the mentioned causes [9] in order to make an accurate interpretation of the degradation processes that plastics may undergo and provide adequate conservation conditions. However, this task is not easy for professionals concerned with conservation of cultural heritage due to the huge variety of materials and formulations existing.

The multiple denominations, trade names and brands available in the market during the nineteenth and twentieth centuries to designate plastics can also become a complication factor that often obscure the actual substance behind different commercial names [8]. These denomination problems may lead to incorrect or imprecise cataloging or the characterization of those materials under generic terms such as "plastic" or synthetic resin [116].

Even though some plastics' degradation processes should be individually monitored and engaged, most museums and art institutions usually apply general standards directed to fragile organic materials for most of them, keeping a relative humidity of around 50 %, temperature of 18-20 °C and low light levels of around 50 lux [81, 117].

The implementation of low temperature conditions with some plastics or the use of absorbents and adsorbents is also an expanded conservation practice in museums and collections to prevent further degradation due to the presence of pollutants or oxygen [8, 118-120]. In extreme cases, objects can be enclosed in oxygen-impermeable transparent bags composed of Escal, a ceramic-coated plastic film, together with sorbents as silica gel, zeolites or activated carbon in order to create an anoxia type environment to slow down oxidation processes and keep moisture under control [72].

Modern and contemporary costume and fashion collections are characterized by the quantity and complexity of the materials that constitute them, and clearly, plastic elements and objects are part of them. Early detection of these elements in costume collections is essential in order to catalogue and contextualize these works properly and, specially, to provide an adequate environment and conditions for their preservation in the future. As there is not a single conservation and storage strategy that is ideal for every plastic [59], for most of the objects and elements reviewed here, preventive conservation measures and optimum storage currently represents the only chance of survival.

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