(Poly)Saccharides in cosmetic products – From alginate to xanthan gum

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Polysaccharides are omnipresent ingredients of cosmetics. They do an absolutely reliable job in silence and far away from the all-too-fleeting active agents and that is why we are no longer aware of them. How important they really are and where they are actually used is explained in the following survey.

The prefix "poly" makes us think of synthetics which are formed by polymerization of smaller units (monomers). As a matter of fact, polysaccharides are biopolymers composed of differently linked single sugar molecules. As a result the characteristics of the sugars completely change. The best known **monomer sugars (monosaccharides)** are glucose (dextrose, grape sugar), fructose and galactose. Monosaccharides are water-soluble and have a sweet taste with a few exceptions though.

The same applies for oligosaccharides i.e. compounds consisting of two or more monosaccharides like e.g. saccharose (sucrose, cane sugar), lactose (milk sugar) and maltose (malt sugar). Saccharose is build up by glucose and fructose, lactose consists of glucose and galactose, and maltose is composed by 2 glucose units.

Polysaccharides like cellulose (glucose chains) and chitin (see below) have no specific flavor and are water-insoluble. There are others that only swell like e.g. starch (linear or branched glucose chains). As polysaccharides are inexpensive and easily available due to their natural sources, they have been used in cosmetics for a long time already. Alginates, pectins and xanthan gum represent many others that are not mentioned at this point. In addition, chemical industry has modified and customized the natural substances and has generated refined raw materials with new characteristics. The following substances are used in skin care products:

Agar: A galactose-polymer with some sparse sulfate groups dominates in this gelling agent which is extracted from red algae. Agar is used as a consistency and bonding agent.

Alginic acid (algin) is gained from brown algae. The polysaccharide is composed of varying ratios of the saccharic acids (uronic acids) mannuronic acid and guluronic acid and is characterized by molecular weights up to 200,000 Daltons (Dalton = unit for the relative molecular mass). Saccharic acids derive from monosaccharides by oxidation of the aldehyde group. Alginic acid and its calcium salt (calcium alginate) are water-insoluble however they can swell; thus, similar to hyaluronic acid the substance can absorb more water than several hundred folds of its weight. Hence, it fulfills several cosmetic functions at the same time. Alginic acid is used as a consistency agent, forms a moisture-retaining surface film and can bind heavy metal ions which are involved in oxidative processes and the formation of radicals. A slightly tightening effect is also experienced during the superficial filming process. Both sodium and potassium salts of the alginic acid are water-soluble. By increasing the consistency alginic acid stabilizes the oil phase in emulsifier free cosmetics. Alginates are not absorbed. Propylene glycol alginate (E 405) is the ester of propylene glycol with alginic acid and is used like alginic acid.

Carrageen (Carrageenan): These polysaccharides of different composition are gained from red algae, among others. An important element is galactose which is partly esterified with sulfuric acid (cf. agar) which is the reason why it can form sodium, potassium and calcium salts. These salts are used for instance as gelling agents in tooth pastes. Furcelleran which has a similar structure and similar field of application also belongs to the Carrageens and is gained from the dulse (Furcellaria fastigiata).

Chitin is formed by a continuous acetyl-D-glucosamin chain (cf. hyaluronic acid) and responsible for the flexibility of insect shells for instance. By deacetylation chitosan is obtained and in combination with acids it forms water-soluble salts that are used for hair conditioning purposes (shampoos, hair gels), as bacteria-inhibiting components in tooth pastes and mouthwashes as well as a cationic filming agent in skin care products.

CM-Glucan: Glucans generally are biopolymers of the glucose. There are alpha- and beta-glucans. Starch and glycogen (see below) e.g. belong to the alpha-glucans whereas cellulose is a beta-glucan. CM-glucan is a specific glucan which is gained from the cell walls of baker's yeast and then modified in a chemical process (**c**arboxy**m**ethylation). As a result, the polysaccharide can form water-soluble sodium salts (INCI: Sodium Carboxymethyl Betaglucan). CM-glucan has skin-protecting and tightening features. It is an appropriate substance for the sensitive skin as it provides basic protection against UVA radiation. It is used for the skin care after peeling and laser treatments, after shaving as well as an additive for body lotions.

CMC is the abbreviation for carboxy methyl cellulose which is also called sodium cellulose glycolate. CMC is gained by chemical modification of cellulose similar to the CM-glucan processing. It forms water-soluble sodium salts which have thickening properties and are used in cleansing and washing products as highly effective carriers for dirt particles.

Dextrins are gained from starches by treatment with heat and acids. The fractions formed this way are water-soluble in contrast to the raw materials and have differently sized chains depending on the manufacturing process. Interesting for the cosmetic use above all are cyclodextrins which are formed by enzymatic degradation of starch. Cyclodextrins have cylinder-shaped cavity structures and may encapsulate organic compounds with the effect that their solubility in water is increased. They absorb scents (deodorant products) however can also retain perfumes which they slowly release then. Due to these characteristics they are also used as active agent carriers.

Glycogen is a widely branched polysaccharide with a molecular mass of 1 –10 mega Dalton and apart from a rather low percentage of proteins it mainly consists of glucose and forms the natural energy reserve of the body. Its structures partially match with the branched amyl pectin which, along with the linear amylose is one of the two elements of vegetable starch. Like microcrystalline cellulose, starch is an additive for powders.

Guar gum gained from the guar bean (Cyamopsis tetragonoloba) is a component of tenside containing products especially shampoos. It has anti-static effects and gives hair a good grip. Main component of guar gum is the polysaccharide guaran with mannose and galactose at a 2:1 ratio. Carob bean gum (Ceratonia siliqua) has a similar composition.

Gum arabic from the Arab gum tree (Accacia Senegal) consists of intricately branched polysaccharide chains which contain different monosaccharides like galactose and arabinose as well as glucuronic acid which derives from glucose. The polysaccharide originates from the juice of different African accacia species. Its alkali and alkaline earth salts are used as thickening agents.

Hydroxypropyl Starch Phosphate (HSP) (E 1442) is gained by esterification of hydroxypropyl starch (modified starch) with phosphoric acid. Both substances are found in food products and cosmetics as thickening agents and stabilizers of emulsions. Analogous to hydroxypropyl cellulose (HPC), hydroxypropyl starch (E1440) is produced by a reaction of propylene oxide (PO) with starch.

Hyaluronic acid is a natural polysaccharide of the body consisting of D-glucuronic acid and N-acetyl-D-glucosamin units on a rotating basis. Nowadays it is produced biotechnologically and can retain considerable amounts of water. Compared with other polysaccharides it excellently adheres to the keratin of the skin and thus forms a very flexible film on the skin surface which has plumping and smoothing effects. Low molecular hyaluronic acid fractions are also released as signal substances during inflammations. Further details can be found in Kosmetische Praxis 2008 (4), 16-18.

Hydroxyethyl cellulose (HEC) is gained by chemical derivatization of cellulose with ethylene oxide (EO). Together with hydroxypropyl cellulose (HPC) and hydroxypropylmethyl cellulose (HPMC, hypromellose) it is a widely used thickening agent in aqueous formulations. Depending on manufacturing conditions and quality, HEC may contain EO side chains if it continues to react with ethylene oxide. In contrast to other cellulose derivatives like methyl cellulose, the HEC in skin care products forms flexible water retaining films. Depending on the manufacturing process in both HPC as well as HMPC side chains may form as by-products like in HEC which is caused by the reaction of cellulose with propylene oxide (PO).

Methyl cellulose (MC) develops by etherification of free cellulose hydroxyl groups. As a result the cellulose becomes water dispersible and can form gels on the one hand; on the other hand the lipophilicity will increase with the methyl groups. This leads to the fact that it also obtains emulsifying features. Hence, it offers a wide range of applications from wall-paper paste and food additives up to thickening agents for shampoos and liquid soaps. This also applies for ethyl cellulose (EC).

Mucopolysaccharides (glycosaminoglycans) contain amino sugar units as e.g. N-acetyl-D-glucosamin which alternate with diverse monosaccharides or their deriving relatives. They are significant components of the connective tissue as they are able to retain water in such a way that the tissue can resist to external pressure. Hyaluronic acid (see above), heparin and chondroitin belong to this substance group. They are characterized by a multitude of biological functions. Hyaluronic acid e.g. serves as a "lubricant" for the joints. Mucilages are also widely spread in the vegetable kingdom. Acemannan which is found in aloe vera extracts belongs to the mucopolysaccharides and potentially stimulates the antibodies in viral infections.

Pectin consists of galacturonic acid chains. It is found in fruits like e.g. apples. Its composition varies depending on the specific fruit species. Pectins are gelling agents and increase the viscosity in gels and creams. Besides other mucilages, pectins are a main component of quince mucilage.

Sugar tensides: Synthetic alkyl polyglycosides (APG) with chains consisting of glucose molecules that are etherified at their ends with fatty alcohols belong to this group. APGs are characterized by a pleasant sensation on the skin specifically in shampoos and can be used in micro emulsions. Coco glucoside (INCI) e.g. is a sugar with $C_{8\text{-}16}$-alkyl groups. Although these tensides are rather mild they are excellent carriers for dirt particles. Besides sugar ethers there are also sugar esters. In sucrose cocoate (INCI) e.g. saccharose and coco fatty acids are linked.

Tragant (E 413): This gum like vegetable juice extracted from the tragant plant consists of the polysaccharides tragacanthin which is water-soluble and bassorin which only swells if combined with water. While tragacanthin forms a galacturonic acid main chain with different branches consisting of the monosugars xylose, fucose and galactose similar to pectin (see above), bassorin is composed of an elongated molecule consisting of arabinose, galactose, rhamnose and galacturonic acid methyl ester. Tragant is used as a binding agent in tooth pastes. Karaya gum which is extracted from the Indian tree Sterculia ureus is labeled as Indian tragant. Its mucilages react slightly acidic. It is used in hair conditioners.

Xanthan Gum is a biotechnologically produced polysaccharide consisting of a main chain of glucose units frequently with a side chain composed of mannose, glucuronic acid and ketalized pyruvic acid at every other glucose molecule. Acetic acid too can be ester-linked. Xanthan gum has thickening properties and improves the gliding characteristics of gels. Similar to hyaluronic acid xanthan has gentle skin-smoothing properties combined with moisturizing characteristics. The TEWL (transepidermal water loss) is slightly reduced if there is a superficial film on the skin.

Ubiquitous and multifunctional

(Poly)saccharides are widely used in natural cosmetics and physiologically oriented products. Their applications range from peelings with candy sugar crystals and treatments of dry eye syndrome with hyaluronic acid up to cleansing products with a multitudinous number of binding, gelling and consistency agents. Even honey which contains, among others, a mixture of mono and oligosaccharides is occasionally used in a number of different products. Interesting applications are gelling masks that are spread on the skin in liquid form and then removed after they have solidified into a rubbery substance. Alginic acid is most appropriate for this purpose. Many of the swelling polysaccharides are also used as disintegrating agents as e.g. in bath tablets. Most of the above mentioned polysaccharides and their chemical derivatives are approved as food additives and frequently used in combinations even if the appropriate E-labeling has not consequently been mentioned in this article. The only disadvantage of many of these regrowing raw materials is that their composition may vary depending on their geographical origin and the manufacturing process with the result that there are differences in quality and chemical purity which even can lead to isolated cases of skin reactions. The chemical analysis of polysaccharides and their by-products in finished products is extremely difficult especially if more than one substance is used in the product.

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