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Article

The Malleable Glass of the Ancients

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Abstract: For centuries, alchemists tirelessly sought to create a transparent material that was at the same time flexible, i.e. the 'malleable glass' of ancient times. The intensive work of our forefathers in alchemy was in fact not in vain, because it led to the transmutation, not of base metals into gold, but rather of a secret, hermetic, cryptic and often obscure field of activity into modern chemistry and polymer science, with all its astonishing contemporary success.

Keywords: *Malleable, glass, alchemy, casein, Franz Patat, Werner Staudinger, Georg Christoph Lichtenberg, transparency, flexibility, Bartholomäus Schobinger, Wolfgang Seidel, silicone glass,*

1. Introduction

Franz Patat,[a] one of the protagonists of early technical-chemical Polymer Science in Germany, wrote in 1959 (translated): "*Plastics, especially the fully synthetics, are quite young children of chemistry. No alchemist experimented with them, looked for them, dreamed of them".*[1]

For synthetic polymers he was right of course. The first successful, fully synthetic polymeric material was the phenol-formaldehyde resin Bakelite®, submitted by Leo Baekeland in 1907, patented in 1909 [2] and first manufactured in 1909/1910 in Erkner near Berlin [3,4] and later on in USA.[5] However, the beginnings of polymer science were established in 1920 by Hermann Staudinger with the concept of macromolecules.[6]

Astonishingly, Franz Patat stated as early as in 1959 (translated): "*The denomination* (German: 'Kunststoffe') is *actually highly unfortunate, because 'Kunststoffe'* (artificial material, plastics) *are neither artificial 'Ersatzstoffe'* (surrogates) *like artificial honey, nor have they anything to do with art (Kunst). ... In*

[a] Prof. Dr. Franz Patat (1906-1982), from 1956 until 1970 head of the Institute for Chemical Technology, Technical University Munich, Germany.

fact, their denomination being derived from artificial instead of natural material is all the more arbitrary. ... The connection between natural materials, like cotton, wood, casein, etc. with plastics, due to their in principle similar structure and organisation, is the reason why plastics started out as modified natural products and that they - today mostly 100% children of the chemical retort - exhibit substantial ancestors like leather, rubber and linoleum".[1]

In the course of the present article, we shall explore the extent to which the 'ancients' were interested in different polymeric materials. Contrary to Patat's statement (cf. above), alchemists certainly did experiment with them, sought them and dreamed of them (cf. chapters 3, 4).

2. Vitrum Malleabile

The name alchemy is coming to us via the Arabic *al-kīmiyā* from the hieroglyphic *kem-it*, figurative for Egypt,[7] signifying its origins.

Figure 1 Alchimia, the embodiment of alchemy; 1574.[8]

Several aspirational themes can be identified in alchemy. Among them are the *lapis philosophorum* (philosopher's stone, legendary substance capable of '*chrysopoeia*', i.e. the transmutation of base metals into gold),[9,10] the *elixir vitae* (elixir of life, for rejuvenation and immortality), *panaceas* (a remedy that would cure all diseases and give immortality), *alkahest* (a hypothetical universal solvent), *vitrum aureum* (golden glass, glassy gold) and *vitrum malleabile* (malleable, i.e. ductile, flexible glass).[11]

With respect to the latter, the famous Egyptian Muslim historian Ibn 'Abd al-Hakam (AD 803-871) relates that king 'Saurid' from Egypt (pharaoh Khufu/Cheops, 2589–2566 BC) deposited in his pyramid, among other precious things, bendable and non-breakable, i.e. malleable glass.[12-14]

Flexible, non-breakable glass was also mentioned in the '*Kenyon'* papyrus (AD 3rd century).[15,16]

In Roman time, it was said that a craftsman made a bowl of flexible glass (*vitrum malleabile, vitrum flexile*) and was allowed to show it to the Roman emperor Tiberius (AD 14 - 37). The emperor tried to break it, but the material was only dented. The inventor easily corrected the damage by embossing it. He claimed to be in sole possession of its secret recipe. Upon learning this, Tiberius ordered the artisan to be beheaded, so that the secret might die with him. The emperor feared that such a material would be more precious than gold, thus reducing drastically the value of the precious metal.[17,18] The story was first reported by Titus Petronius Arbiter (AD ~14-66) in his *Satyricon 51,* then critically commented on by Pliny the Elder (AD ~23-79),[19] similarly described by Cassius Dio (AD ~163-229) [20] and later on reported again by Isidore of Seville (AD ~560-636).[21]

A related story was told much later in France: a bust of malleable glass was presented to Cardinal Richelieu (1585-1642). On the premise that the invention would damage the glass manufacturing industry, the discoverer was doomed to perpetual imprisonment.[22]

Apparently, the 'malleable glass' story was strongly alive and its experimental realisation indeed represented a dream from antiquity through the whole of the Middle Ages and Renaissance, like creating gold. Samuel Hartli(e)b (~1600-1662), a German born 'polymath' ('The Great Intelligencer of Europe'),[23] indeed specified in a list of inventions "those which have been lost and ought to be researched and restored" (translated): *a flexible or ductile glass* ("*vitrum flexile seu ductile*").[24]

But already in 1752 in the Age of Enlightenment, Hieronymus von Ludolf, a physician and chemist wrote in his 'Introduction to Chemistry' (translated): "*Many chemists go to great efforts to make a malleable glass*" [25] (cf. furthermore chapter 4, J.G. Lichtenberg).

3. What does malleable mean? What does glass mean?

At this point, we have to define what 'malleable' means. We have already seen the first significant property that the desired material was originally to be forgeable, i.e. to be formed, perhaps by a hammer. That is why the term 'malleable' originates from *malleus* (Latin for hammer). In consequence, a malleable material must then also be formable, deformable, processable, tractable, pliable, flexible, ductile and to a certain extent soft and plastic. The latter properties could already be achieved in ancient times by heating inorganic materials like metals, glass or crystals to high temperatures. On the other hand, pre- or proto-historic organic polymeric materials like birch bark pitch, bitumen, or tar,[26] lacquers (shellac) and not fully crosslinked resins like copal and even amber could be softened by heating them to only slightly elevated temperatures.[27]

Furthermore, we have to ask what *vitrum* or glass means? *Vitrum*, the classical silicate glass, is an inorganic, crosslinked polymeric material in a non-ordered non-crystalline, so-called amorphous state. Therefore, a glass is defined by scientists as a liquid or fluid state, frozen below its 'glass transition temperature' T_g, which at the same time signifies its softening temperature range. T_g of silicate lies around 1000 °C.[28] Of course, alchemists wanted to have it much lower.

One of the fundamental properties of amorphous silicate glass is its optical transparency. But this phenomenon can also be achieved by inorganic crystalline compounds, i.e. minerals, if their physical properties allows them to let pass visible light, e.g. in pure crystalline berg crystal (quartz).[28] But even natural organic, i.e. biogenic polymeric materials, known much longer than glass, e.g. the above mentioned amber or other natural resins, may exhibit optical transparency. This behaviour is demonstrated by Tacitus' (AD ~55-~120) early use of the term *glaesum* for Baltic amber, which was derived from the Germanic *glezan* (glazed, glassy, glossy, vitreous), because of the transparent appearance of amber after polishing.[26] Hence, a transparent material need not necessarily be an inorganic crystal or silicate glass.

Now we can combine both arguments and may deduce that alchemists, interested in *vitrum malleabile*, were looking for materials combining mainly two major properties - being soft and deformable at ambient or slightly increased temperature (e.g. that of cooking water) and being optically transparent - whereupon the material class itself may not have been really in the focus of alchemists, given that knowledge of material science had simply not yet developed.

And indeed, we find alchemical descriptions extending experiments to material combinations or other materials beyond true 'silicate glass'.

4. Malleable 'glassy' materials

At the beginning of the 18th century it was still reported that mixtures of glass and a certain *spiritus* resulted in a soft material, from which "*pictures and medallions could be formed*". It was said that such materials were shown at different places, e.g. in the presence of King Casimir IV of Poland (after 1447).[29] Similar stories were known in England and Germany, there a certain *spiritus aquae fortis* being used.[29]

This could be regarded as an early idea to use the concept of a 'plasticiser' or softener in modern terms.

Other 'plasticisers' proposed were 'billy goat or goose blood, *feces* of vinegar, i.e. presumably tartar, or the fat of horse hooves etc.[30]

Sometime after 1576, a craftsman was said to have demonstrated in front of the future Emperor Matthias of Habsburg that he could repair broken glassware by putting and bending them together.[29] This may well be an early indication of the use of glue.

Minera argenti vitrea, ('glassy ore', 'silver glass', i.e. a silver sulphide mineral) [31-33] or *minera argenti cornea* ('horn silver', i.e. a silver chloride mineral) [31,34] in association with layered silicate clay and under fresh humid conditions, are described in 1755 as being (translated): "*transparent or glassy*" and "*soft, pasty*" and "*malleable*", so that "*it could be cut, pressed and shaped*".[31]

The impossibility of a flexible silicate glass was emphasised by an Enlightenment commentator, Georg Wilhelm Wegner (1692-1765), who in 1744 published a treatise under the pseudonym 'Tharsander' about (translated): "*The foolish adept (Adeptus Ineptus) or the uncovering of the famous, false art named alchemy"* (cf. Figure 2). He quoted therein (translated): *"I still know enough of my physics to state that a malleable glass is a contradiction in terms (contradictio in adjecto), much as if I was likewise to speak of dry water*".


Adeptus Ineptus,
Oder
Entdeckung
der
falsch berühmten Kunst
ALCHIMIE
genannt:
Darin
die Nichtigkeit solcher Kunst
klärlich erwiesen,
der Alchimisten Principia untersucht und widerlegt, ihre Betrügereyen eröffnet, und die Unmöglichkeit der Metallen-Verwandlung wenigstens auf das wahrscheinlichste dargethan,
Wie auch
von der Universal-Medicin
und andern vorgegebenen Alchimistischen Kunst-Stücken
gehandelt wird.
Von
THARSANDERN.
Berlin bey AMBROSIUS HAUDE. 1744.

Figure 2 *Adeptus Ineptus*, 1744.[35]

However, as early as in 1721, in a relevant lexicographic collection (cf. Figure 3), it was stated on 'malleable glasses' in general (translated):

"*With respect to the malleability of these glasses, I let everybody believe what he wants, but as for myself I hold that something like that has never been a reality. But I do believe that something which resembles glass in appearance and* *impression, being bendable and pliable, could be found and fabricated*".[30]

The last sentence can be regarded as an astonishing prediction, predating by almost two hundred years Hermann Staudinger's concept of macromolecular science and the subsequent development of transparent thermoplastics like polystyrene (PS), acrylic glass, (PMMA, Plexiglas®), polyethylene terephthalate (PET) and polycarbonate (PC, Macrolon®) etc.[36]

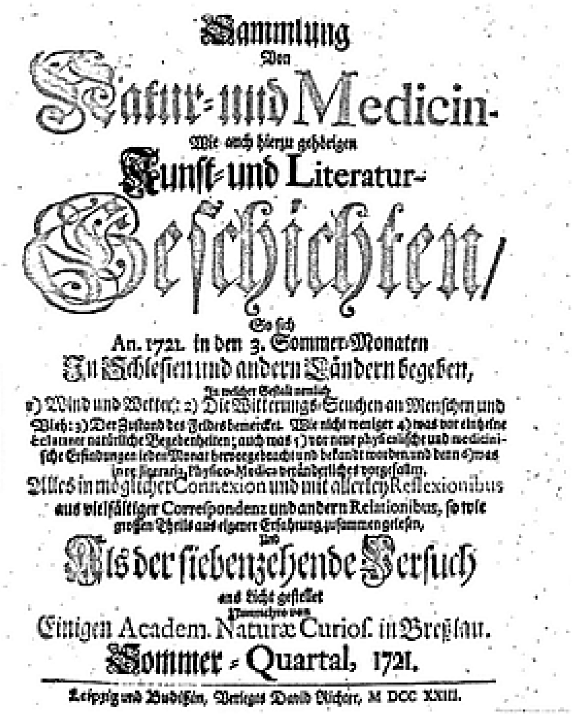
Sammlung Von Natur- und Medicin- Wie auch hierzu gehörigen Kunst- und Literatur-Geschichten,
So sich An. 1721. in den 3. Sommer-Monaten In Schlesien und andern Ländern begeben,
Alles in möglicher Connexion und mit allerley Reflexionibus aus vielfältiger Correspondenz und andern Relationibus,
Als der siebenzehende Versuch ans Licht gestellet
Einigen Academ. Naturae Curios. in Breßlau.
Sommer-Quartal, 1721.
Leipzig und Budißin, Verlegts David Richter, M DCC XXIII.

Figure 3 Collection of Nature-, Medicine-, Art- and Literature-Stories, Summer Quarter 1721.[29]

The possibility of an organic *malleable glass* was mentioned in 1785 by the famous mathematician, physicist and brilliant aphorist Georg Christoph Lichtenberg in Göttingen (1742-1799, cf. figure 4) (translated): "*Castor oil can be thickened by quicklime in such a way that it resembles Chinese Resin. This firm jelly is not affected by water or spirit of wine, so perhaps various, transparent and unbreakable vessels might be fabricated from it. It may even be that this is* ***the malleable glass of the ancients***".[37,38]

Figure 4 Georg Christoph Lichtenberg (1742-1799).[39]

Lichtenberg described a rather interesting observation, because it reflects, in the terms of his time but still very early on, both the transparency and the soft, plastic properties of the gel state of an organic material. From the chemical point of view, it is equally noteworthy, because it could describe a polymeric crosslinking reaction via ricinate formation and a double bond reaction of the castor oil.

However, no one of the authors mentioned above any information about an earlier organic material which *resembled glass in appearance and impression, being bendable and pliable* [30] at reasonable temperatures.

Schobinger's material

Earlier than 1530, the wealthy merchant, scholar and alchemist Bartlome Schobinger (1500 – 1585, St. Gallen, Switzerland, cf. figure 5) [40] established a recipe for the precise manufacturing of a thermoplastic casein material. He committed this recipe to the Bavarian Benedictine monk Wolfgang Seidel, who published it around 1530 (translated):

"*To make a transparent material, like a fine horn, which is as shapeable as you* *like, which remains clear, which can also be dyed. … which - being warm - can be pressed and bent. … but cooled down no bending or crooking is possible, but it cracks like a glass. … one can cast table boards, tableware and medallions. And on the whole whatever you want*".[41,42]

Figure 5 Bartlome Schobinger (1500 – 1585).[43]

5. Modern malleable transparent materials

The thermoplastic, transparent casein material of Schobinger was in principle the direct predecessor of *Galalith®*, invented 365 years later, the semi-synthetic casein resin, chemically crosslinked by formaldehyde. This material was patented in 1897 by Adolf Spitteler and Wilhelm Krische, and was produced from 1904 onwards by the Internationale Galalith Gesellschaft Hoff, u. Co in Harburg near Hamburg until the 1970s/80s. Before WW II, it was one of the most important plastic materials because of its properties: transparent when manufactured without fillers, non-flammable, stainable, and resistant to fatty and oily substances, and to certain organic solvents. Consequently, it was ideal for the production of combs, jewellery objects, belt buckles, door and furniture knobs, penholders, smoking utensils, walking sticks and umbrella handles, etc.[44] From around 1917 onwards, it was also used as a decorative material for furniture inlays by the most influential architect, designer and artist Charles Rennie Mackintosh.[45]

Furthermore, the electrical insulating properties of casein formaldehyde (CSF) led to the production of low voltage items like switches, push buttons and plug contacts etc.

Another CSF product line was the semi-synthetic fibre, i.e. the ‘milk wool’ Lanital®, made in Italy from 1936/37 onwards.[44]

Besides the aforementioned transparent thermoplastics like polystyrene (PS, glass transition temperature T_g: ~95 °C), acrylic glass, (PMMA, Plexiglas®, T_g: ~105 °C), polyethylene terephthalate (PET, T_g: 60-80 °C), polycarbonate (PC, Macrolon®, T_g: 150 °C),[46] one particular kind of plastic recently completely fulfilled the two hundred years old prediction: “*But I do believe that something which resembles glass in appearance and impression, being bendable and pliable, could be found and fabricated*”.[30] This is the “Squishy glassware made of magical crystal clear silicone”, which is perfectly malleable at room temperature, cf. figure 6.

Figure 6 “Squishy glassware made of magical crystal clear silicone”.[47]

6. Conclusion

Over many long ages, innumerable alchemists have dreamed of and worked on malleable glass. Today, it is available as bendable, transparent glassware made from silicone rubber (glass transition temperature T_g: below -85 °C). Two thousand years ago this would have surely been more precious than gold, and the emperor Tiberius would have killed its inventor.

Nevertheless, the feverish work of our forefathers in alchemy was not all for nought, because, even if it did not enable the transmutation of base metals into gold, this secretive, hermetic, cryptic and often occult and obscure field of activity laid the foundation for modern chemistry and polymer science. It formed the basis of an astonishing conversion of age-old dreams into contemporary reality.

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