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Review

Pre- and Protohistoric Biopolymeric Materials [1]

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Abstract:, Fossilised natural polymers like *Siegburgit,* Baltic amber and 'ape hair' were synthesized by nature million years ago. Very early, human species used some of them or even prepared on their part such biopolymeric materials. These comprise leather, birchbark pitch, horn. Later on, the manufacture of papyrus, parchment and natural rubber was realised. Without the use of those early biopolymeric materials for clothes, tools, adhesives, jewelry and many other objects of daily life, the development of human life in its full diversity would not have been possible.

Keywords: Prehistoric, protohistoric, polymers, biopolymers, *Siegburgit*, *Beckerit*, Krantzit, Baltic amber, horn, pitch, tar, bitumen, asphalt, fossil natural rubber, pre-columbian caoutchouc, chewing gum, chicle.

Introduction

The 'awakening' of 'chemistry' is mostly connected with the production and dying of textiles, pottery, mining and manufacturing of metals, glass making and preparation of beer or wine. Their early beginnings lie far in prehistoric times.

The same applies to natural polymeric material used for different purposes since dawn of mankind. Without those early biopolymers, the development of human civilisation and its material history is not thinkable

On the one hand, some natural polymeric substances formed million of years ago will be presented in this review. They have not been utilised by early human species, but can be regarded as the 'ancestors' of modern polymers.

On the other hand, a series of widely used, different biopolymeric material will be described, without considering the large group of textile fibres.

Siegburgit, *Beckerit*, *Krantzit*: fossil, biopolymeric polystyrene

These fossil types of resin originate from the Eocene (ca. 55-35 million years years ago) [2].

Siegburgit was first described in 1875 by A. von Lasaulx [3]. In the sand layers above the seams of Siegburg and Troisdorf (Rhineland region, Germany) brown coal nodular, grey-white clumps have been found. (figure 1). Since long time, they attracted attention of the workers, because of the aromatic smell on combustion. As 'burning stones' and 'marl manikins' ("Mergelmänchen") they were used for mundane coffee cooking and potato roasting, but also - more sacred - burnt as frankincense in nearby churches. *Siegburgit* was further found at the open-cast mining in the Bitterfeld region (Saxony-Anhalt, Germany) [4].

Figure 1 *Siegburgit*, fossil polystyrene, Eocene, ca. 55-35 million years ago (Foto: Naturkundliches Museum Mauritianum, Altenburg, Germany)

First chemical investigations of *Siegburgit* were performed in 1884. After dry distillation, styrene and cinnamic acid were found [5], compounds not existing in e.g. Baltic amber.

New investigations have been performed, together with reference samples of recent *Storax* (from *Levant styrax*, *Liquidamber orientalis*) and of an analogous fossil resin found near Squankum (New Jersey, USA). Gas chromatography/mass spectrometry (GC/MS, Py/GC/MS) and size exclusion chromatography (SEC) revealed a certain additional content of low molecular triterpenoid compounds. The fraction soluble in tetrahydrofuran (THF) exhibit polystyrene with molar masses of at least 1.000.000 Da *, consisting to 80% of atatic polystyrene. The non soluble fraction was shown to be likewise polystyrene crosslinked via different side groups [6].

Beckerit [7], originating from the open-cast mining of Goitzsche (Saxony-Anhalt, Germany) was later on found to be the same as *Siegburgit* [2]. Furthermore, the fossil resin *Krantzit* from the brown coal mining at Latorf (near Nienburg/Saale, Saxony-Anhalt, Germany) [8] is also very similar to *Siegburgit*, exhibiting only different degrees of crosslinking [9]. All three species are now ranked to class III of fossil resinites [9,10]. As polystyrene resins, they differ significantly from various kinds of amber and copal, which do not contain this compound [11] (see below). *Siegburgit*, *Beckerit* and *Krantzit* have been formed as fossilised secretions of broad-leaf trees, which belong to witch-hazel plants (*Hamamelidaceae*) [9].

Baltic amber, *Succinit*: fossil, biopolymeric copolyesters

Similarly to the fossil biopolymers discussed before, the Baltic amber (*Succinit*) originates from the Eocene (ca. 55-35 million years ago) 12,13. It consists of the fossilised resin from Araucaria trees (*Araucariaceae*), belonging to the family of conifers [14].

In earlier times, amber was picked up on the beaches of the Baltic Sea or in shallow water ('amber fishing', "Bernsteinfischen") or digged in shore area ('amber digging', "Bernsteinstechen"). The most important place, where amber is found, lies in the 'blue earth' sediment ("Blaue Erde") near formerly Palmnicken, East Prussia, today Jantarny, district Kaliningrad. In more recent times, amber is extracted there in opencast mining [15].

Baltic amber (*Succinit*) consists of copolyesters of diterpenoid *abietic acid* derivatives with diterpenoid alcohols, e.g. *communol*. The latter is responsible for a partial crosslinking with bifunctional acids (*communic acid*, *succinic acid*) [10].

* Da = the standard atomic or molar mass unit

Amber belongs to class Ia of fossil resinites [10,11,16,17]. It is partially soluble in certain organic solvents, e.g. turpentine. Softening at around 115°C, amber liquefies at around 200 - 250°C without degradation [18]. Hot press moulding of scraps is possible, in fact amber is a thermoplastic biopolymeric material.

In very early periods, amber appeared and was used in human settlement sites.

First artifacts, e.g. perforated discs, needles, originate from the Late Upper Palaeolithic (12000-10000 BC [†]) [19-23]. Also from this time, the first figural amber object - an elk - was found in Weitsche/Lüchow-Dannenberg, Germany (figure 2) [24,25].

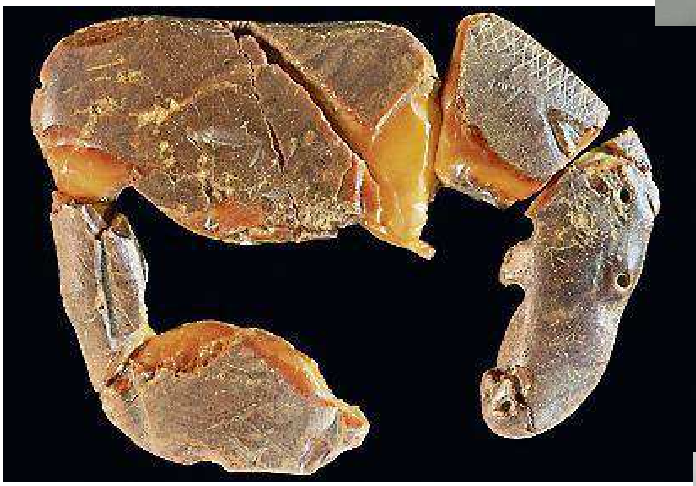

Figure 2 Elk, amber, Weitsche/Lüchow - Dannenberg, Late Upper Palaeolithic, ca. 12000-11000 BC (Foto: Hannoversche Allgemeine)

Later on, figural amber objects are known somewhat more frequently from the Mesolithic (ca. 9500-5500 BC), e.g. a small figurine of a wild pig, described 1884 by Rudolf Virchow [13] or the “Stolper Bär” (‘Stolpe bear’) found 1887 in Stolpe, Germany (figure 3) [26,27].

Since the neolithic period (ca. 5500-2200 BC), use and trading of amber increased considerably. At the end of the latest glacial epoch (ca. 12000 BC), the sea level had slowly risen. Around 5000 BC, the Baltic Sea of today was formed due to a connection with the North Sea. Thus, coastal amber deposits were increasingly washed out [28] and could be more easily collected on the Baltic beaches.

Figure 3 “Stolper Bär”, amber, Mesolithic, ca. 9500-5500 BC (Foto: Stettin, now Szczecin, Muzeum Narodowe, Grzegorz Solecki)

The “Woldenberger Bernsteinpferd” (‘Woldenberg amber horse’), attributed to the Neolithic, ca. 3000 BC, was found 1858 in Woldenberg, now Dobiegniew and published in 1881 [29] (figure 4) [30,31].

Figure 4 “Woldenberger Bernsteinpferd”, amber, Neolithic, ca. 3000 BC (Foto: Museum für Vor- und Frühgeschichte Berlin)

[†] BC = Before Christ; AD = Anno Domini

During the subsequent Bronze Age (2200 – 800 BC), exploitation, trading and use of amber increased extensively. In this period, amber almost came 'in vogue' [32]. Trade occurred westward via France and the Alpes to the western Mediterranean area or via the Danube to central Europe and via the Black Sea into the eastern Mediterranean regions [33].

In classical antiquity, the 'Gold of the North' was in enormous demand. Additionally to the western and central European trade routes, an eastern route from the Baltic via Vistula and Dniester and the Black Sea to the Greek region was established.

All in all, the different ways of transport of the amber trade were referred to as the "Amber Road" [28,33, 34]

The classical Greek denomination *ἤλεκτρον* (*électron)* indicates the static electrical properties of amber.

During the roman period, Aquilaea (today 'Aquileia') became the most important manufacturing centre [34]. At first, Tacitus (AD ca. 55-ca.120) used the term *glaesum* [35], which was deduced from the germanic *glezan*, >glossy, glass<, because of the transparent appearance of Baltic amber after polishing [36]. However, Tacitus and Pliny the Elder (AD 23-79) deduced by the observation of insect inclusions that it must be a solidified sap (*succus*) of trees and renamed it *succinum*.[28,35]

The English term 'amber' developed from Arabian *anbar*, Spanish *ambar*, Middle English *aumbre* [37].

The German name "Bernstein" developed from the Middle Low German *Börnsteen* from *börnen* >to burn< and means in fact 'burn stone' [38] (cf. analogy to the similar properties of *Siegburgit*).

Horn: biopolymeric protein α-keratin

The material 'Horn' should not be mistaken for 'horns' i.e. from antlers of deer, roes, elks, reindeers etc. They are totally different bone materials with a high inorganic content of calcium phosphate [39].

Horn of bovids (*bovidae*) and hoof horn of odd- and even-toed ungulates mainly consists of the biopolymeric fibre protein *α-keratin* [40] It is relatively soft, fibrous, flexible and capable to absorb moisture. In whole pieces or crushed, horn is ductile and mouldable above around 140 °C. The utilisation of these thermoplastic properties is documented only since medieval times.[41]

But already in prehistoric periods, horn was commonly used [39]. However, for this only indirect evidence is possible, because of the quick and quite effective microbial degradation of the uncrosslinked, biopolymeric material.

In the Stone Age, wild *bovinae* (aurochses, European bisons/wisents) were important hunted animals, as shown in the paleolithic cave paintings, e.g. Chauvet cave, France; ca. 31000 BC [42]). Those pictures symbolise life, power and strong virility. They received cultic worship for long historical epochs [43]. These ideas were also partially transferred to the material. The earliest illustration of a bovine horn originates from the Upper Palaeolithic (*Gravettien*, ca. 24000 BC). On a limestone relief, the so-called 'Venus of Laussel' (Dordogne, France) holds up a horn with her right hand (figure 5) [44].

Among the most early existing artifacts are decorated bovine horns from the Neolithic (Catalhöyük, Turkey; 7400-6200 BC) [43,45].

In the closed find deposits of 'Ötzi', the 'Iceman' or 'Similaun Man' (Hauslabjoch, Ötztal Alps, Italy/Austria), several artifacts of horn material are found (Late Neolithic/Chalcolithic, ca. 3250 BC) [46].

Furthermore, an intensive use of horn material is known since celtic times [47], e.g. drinking horns decorated with golden ornaments (Burial Chamber of Hochdorf, Germany, Early Iron Age/Hallstatt culture, ca. 530 BC [48,49]; cf. figure 6).

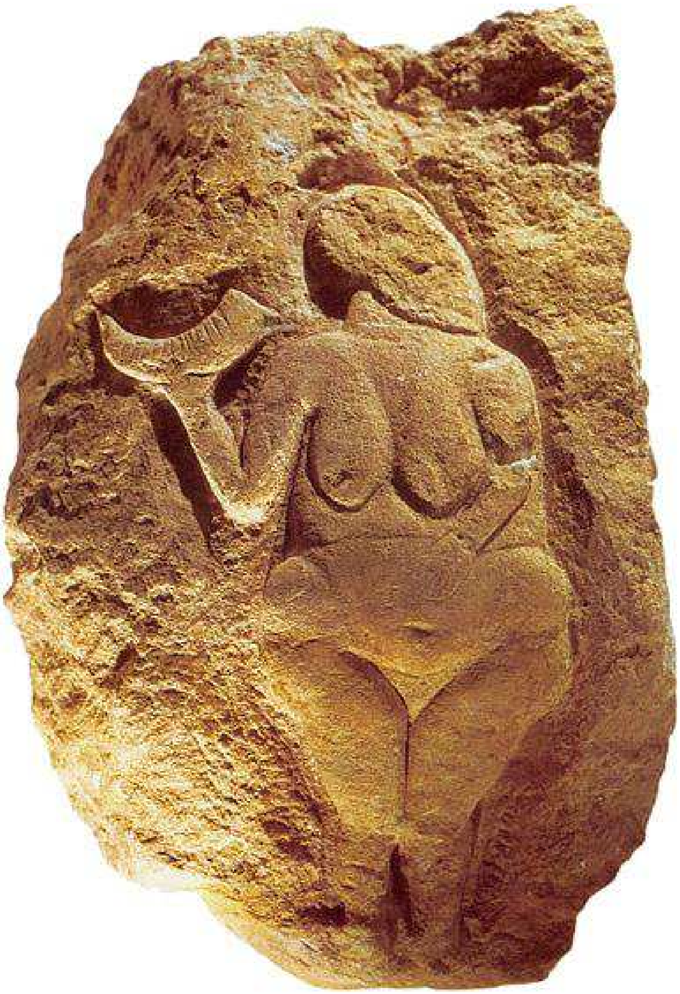

Figure 5 'Venus of Laussel', Dordogne, France, Upper Palaeolithic (*Gravettien*), ca. 24000 BC (Foto: Wikipedia)

Figure 6 Reconstructed drinking horns, original gold ornaments, Burial Chamber of Hochdorf, Germany; Early Iron Age/Hallstatt culture, ca. 530 BC (Foto: Frankfurter Allgemeine, 20.09.2012)

Leather, parchment: biopolymeric protein fibres and their conservation processes

Leather

In principle, the transformation of animal skin into leather is a consecutive, complicated process with manifold steps. The 'unhairing' (in earlier times in human urine or after being putrefied for several months) and the removal of the *epidermis* ('bucking' with e.g. wood ash and water) is followed by removal of the *subkutis* ('fleshing'). After a controlled degradation of the collagen fibres in the *corium* to losen them for more flexibility and to create more reaction sites for tanning agents ('pickling', in earlier times with dog faeces and bird dung), the rawhide is tanned, dyed, dried and oiled or regreased [50,51].

The *corium* in its upper part consists of fine, long fibres of the highmolecular protein *collagen*, which is - together with *cellulose* and *lignin* - the most commonly occurring natural biopolymer on a quantitative basis [52]. In the lower part of the *corium* bigger, elastic fibres of the proteins *elastin* and *fibrilin* are present. In the actual tanning process the amino or carboxylic groups of the protein fibres are chemically or physically crosslinked through the tanning agent [52-54]. Hereby and through reduced water absorption (swelling capacity), leather can no longer be degraded by microbial activities under the necessary humid conditions. The preservation by maintaining flexibility, elasticity, ductility and softness is the principal purpose of tanning.

A simple drying of coats and skins in open air or with salt, without applying pickling and tanning processes, is likewise able to decrease the water content. Under these conditions, the *collagen* fibres are packed more densely and stick together [52]. The material gets hard, brittle and stiff. Treated in such a way, dried furs and skins are stable at first againts microbial attack. However, contrary to real leather, simple dried skins exhibit a considerable capability of water absorption, so that subsequently rotting processes can recur easily. [52].

Furs and rawhide rank among the earliest biopolymeric materials used by mankind. At the latest from the glacial period beginning at around 400000 years ago [55] and during the following glacials, fire and clothing was essential for surviving, particularly in Europe. Primarily, furs and skins of hunted wild animals, cleaned and simply dried, served as clothing and footwear [56]. As mentioned, the material was not too stable against biodegradation. Improvement was achieved by pre-stages of a real tanning, like smoke or fat treatment, which facilitates the drying process, making the skins additionally more water repellent and flexible. Someday, the *Homo*-species prolonged the exposure with smoke and its components phenol and formaldehyde, which are disinfectants and react with proteins under crosslinking. Furthermore, they used instead of tallow the brain of terrestrial mammals or also fish oil, both containing unsaturated fatty acids with double bonds, capable of reacting and polymerising on air [[53,57]]. Herewith, a smooth transition to the real smoke and fat tanning processes began. These techniques rank among the oldest (bio)chemical processes, utilised by mankind [58]. To speak in this context of an early 'half' or 'pseudo' tanning [59], seems not to be helpful, the more so as these terms have been coined at the beginning of 20th century, before the concept of macromolecules was established by Staudinger [60], i.e. when nothing was still known about crosslinking of polymer chains.

Much more later on, 'vegetable tanning' or 'tawing', and mineral tanning' were used (see below).

Vegetable tanning comprises the treatment with plant saps or acqueous extracts of wood and bark (oak tree), leaves, roots and fruits, but also e.g. oak apples. Most of these ingredients contain polyphenolic tannins, capable of reacting with appropriate functional groups of proteins under crosslinking.

Mineral salt tawing in general is the youngest among the mentioned kinds of tanning. Compared to the earlier methods, tawing with *alum* is more laborious and can take long time over days and even months.

With the arrival of *Homo sapiens sapiens* in Europe, (since ca. 40000 BC, *Aurignacien*, Upper Palaeolithic), coincident with the disappearance of the last Neandertals (*Homo sapiens neanderthalensis*) [61], the first indirect evidences for clothes appeared. On a figural mid-relief from the "Geißenklösterlehöhle" ('Geißenklösterle cave'), Alb-Donau-district, Germany, ca. 30000 BC, a loincloth is identified [56].

The earliest fragments of fur and skin clothes (shirt, trousers, shoes and a cap) were found in Sungir (east of Moscow, Russia). The burial artifacts were dated to ca. 23000 BP[‡] [62]. Apparently in this time, the oldest methods of smoke and fat tanning to preserve leather were developed.

The up to now oldest artifact of an entire sandal of plant fibres and leather originate from the Arnold Research cave in Missouri, USA, dating to ca. 5000 BC [63] (figure 7).

[‡] BP = Before Present; time scale in geology and other disciplines, according to either stratigraphic or calibrated radiocarbon dating, fixed to 1950 AD

Figure 7 Up tp now the oldest sandals with leather, Arnold Research cave, Missouri, USA, ca. 5000 BC (Foto: http://benedante.blogspot.de)

Leather strips were found in tombs of the upper Egyptian Chalcolithicum [64], following to the local neolithic period (*Naqada I*, ca. 4500-3500 BC [65]).

The oldest Eurasian leather shoe derives from Areni-1 cave, Armenia, dating to the local Neolithic, ca. 3500 BC (figure 8) [61].

Figure 8 Up tp now the oldest Eurasian leather shoe, Areni-1 cave, Armenia; local Neolithic, ca. 3500 BC (Foto: Welt online 10.06.2010; AFP)

At the same time (ca. 3500 BC), in Mesopotamia and Egypt vegetable tanning was verifiably practised [58,59,66,67].

Tawing with *alum* became known in Mesopotamia since ca. 2200 BC and in Egypt since the 2nd millennium BC [68]. In Egypt, *Alunite* (basic potassium aluminium sulfate) or *alunite*-containing earths found in oases, were recovered by digging [69] and treated with big expenditure of technology. After calcination and leaching out with hot water, insoluble alumina remained and the *alum* recrystallised on cooling down from the solutions. Such a process was later on described by Pliny the Elder (AD 23-79) in his *Historia Naturalis* [68,70].

Parchment

Though papyrus was the predominant writing material in old Egypt, parchment was already used to a certain extent. The oldest artifacts date from the Old Kingdom (Fourth Dynasty, ca. 2700 BC) [71], but also scripts on parchment from the late Twenty-First Dynasty (ca. 970 BC) are known [72]. Furthermore, parchment scrolls are found in Qumran at the Dead Sea. (figure 9). The earliest examples were radiocarbon dated to a period at around 272 BC (mean value of the methodic error range) [73].

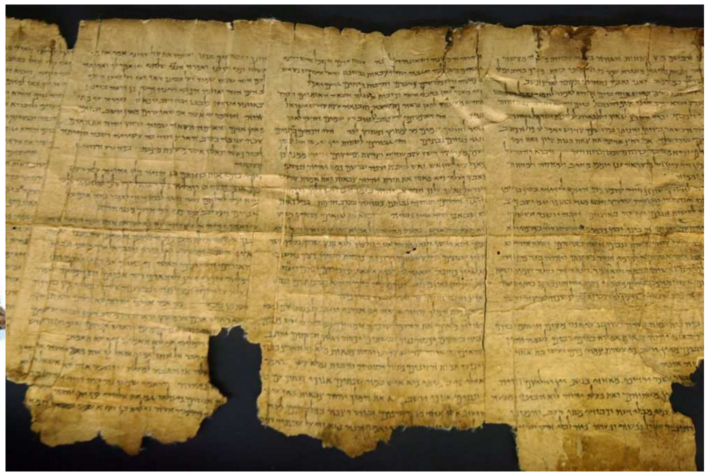

Figure 9 Part of the der Great Isaiah Scroll, parchment, Qumran, ca. 125 BC, (Foto: The Israel Museum, Jerusalem; URL: http://dss.collections.imj.org.il/Isaiah)

The present name 'parchment' originates from the greek town Pergamon in Minor Asia, which - since the 2nd century BC - became the most important centre of parchment manufacturing with essential improvement of production and temporary market dominance [74,75].

The fabrication process includes the same starting procedures as for leather (unhairing, bucking, fleshing) also of pigskin, but mainly of calfskin, goatskin and lambskin. After treated with lime solution ('liming', for unhairing and bucking) and fleshing, the rawhide is made plane and even and finally dried under strong tension

[76]. Hence, the preparation of parchment does not result from a simple drying process, neither through pickling and conventional tanning procedures. However liming, acting not only for unhairing and bucking, should effect additionally a (thermoreversible) crosslinking between the proteins of the tension-aligned collagen fibres via bivalent calcium complexes – in analogy to the formation of water insoluble calcium caseinates [77] using lime-casein paint [78,79].

The long-lasting, hard, uniform, pale and sometimes even translucent parchment absorbs only small amounts of moisture. Because it can be flattened but also deformed thermally, it still exhibits certain thermoplastic properties [80].

Papyrus, papyrus-cartonnage: bio-polymeric cellulose fibres

Papyrus

The greek name *πάπυρος* (*pápyros*) originate from the old-egytian *pa-en-per-aa*, which figuratively means >writing material from the administration of the Pharaoh< [81].

For papyrus sheets, the decorticated, fibrous stalk pith of the papyrus plant (*Cyperus papyrus*) was used. The pith, consisting mainly of cellulosic fibres, was cut in stripes, beat flat and and laid over-lapping side by side. Above, a similar second layer was placed, however turned 90°. By pressing, the starchy plant sap sticks the double layer together. The so formed papyrus sheet was coated with (biopolymeric) liquid glue, flattend, dried and polished. Normally 6-10 papyrus sheets, treated in such a way, were adhered together side by side and rolled in. After this the papyrus scroll could be inscribed [82]. Today, one would term such a material a bidirectional double layered composite fibre mat.

Because of its porosity and high moisture-sensitivity, papyrus is susceptile to environmental influences and ageing. In consequence, it becomes brittle and breaks easily into pieces, so that antique papyri are only preserved in the dry climate of Egypt and not in Greek soil [82].

The earliest papyri are found as burial objects, dated to ca. 3000 BC (First Dynastie, Old Kindom) [83].

In figure 10, a part of the oldest com-plete papyrus, the seven meter long, well preserved Papyrus ‘Prisse’ is shown, dating to the Thirteenth Dynasty at the end of the Middle Kingdom, ca. 1800 BC [84].

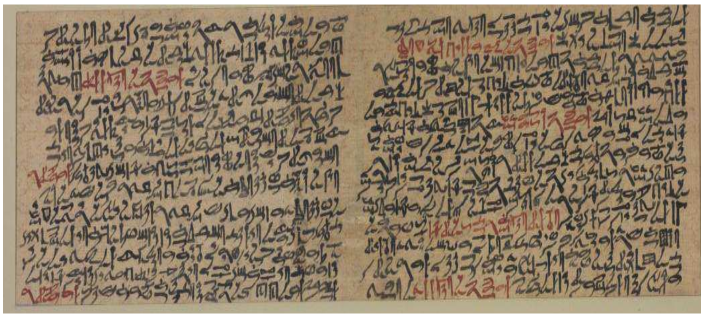

Figure 10 Part of Papyrus ‘Prisse‘, Thirteenth Dynasty, ca. 1800 BC (Foto: Bibliothèque Nationale de France; URL: http://gallica.bnf.fr/ark:/12148/btv1b8304612b.r =papyrus+prisse. langDE)

First papyri in book-form (*Codices*) instead of scrolls appear at ca. 700 BC (Twenty-fifth Dynastie, Nubian time, Third Intermediate Period) [83].

Starting from Egypt, papyri spread out all over the antique world. The relevant most important trade centre was the Phoenician sea port Byblos. Herefrom came the Greek name *βύβλος* (*bublos*) >book< and *βιβλίον* (*biblion*) >Bible< for the ‘Book of Books’ [83].

Papyrus-cartonnage

Though papyrus-cartonnage was already known since the Middle Kingdom (2000-1700 BC) [85], the Graeco-Ptolemaic Period (323 BC – AD 30) began to recycle intensively old papyri. The innumerable administrative documents of the old pharaonic kingdom had become futile, because the popular Demotic script was used more and more. The ancient script types Hieroglyphic and Hieratic were no longer understood commonly. Further-more, Greek replaced to a considerable extent the Egyptian as administrative language. And finally in pagan-roman time (AD 30 – 380) the Demotic transformed slowly to an alphabetical administrative script, derived from Greek [86]. Therefore, in the archives of the administration authorities very large amounts of public record papyri piled up, becoming useless. Hence, coffin makers bought them *en gros* as ‘maculature‘, i.e. scribbled, dirty, rubbish ‘waste-papyri’ to use them for mummy coffins und masks. After being torned and cut in pieces, papyri were soaked in water and either pressed in six to eight layers or stuck together over a mould. Finally, they could be painted, optionally leaf gilded and decorated with glass or faience inlays. (figure 11) [87,88].

Figure 11 Mummy mask, papyrus-cartonnage, Ptolemaic, 3rd century BC (Foto: mannaismayaadventure)

Though produced in series to some extent, mummy masks still cost between half and two and a half times of a worker’s average monthly wage [89].

Papyrus-cartonnage can be regarded as an early multidirectional layered composite material. Presumably pollution control or environment protection still was out-of-focus, but a first, reasonable re-cycling technique was practised to a large extent with respect to the originally valuable papyri of the innumerable ad-ministrative documents of the old pharaonic kingdom.

Birchbark pitch: biopolymeric adhesive

The term pitch came from Greek *πίσσα/πίττα* (*píssa/pítta)* >in general: dripping liquid, here: liquid tar< or *πίττοσ* (*pitos*) >solid resin< respectively [90], to latin *pix* [91] (Old High German *beh*, German: “Pech”).

Mostly, pitch was obtained by oxygen free smouldering at 340-400 °C of resin rich wood of conifers and bark (e.g. birch). On cooling, the product solidifies to pitch. Alternatively, ‘synthetical’ pitch also can be generated as distillation residue from peat, brown coal and stone coal, beside the liquid fractions of tars, e.g. wood tar, coal tar [92].

Especially birchbark pitch was produced very early, being particularly suitable because of its good hardening properties. Birchbark pitch is a complex mixture of low and high molecular esters of mainly tripterpenoid diols, e.g. *Betulin* (typical marker compound) with aliphatic acids [93]

Already the Neandertals have produced birchbark pitch by a deliberately developed procedure and used it for stone tools. So, for example different lithic flakes have been stuck together (figure 12). The corresponding archeological findings have been made in Campitello/Bucine (Tuscany, north eastern of Siena), later on investigated and dated to ca. 220000 years ago (Late Lower Palaeolithic) [94].

Thus, birch bar pitch is the oldest man-made polymeric material (thermoplastic) in human history, found until now.

Without modern technical equipment, the procedure is very difficult to control, as have shown experiments in the open-air museum “Museumsdorf Düppel” in Berlin [95]. Instead of the there applied ceramic vessels, originally earth cavities could have been used as ‘alembics’ [96].

For such operations, the competence for conceptual thinking and target-oriented action is necessary, as well as the ability to communicate complex knowledge. Because this could not be done by gestures alone, it can be deduced that the Neandertals could have had an oral communication system, i.e. a language [97,98].

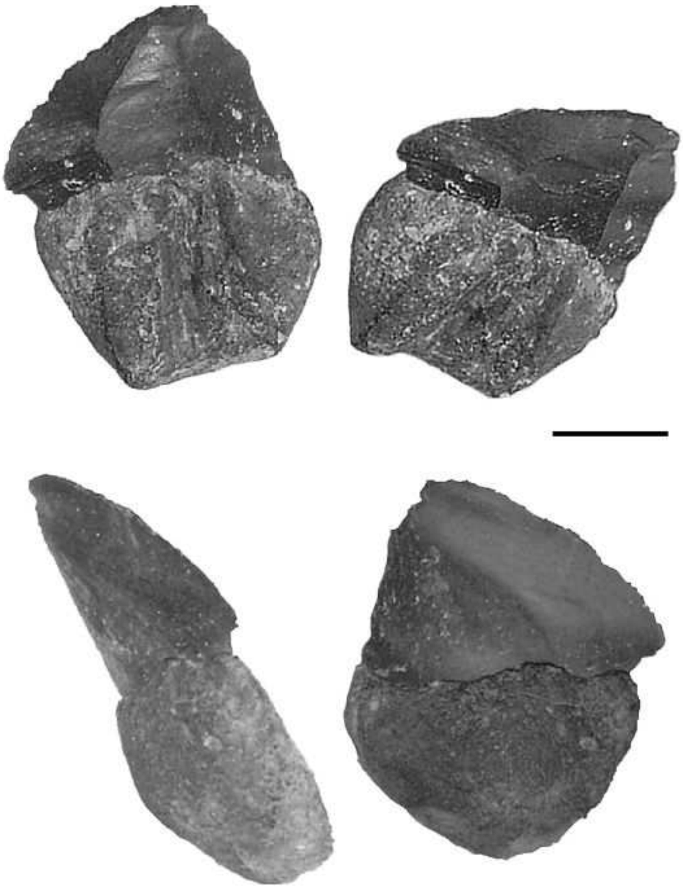

Figure 12 Stone tool, hafted with birch bar pitch, Campitello/Bucine, Valdarno Basin, Italy, *Homo neanderthalensis*, Late Lower Palaeolithic, ca. 220000 years ago (Foto [94])

Other artifacts of stone tools with remnants of birchbark pitch originate from Inden-Altdorf (Rhineland, Germany) [99,100], dated to 120000 years ago (*Moustérien*, Middle Palaeolithic).

In Königsaue (Saxony-Anhalt, Germany), artifacts exclusively of birch pitch were detected and dated to 80000 years ago [97,98,101,102]. Here as well, the producers should be Neandertals or eventually an early, temporally isolated population of *Homo sapiens* [103]. The objects were used to fix e.g. stone points onto a wooden shaft, its imprint is shown in figure 13c. Additionally, in figure 13b, dermal papillae are observed, apparently imprinted in the warm, plastic state. They seem not to be from a fingerprint but from the heel of a hand below the pinkie.

The technology of the birchbark pitch preparation was taken over later on by the *Homo sapiens sapiens* in Europe, ca. 45000 years ago [104]. Stone tools with adhesions of birch pitch were found in Les Vachons, France, late *Aurignacien*, Upper Palaeolithic, ca. 31000–28000 years ago [96].

In Altscherbitz near Schkeuditz, Saxony, Germany, vessels from the ‘Bandkeramik‘ culture (Early Neolithic, 5100 BC) were found. They have been glued together, coated and inlay ornamented with birchbark pitch (figure 14) [105,106].

Birch tar and pitch for adhesive, tanning material and disinfectant was used in stilt-house settlements (Switzerland, Late Neolithic, 3900-3500 v.Chr.) [107].

‘Ötzi‘, the ‘Iceman’ (Ötztal Alps, Italy/Austria), owned arrowhead stone points and copper axes, fixed with birch pitch to their hafts, Late Neolithic/ Chalcolithic, ca. 3250 BC, (figure 15) [108].

From the beginning of the Bronze Age (2200-1900 BC) a brown mass of birchbark pitch and eventually amber was found as inlay ornamentation of knobs and swords [109,110].

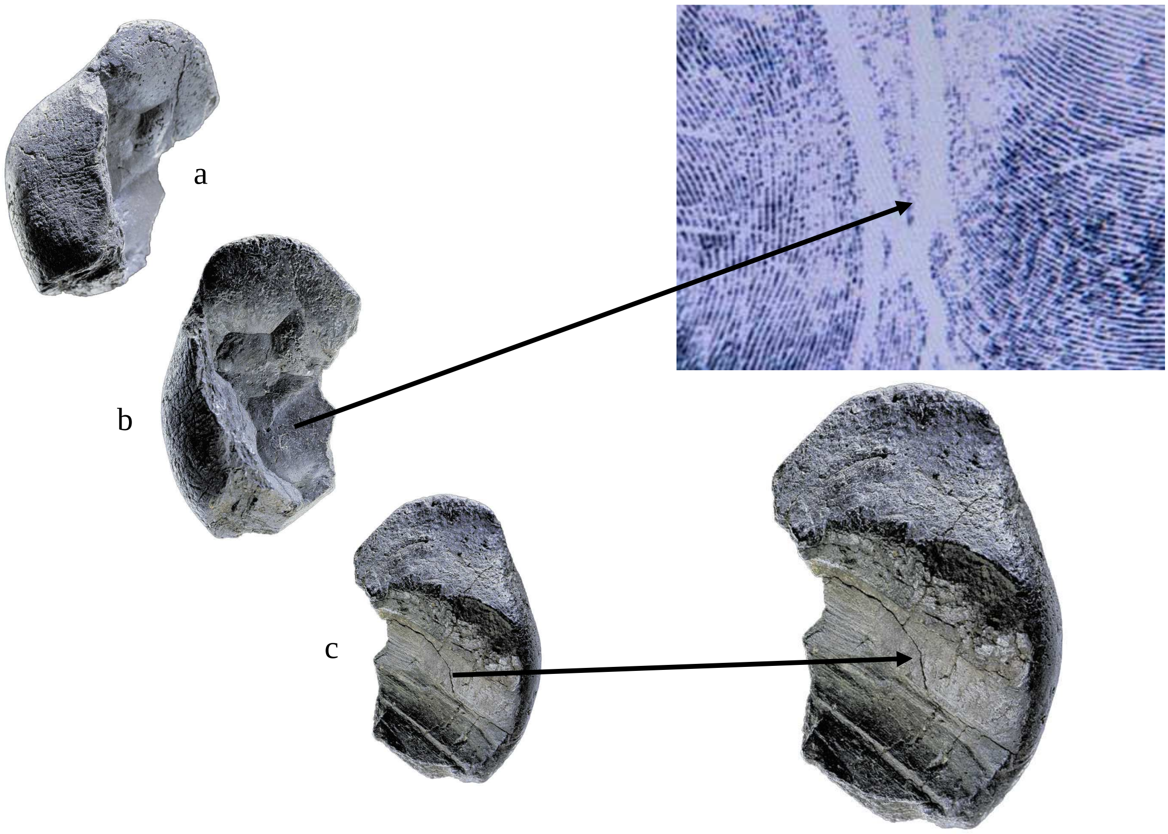

Figure 13 Pieces of birchbark pitch, Königsaue, Germany; Middle Palaeolithic, ca. 80000 years ago (Foto: LDA Sachsen-Anhalt, Jural Liptàk; WDR)

Figure 14 ‘Bandkeramik’ Vessel, birchbark pitch inlaying, Altscherbitz, Germany, Early Neolithic, ca: 5100 BC (Foto: Landesmuseum für Vorgeschichte, Dresden)

Figure 15 ‘Ötzi’s‘ arrowhead, hafted with birchbark pitch, Late Neolithic/Chalcolithic, ca. 3250 BC) (Foto: ARD)

Bitumen, asphalt: fossil, biopolymeric material

Natural bitumen was called *mumia* by the Old Persians and Greeks [111], which signifies its special use in mumification. In latin *pix tumens* means >bubbling pitch< [112], indicating natural seeps in the Near and Middle East.

The term asphalt originate from greek *ξἄσφαλτος* (x*ásphaltos*), which means originally >indestructible< [91,112,113]. It turned into latin *asphaltum*.

Especially in the Anglo-american language use and literature, the terms bitumen and asphalt unfortunately are often mixed, though a clear distinction can be given (see below).

Furthermore, an exact differentiation between bitumen, asphalt and tar/pitch should be made.

The more liquid tar and more solid pitch is always produced from wood or coals (fossil remains from plants) etc..

However, bitumen and asphalt originate from fossil fuel (petroleum), which itself is formed by fossilized marine sediments from zooplankton and algae [112,114]. Therefore, the term 'mineral' oil is not correct. When *in situ* fossil oil has slowly evaporated, liquid to solid natural bitumen remains. 'Synthetic' bitumen can be obtained as the residue fraction during the distillation of recovered crude oil.

Natural bitumen can consist of several groups of compounds in varying percentages. They differ by their solubility or insolubility respectively, their content in oil, their ageing processes, their chemical composition and varying physical properties [115,116]:

1) *Asphaltenes:* insoluble in hydrocarbon solvents, high-molecular (1000-20000 Da), highly condensed aromatic hydrocarbons: e.g. *asphaltite*
2) *Malthenes:* soluble in hydrocarbon solvents
   a) *Naphthenes:* low molecular, liquid cycloalkanes.
   b) *Paraffines*: more solid, saturated linear alcanes, e.g. earth wax
3) Solids with in general low solubilty: e.g. *Impsonite*
4) Rest of ca. 5%: sulfur, nitrogen and oxygen containing compounds.

Natural asphalt consists of natural bitumen of different composition together with mineral admixtures (sand, clay, stones, pieces of rocks (limestone etc.) [112].

'Asphaltgoudron' is asphalt, which was heated several hours to ca. 250 °C. From this and added, crushed asphalt containing rocks 'mastic asphalt' or 'asphalt concrete' with a higher content of split or stones etc. is produced for modern road construction.

Like tar and pitch, optically resembling bitumen, but of different origin (wood and coal, see above), natural bitumen and asphalt was also very early used by the human species.

Bitumen coated flint tools for fixing them onto handles, used by Neandertals, have been documented in the archaeological sites of Umm El Tlel, Syria. They have been dated to the *Mousterien*, Middle Palaeolithic, ca. 70.000 years ago [117,118].

Since the Neolithic, 7000-6000 BC, bitumen was exensively used in present day Iran, Iraq and the Dead Sea region to conserve wooden piles, to make screeds, to make watertight baskets, ceramic vessels, storage pits, reed and wood boats, sarcophagi, coffins, and urns [118,119].

Since 4500-3600 BC, sealing or adhesive repair of broken vessels was peformed with bitumen in Mesopotamia [120].

Already since 3000-2000 BC, Bitumen was exported from the Dead Sea to Egypt for the preparation of mummy balms (see above the name *mumia)* [118].

Around that time from the fourth to the 1st millenium BC, an extensive use of sculptured local natural asphalt flourished in Susa. In much smaller quantities, natural bitumen was also thermoplastically moulded. Susa, the future capital of the ancient Elam kingdom was closely situated to Mesopotamia, in today Iran near the Iraq border. There, an enormous amount of everyday objects like spindle-whorls, game pieces, discs, spools, knobs etc., but also a rich variety of cylindrical seals, bowls, vessels, relief plaques, statuettes were produced [121]. In figure 16, a plaque (ca. 2500 BC), in figure 17 a cup (2000-1940 BC) are shown, both carved from natural asphalt [121].

Figure 16 Relief plaque, natural asphalt, Susa, Old Elamite Period, ca. 2500 BC (Foto: Louvre Museum, Paris [121]

Artifacts from the royal tombs of Ur (2600-2500 BC) showed that bitumen was used for adhering eye stone in statues and for precious inlay work [118,122].

Around 2250-2200 BC, a refined rock asphalt watertightened the Great Bath of Mohenjodaro, Indus Valley. This Civilisation in today Pakistan, had some contacts to Mesopotamia [123],

Figure 17 Tripode cup, natural asphalt, Susa, Old Elamite Period, 2000-1940 BC (Foto: Louvre Museum, Paris, Hervé Lewandowski)

where bitumen/asphalt 'technology' had already been developed during a long time.

With bitumen/asphalt as mortar for brick walls were built the first Ziggurat of Babylon (*Etemenanki*, 'Tower of Babel' (2nd millenium BC) [118,124], the Assyrian North Palace in Tell Halaf at ca. 820 BC [125] and one of the future Seven Wonders of the World, the Hanging Gardens of Babylon (Nebuchadnezzar II, 640-562 BC) [118,119]. Nebuchadnezzar's famous Processional Way to the Ishtar Gate in Babylon had already a quite modern asphalt pavement [118,119].

Rubber, caoutchouc, chewing gum (chicle): biopolymeric cis-1,4-polyiso-prenes

"Affenhaar" ('ape hair'): fossil rubber/caoutchouc

Together with *Siegburgit* and Baltic amber (cf. above), the so-called "Affen-haar" ('ape hair'), a fossil rubber/ caoutchouc, ranks among the oldest known polymeric materials with respect to the period of formation.

Many a time, in older brown coal layers (Eocene, ca. 55-35 million years ago) of the Central German coal-mining districts around Köthen, Nachterstedt, Geiseltal and Oberröbling a kind of flat material with thin, yellow-brownish fibres were found. The miners called it "Affenhaar" (figure 18) [126]. This 'fibrous coal' was first mentioned 1848 by T. Hartig and already at that time described as fossil vascular latex bundles [127]. Later on they were newly classified as bast fibres from plant stems and denominated "Faszikulitenkohle" ('fascicle coal') [128]. However, the colour of the fibres was already contradictory to this new indexing. As bast fibres, they should consist of cellulose and lignified material, having adopted a dark brown to black colour. First analytical investigations were performed in 1924 [126]. Contrary to cellulose, the fibres showed in preliminary tests a very quick burning with an aromatic smell, reminiscent of resin or burned rubber. Extraction with acetone, alcoholic caustic soda solution and benzene gave evidence that the single de-resinified strands have not been dissolved, but became elastic after drying. With that, they resembled thin rubber threads [129]. Elemental analysis revealed the presence of ca. 2% sulfur.

The evidence of being a rubber indeed began 1924 through investigations by R. Weil in the laboratory of "Continental Kautschuk und Guttapercha Kompagnie" in Hannover [126]. In analogy to Harries' experiments, he converted the material chemically to caoutchouc ozonide [130] However, the real constitution of this compound as a highmolecular ozonide was verified one year later - 1925 - by Staudinger [131]. The investigations of "Affenhaar" have been indeed highly topical and coincide exactly with the period of establishing the concept and proof of macromolecules.

50 years later, new investigation on similar samples likewise from the Central German coal-mining districts confirmed with ^{13}C-NMR the existence of cis-1,4-polyisopren structures, analogous to those from the latex of *Hevea brasiliensis*. Scanning electron microscopy (SEM) revealed a thickness of the single strands of ca. 100 µm with a length of many centimeters. The sulphur content varied here around 4 to 11%, indicating the degree of vulcanisation [132].

Alltogether, the existence of "Affenhaar" as rests of fossil vascular latex threads of *angiosperms* was demonstrated. The plant species itself could not be determined [133]. An application is not known.

Figure 18 "Affenhaar", vulcanised rubber as content of vascular latex threads of fossil rubber trees, on brown coal flades, Eocene, ca. 55-35 million years ago (Foto: D. Linke, Berlin)

Pre-Columbian caoutchouc/rubber

The name of ‘caoutchouc‘ originates from the pre-Columbian Indian word *kaa-ochoe* or *cahuchu* >weeping tree< [134,135].

The expression ‘rubber’ was created 1770 by the instrument maker Edward Nairne, who discovered that instead of the usual wax pieces or breadcrumb cubes, natural caoutchouc could erase (rub off) pencil writing. He called them ‘rubbers‘ and sold them at his shop in London. The chemist Joseph Priestley, England, published this property [136]. Therefore, he is sometimes misleadingly regarded as the inventor.

For the first time, natural rubber was used in the mesoamerican La-Venta civilisation at around ca. 1600 BC by the ‘Olmecs’, which means in later Aztec language (*Nahuatl*) ‘rubber people’ [137]. From that time, twelve balls of solid rubber were found in the archaeological site of Manatí (Mexico) and dated by radiocarbon method (figure 19).

The first, simple Olmec ball game play ground was excavated in Chiapas (Mexico) and dated to 1400 BC [138].

Figure 19 Solid rubber ball, archaeological site of Manatí (Mexico), Olmec, ca. 1600 BC (Foto: Kenneth Garrett, National Geographic)

The Maya (ca. 800 BC - AD 950 [139,140]) and other mesoamerican peoples took over the production and use of rubber. The oldest Maya artifacts dates to 300 BC - AD 250 (figure 20 a). Beside balls, also rubber tapes to wrap and fix stone axes onto shafts, figurines, flasks, tubes and clothes were produced [138,141].

Since the 3rd century AD, the Maya ball courts were built of stone. Such regular ‘stadiums‘ have been excavated to several hundreds in many places of the Yucatán Peninsula (figure 20 c).

Different kinds of pre-Columbian ball games are known: early versions of stickball, handball and ‘hip-ball‘. The latter (in Maya language: *pitzi* or *pok-ta-pok*) was played making use of arms, shoulder, hips, or buttocks (hands, feet or head were not allowed) [142]. The ballcourt goal in later periods was a vertical stone ring attached in considerable height (figure 20 d), somewhat in analogy to the horizontal ring of basketball today. Teams of different cities, princedoms and states compete against each other [143]. The games were accompagnied by festivals, markets, music, sports betting etc., as shown in numerous scenes on reliefs and paintings on walls and ceramics (figure 20b) [143], but also in the few preserved codices [142,143].

In pre-Columbian cultures, ball games were something like a mixture of Olympic Games in ancient Greece, Roman gladiatorial combats and today soccer or baseball championships. Moreover, an important cultic-religious, ritual background existed, sometimes linked with the sacri-fice of the losing players (enemies, slaves) [141,142, 144].

From the high cultic ceremonial-reli-gious, political and athletic importance of the ball games [144,145] itself, one can conclude the considerable significance of the ‘rubber technology‘ in pre-Columbian Central America over many centuries. [138].

a b c d

Figure 20 Pre-Columbian ball games.

a) Rubber ball and catcher's stone dish (*manopla*), Maya, archaeological site Kaminaljuyu, 300 BC-AD 250 (Foto: Madman 2001)
b) Two princes, playing *pitzi/pok-ta-pok*, polychromic vase, Maya, AD 750-800 (Foto: Dallas Museum of Art, Justin Kerr)
c) Ball court in Monte Albán, Zapotecs, ca. AD 800 (Foto: Wikipedia)
d) Stone ring goal, Great Ball Court Chichén Itza, Maya, ca. AD 500 (Foto Wikipedia)

To produce natural rubber, Meso-american native peoples gained latex from the rubber tree *Castilla elastica* by incising its bark and collecting the dropping fluid in vessels, equivalent to modern ‚tapping' of natural rubber. Adding the sap of the moonflower *Ipomea alba* (ca. 5 Vol%), the emulsion was coagulated. The precipitated pale rubber mass was heatened up and directly brought into the desired form. Moreover, the sap of *Ipomea alba* contains organic compounds with sulfonic acid and sulfonic acid chloride groups. These reacted with the double bonds of cis-1,4-polyisoprene under crosslinking. Through this, the rubber objects obtained their typical elasticity. Non-treated, dried up latex is only brittle and crumbly [138].

The last mesoamerican empire, the Aztecs (ca. AD 1350-1521 [146]) took over the hip-ball game (in *Nahuatl*, i.e. Aztec language: *ulama*).

Via the Spanish conquistadors, the first knowledge of rubber material came to Europe at the beginning of 16th century [147]. The historian Antonio de Herrera Tordesillas reported 1601 [148] that 1495 Columbus observed during his second trip to Hispaniola indigene people during a match, using balls of dark and elastic material which "jumped better than Castilian wind balls" [141] ('wind balls' are most probaly animal bladders, filled with air and covered with leather, often used for ball games, e.g. already since the beginning of the 14^{th} century in France [149]).

1522/23 Peter Martyr d'Anghiera collected eye witness reports of the New World's discoveries [150] and gave the first direct, written information on the use of elastic rubber balls by the Aztecs and other natives [151].

1535, a further early report on rubber ball games came from the historian Gonzalo Férnandez de Oviedo y Valdés [152], who participated on the first trip of Columbus to America, later on travelling several times more to the New World [141,153].

With respect to rubber history, one can state finally that in pre-Columbian Central America rubber elasticity through crosslinking was detected and used a very long time before the invention of modern 'vulcanisation' by Charles Goodyear, 1839 [154].

Kaugummi (Chicle)

The latex of 'Sapodilla-tree' (*Manilkara zapote*, *Sapotaceae*) contains up to 20-40% of a rubbery substance, consisting of ca. 20% of cis-1,4-polyisoprene with an average molar mass of around 130000 Da. This is somewhat higher than that found for natural rubber of classical rubber trees (*Hevea brasiliensis*, ca. 55000-100000 Da.) [155]. 50-60% of the Sapodilla latex consist of resins and further ca. 17% of sugars and starch [156].

Sapodilla tree latex was used already by the Mayas (ca. 800 BC – AD 950 [139,140]) [157]. The caoutchouc mass was coagulated through heating, mashed, boiled with water and purified. After adding flavourings and aromatic resins, the product was used as chewing gum [156,158].

The spanish denomination ‚chicle' comes from the Mayan *tzicte* and the Aztec/*Nahuatl tzictli*. The Maya people chewed it because of oral hygiene, ascribing to it likewise an effect, appeasing one's thirst and hunger. For the Aztecs (ca. AD 1350-1521 [146]), the use of chewing gum was socially strongly controlled. Mostly, chewing was allowed only for women, but in no case in public [157].

Chewing gum was passed to the whole world indeed, but apparently not in such a strictly regulated form.

Summary

Fossil polymers were made millions of years ago by nature.

Different human species used very early biopolymeric materials. Without them, the development of human life would not have been possible in its diversity. Such natural or naturally obtained polymers were used as rigid or ductile materials, fibres and adhesives for numerous items of daily life, such as clothing, tools, adornment etc.. Already in the time of the Neandertals, far before the appearence of modern *homo sapiens*, i.e. since the Late Lower Palaeolithic (ca. 220000 years ago) the use of birchbark pitch began. Later on, leather, horn, bitumen and amber were added to the knowledge of mankind. Much later, the preparation and use of papyrus, parchment and caoutchouc became evi-dent. With these polymeric materials from pre- and early history, astonishing tech-niques emerged with respect to exploitation and production, followed by use and trade. All this formed – together with the early knowledge of natural dyes, binding agents and elixirs – the first human treasure trove of experience, which was in principle the base of much later arising chemical technology and science.

Zusammenfassung

Fossile natürliche Polymere sind bereits vor Millionen von Jahren entstanden.

Verschiedene menschliche Spezies benutzten sehr früh biopolymere Materialien. Ohne sie wäre die Entwicklung menschlichen Lebens in seiner Vielfalt nicht möglich gewesen. Solche frühen, natürlichen bzw. aus der Natur gewonnenen Polymere wurden als Formmassen, Fasern und Klebstoffe für allerlei Dinge des täglichen Gebrauchs wie Bekleidung, Geräte, Werkzeuge, Schmuck etc. verwendet. Bereits in der Zeit der Neandertaler, noch weit vor Erscheinen des modernen *Homo sapiens*, d.h. seit der letzen Periode der Frühen Altsteinzeit (Altpaläolithikum, ca. 220.000 vor heute) setzt der Gebrauch von Birkenpech, ein. Später wird der Gebrauch von Leder, Horn, Bitumen und Bernstein dem Wissen der Menschheit hinzugefügt. Sehr viel später kamen dann noch Papyrus, Pergament und Kautschuk hinzu. Mit diesen vor- und frühgeschichtlichen, polymeren Materialien entwickelten sich erstaunliche, frühe Techniken hinsichtlich Gewinnung und Verarbeitung, gefolgt von Handel und Gebrauch. Dies alles bildete - zusammen mit der frühen Kunde über natürliche Farben, Binde- und Heilmittel - den allerersten menschlichen Erfahrungsschatz, auf dem dann letzlich auch die chemische Technologie und Wissenschaft aufbauen konnte.

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