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## Abstract

Skin hydrating polysaccharides are derived from several natural sources. This biopolymer is constructed with simple sugar building blocks that are easily hydrated in an aqueous environment, thereby creating the gel structure called hydrogel or hydrocolloid. Polysaccharide that is a biodegradable polymer is excellent in compatibility with the biological tissues and largely meeting the consumers' preferences toward natural products. In this chapter, applications of biopolysaccharides in cosmetics are subjected to be summarized especially skin hydrating biopolysaccharide that is incorporated as the active ingredient in cosmetic product. Mechanisms of skin hydrating effect and *in vivo* instrumental evaluation are addressed. Commercial biopolysaccharides are summarized for further reference in addition to some potential candidates, particularly botanical polysaccharides. The potential biopolysaccharides, with *in vitro* activities, are additionally included. Health benefits of this biopolymer in sufficiently suppressing dryness of the skin and potentially protecting from and/or treating wrinkles of the skin acting as antiaging ingredients are highlighted.

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**Keywords**

Biopolymer • Biopolysaccharide • Hydrogel • Hydrocolloid • Moisturizer • Polysaccharide • Skin hydration

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## 1 Introduction

Polysaccharides are composed of multiple saccharides forming a large branched or unbranched chain. They are simply classified as homopolysaccharide (same monosaccharide unit) and heteropolysaccharide (different monomeric units). Thus, they are accounted as polymers. This naturally derived polymers constructed with simple sugar building blocks are hydrated in an aqueous environment, thereby creating a gel structure called hydrogel or hydrocolloid. This system, in which water is immobilized by insoluble polymers, is imparting moisturizing effect consequently. The moist gels are highly compatible with the biological tissues and are biodegradable according to their natural occurrence (Brode 1991), classifying them as biopolymer. These are inexpensive and vastly available from natural sources which enlighten their importance in health benefit applications, including cosmetics. These strengthen the consumers' preferences toward the safety and efficacy of biopolysaccharides. In this chapter, application of polysaccharides in cosmetics will be classified into functional and active polysaccharides. Functional polysaccharides in cosmetics are claimed on the basis of their functionalities in the formulation technology such as film former, gelling agent, thickener, suspending agent, conditioner, and emulsifier, of which it mainly relies on the physicochemical properties of the biopolymer. On the other hand, cosmetic active polysaccharides are role by the ability of hydrogel or hydrocolloid mobilizing water to the contacted skin (Goddard and Gruber 1999). The skin hydrating benefit is the main object to be exclusively discussed herein. Mechanisms of this skin hydrating agent are included with *in vivo* efficacy evaluation. Furthermore, biopolysaccharides with skin hydrating effect, including those of potential ones with *in vitro* activities, are also included, of which botanical polysaccharides are mainly the focus in this chapter. However, preparation, characterization and physicochemical analysis of polysaccharide, and modification will be out of the scope of this chapter. Antioxidant and antibacterial activities of biopolysaccharides will also not be included, as well as their application as delivery systems.

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## 2 Classification of Polysaccharide in Cosmetics

Polysaccharides applied in cosmetics are classified on the basis of their actions in the products that are functional and active polysaccharides.

## 2.1 Functional Polysaccharide

Polysaccharides are incorporated into cosmetic product to function as gelling agent, viscosity adjuster, thickener, and emulsifier as well according to its polymerized network holding water by means of its swelling capability. Therefore, functional polysaccharide is traditionally classified on the basis of its electrochemical charges in the structure as follows.

### 2.1.1 Anionic Polysaccharide

Cosmetically interesting anionic polysaccharide is predominantly comprised of a group of naturally occurring materials. A majority of this group is xanthan gum with a  $\beta$ -(1-4)-D-glucopyranose glucan skeleton. It is naturally synthesized and composed in the cell wall of bacteria and is isolated by bacterial fermentation. In water, xanthan polymerizes forming viscous liquids which crystallized giving the unique ability to emulsify the suspensions. This pseudoplastic fluid, with a shear-thinning property, is commonly used in cosmetic preparation to enhance the stability against freeze-thaw challenge.

### 2.1.2 Cationic Polysaccharide

This cosmetic important group of polysaccharide mainly relied on synthetically altered polyglycans. They have unique advantage to bind tightly with protein (negative charge) of the human skin and hair. Cationic polysaccharide therefore has been found to be very useful as film-forming agent popularly applied for damage controls in hair and skin-conditioning products in addition to the vast application in hair fixative preparations. Among natural-derived cationic polysaccharides, chitosan is the main commercialized polyglycan with a cationic nature. This seminatural polysaccharide is partially deacetylated (>50 %) of naturally occurring chitin to improve solubility.

### 2.1.3 Nonionic Polysaccharide

This polysaccharide is not charged and thus less affected by negatively or positively charged compounds as surfactants. Starch as one of the most used and least expensive natural nonionic polysaccharides is mainly used as thickener. Guar gum is another nonionic polysaccharide which has found broader appeal as a natural thickener isolated from seed of plants in the Leguminosae family. Guar gum consists of two different sugars, which are mannose and galactose. Its chelating effect with metal ions enables gel thickening in alkaline media. Seminatural nonionic polysaccharides are mainly ethers of cellulose- or guar-based materials, for example, hydroxycellulose, methylcellulose, etc., that are widely used as thickeners and film formers in nail products.

### 2.1.4 Amphoteric Polysaccharide

Positive and negative charges are present in the same molecule naming the group of this biopolymer to amphoteric polysaccharides. There are few naturally

occurring amphoteric polysaccharides used in cosmetics. The most frequently applied are seminatural derivatives which is carboxymethyl chitosan.

## 2.2 Active Polysaccharide

In addition to the above functioning polysaccharides, application of these biopolymers acting as active ingredient is widely adopted in cosmetics. Polysaccharides are pharmaceutically and cosmetically classified on the basis of skin hydrating effect as follows.

### 2.2.1 Cellulose

Cellulose is the most abundant renewable polymer composed of repeating units of monosaccharide that is known as cellobiose. This anionic water-insoluble polymer is extracted from natural source, mainly plants with hemicelluloses, lignin, and other extractives. It is a hygroscopic material that is implied in skin-conditioning products particularly skin hydrating cosmetics.

Although plant is the major producer of cellulose, microorganisms such as algae, bacteria, and fungi are of economically important sources as manipulation of the cellulose structure with different properties and functions can be controlled by means of the biosynthetic modification especially in skin tissue-repairing products (Fu et al. 2013). Cellulose ethers are the modified cellulose and enlarge cellulosic application in cosmetics with optimal physicochemical properties available for a wider choice of dosage forms particularly those of methyl and ethyl cellulose derivatives (Chen et al. 2012; Vandamme et al. 2002).

### 2.2.2 Starch

Starch is a glucose polymer biosynthesized in plants for energy preserving aspect. It is the modified flour with a primary constituent of carbohydrates that differentiated by the proportion of amylose and amylopectin varied by source in similar to size, structure, and pharmaceutical property. Commercial highly pure starch is mainly isolated from cereal (wheat, rice, corn, oat, sorghum, and barley), legume (lentil, bean, and pea), and tuber of potato and tapioca. Similar to cellulose, modified starches are widely used in cosmetics, for example, hydrolyzed corn starch, hydrolyzed wheat starch, hydroxypropyl corn starch, sodium carboxymethyl starch, etc. In addition, those of novel application forms of starch in microcapsules, nanoparticles, and composites are recently emerging in the cosmetic industry (Rodrigues and Emeje 2012).

### 2.2.3 Pectin

Pectin is a non-starch water-soluble linear polysaccharide found in higher plants, particularly in fruits and vegetables. Commercialized pectin mostly relied on food industry by-products, e.g., apple pulp and citrus peel. Its structure governs property with the appointed various applications depending on its source.

**Table 1** Gum in skin nourishing cosmetics

Gum	CAS number	Mannose-galactose
Guar hydroxypropyltrimonium chloride	65497-29-2	2:1
C18-22 hydroxyalkyl hydroxypropyl guar		
Locust bean hydroxypropyltrimonium chloride		4:1
<i>C. spinosa</i> gum	39300-88-4	3:1
<i>C. spinosa</i> hydroxypropyltrimonium chloride	742071-24-5	
<i>T. foenum-graecum</i> hydrolyzed trimonium chloride	742071-24-6	1:1
Cassia gum		5:1

### 2.2.4 Gum

This plant hydrocolloid can be either anionic or nonionic polysaccharides including salt polysaccharide. It is biosynthesized as plant protector, following an injury or attack. This class of polysaccharide has long been served in pharmaceutical applications which are gum arabic or acacia gum from *Acacia* sp., gum tragacanth from *Astragalus gummifer*, gum karaya from *Sterculia urens*, and gum ghatti from *Anogeissus latifolia*, of which gum acacia and tragacanth were reported for their emollient property (Raymond et al. 2003) contributing to their hydrating effect.

In addition to the above gum, those of legume polysaccharides which are *Cyamopsis tetragonoloba* or guar gum, hydroxypropyl guar, C18–22 hydroxyalkyl hydroxypropyl guar, guar hydroxypropyltrimonium chloride, hydroxypropyl guar hydroxypropyltrimonium chloride, carboxymethyl hydroxypropyl guar, hydrolyzed guar, *Ceratonia siliqua* gum, locust bean hydroxypropyltrimonium chloride, hydrolyzed *C. siliqua* gum extract, *Caesalpinia spinosa* gum, *C. spinosa* hydroxypropyltrimonium chloride, hydrolyzed *C. spinosa* gum, *Trigonella foenum-graecum*-hydrolyzed trimonium chloride, cassia gum, and cassia hydroxypropyl trimonium chloride are used and commonly called galactomannans. Those of guar, carob, tara, fenugreek, and cassia gums with skin-conditioning effects are summarized in Table 1.

### 2.2.5 Mucilage

This viscous polysaccharide is extractable from Leguminosae plant such as okra, psyllium, and flax. Mucilage is traditionally applied in topical products as functional ingredient. This water-soluble polysaccharide, similar to gum, is widely used in cosmetics due to its high water absorption capacity.

### 2.2.6 Seaweed Polysaccharide

Alginates are one of the most well-known marine polysaccharides prepared from brown seaweeds in the Phaeophyceae family, out of which *Macrocystis pyrifera* is a major commercialized seaweed for alginate production. In addition, *Laminaria hyperborea*, *L. digitata*, and *L. japonica* are becoming important sources of good quality alginates.

Marine red algae (Rhodophyceae family) largely produces carrageenans. Carrageenan is a hydrocolloid that can be classified into  $\kappa$ -,  $\iota$ -, and  $\lambda$ -carrageenans.

Red-purple algae of the Rhodophyceae additionally synthesizes agar of which *Gracilaria* and *Gelidium* spp. are the major grown genera for agar production.

### 2.2.7 Microbial Polysaccharide

This class is interchangeably known as exopolysaccharide. Xanthan gum produced by *Xanthomonas campestris* is highlighted as the main significant bacterial exopolysaccharide accounted for more than 6 % of the total market value of these categorized polysaccharides (Imeson 1997). Pullulan, a water-soluble extracellular polysaccharide, from *Aureobasidium* especially *A. pullulans* and gellan from *Auromonas elodea* are additional microbial polysaccharides that are also widely used in cosmetics. The principal commercialized pullulan is produced by Hayashibara, the Japanese company, that deals in this polysaccharide preparation since 1976. In addition, dextran, glucan, and fructan are microbial producible and largely used in cosmetics. Those of skin hydrating microbial polysaccharides that act as humectants used in cosmetics are included in Table 2 with the incorporated content as exemplified in Table 3.

**Table 2** Microbial polysaccharides in moisturizing cosmetics

Polysaccharide	Strain	CAS number
Xanthan gum	<i>Xanthomonas campestris</i>	11138-66-2
Xanthan gum cross polymer		
Xanthan gum hydroxypropyl trimonium chloride		
Sclerotium gum	<i>Sclerotium rolfsii</i> , <i>S. glucanicum</i>	39464-87-4
Biosaccharide gum-1		223266-93-1
Biosaccharide gum-2		758716-52-8
Biosaccharide gum-3		896736-76-8
Biosaccharide gum-4		283602-75-5
Biosaccharide gum-5		
Pseudoalteromonas exopolysaccharides	<i>Pseudoalteromonas</i>	
Dextran sulfate	<i>Leuconostoc mesenteroides</i>	9042-14-2
Beta-glucan	<i>Aureobasidium pullulans</i> , <i>Agrobacterium biohar</i> , <i>A. radiobacter</i>	55965-23-6, 53238-80-5
Beta-glucan hydroxypropyltrimonium chloride		
Beta-glucan palmitate		
Hydrolyzed beta-glucan		
Oxidized beta-glucan		
<i>Alcaligenes</i> polysaccharides	<i>Alcaligenes latus</i>	188846-47-1

**Table 3** Microbial polysaccharide content in cosmetics

Microbial polysaccharides	Concentration (%) in cosmetics		
	Leave-on	Dermal contact	Baby products
Xanthan gum	0.001–6	0.001–6	0.2–0.6
Xanthan gum cross polymer	0.03–5	NR	
Biosaccharide gum-1	0.002–6	0.002–6	NR
Biosaccharide gum-2	1	1	
Biosaccharide gum-4	0.004–5	0.00001–5	
Dextran sulfate	0.01–0.1	0.01–0.1	
Sclerotium gum	0.003–2	0.003–2	
Hydrolyzed sclerotium gum	1	1	
Beta-glucan	0.0002–0.1	0.0002–0.1	
<i>Alcaligenes</i> polysaccharides	0.3	0.005–0.3	

NR no reported uses

### 2.2.8 Animal Polysaccharide

Chitin is the second most abundant biopolymer after cellulose with the similar structure formed in the exoskeleton of arthropods or in the cell walls of fungi and yeast including other lower plants and animals for reinforce and strength proposes. Chitosan is a chitin derivative which is vastly applied in pharmaceuticals and cosmetics. Partial deacetylation of chitin in basic condition or by enzymatic hydrolysis conducted by a chitin deacetylase yielded the modified compound chitosan. Chitin is not only used for chitosan production but also a raw material for glucosamine and oligosaccharide manufacturing (Sandford 2003). Significant water evaporation reduction of the skin treated with high molecular weight chitosan ( $10^4$  to  $10^6$  Da) was reported (Dee et al. 2007). This skin hydrating effect is regulated by occlusion of chitosan on skin layer. Furthermore, chitin is claimed to reduce a risk of scar formation (McCarthy 1996) with an ability to enhance synthesis of skin matrix acting as the mucopolysaccharide templates as examined in mouse (Bakkers et al. 1997; Varki 1996).

In addition to chitin and chitosan, mucopolysaccharide is produced from the vertebrate particularly in mammalian. Mucopolysaccharides are the term designated to hexosamine-containing polysaccharides present in animal tissue in free sugar polymeric form or that bind with proteins (Meyer 1938). These heteropolysaccharides are different from cellulose, starch, and chitin that are based on a single monosaccharide by their structural repeating units of disaccharide. Hyaluronic acid or hyaluronan (HA) is a natural polysaccharide found in the intercellular matrix of most vertebrate connective tissues including the skin. Together with other glycosaminoglycans (GAGs) that are dermatan sulfate, chondroitin sulfate, and keratin sulfate are represented as the prominent fluid in the skin responsible for skin elasticity. HA is found in the dermis at a greater amount than the epidermis ( $\approx 0.5$  and  $0.1$  mg/g wet tissue) (Koshiishi et al. 1999). This polysaccharide therefore mainly regulates elasticity of the skin. Commercialized HA isolated from the

synovial fluid, umbilical cord, skin, and rooster comb of animal source is available with various molecular weights, the highest being 5,000 kDa (Milas et al. 2001). This biodegradable viscoelastic polymer has several health benefits according to its physiological roles leading to versatile applications including cosmetics (Manuskiatti and Maibach 1996).

However, recent advance in biotechnology enables production of specific polysaccharides from the certain strain of microorganism that is more economically feasible with a shorter time of production of these biopolymers and within a reduced space. In addition, nanotechnology is highly emerging in cosmetics recently including skin hydrating products that nanovesicles and cubosomes showed superior efficacy over the casual cosmetic formulation (Esposito et al. 2007) including the liquid crystal moisturizer (Tsai et al. 2010). In addition, penetration enhancement would be greater than topical application of the classical product with massage that was misunderstood to improve the efficacy of the skin hydrating formulation (Hamed et al. 2012).

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### 3 Skin Hydrating or Moisturizing Effect

Dryness of the skin aesthetically draws back the individual's confidence with adverse experiences as follows:

1. Sensory characteristics: feels dry, uncomfortable, painful, and itchy, stings, and tingles
2. Visible characteristics: redness, a lackluster surface, dry white patches, flaky appearance, cracks, and even fissures
3. Tactile characteristics: rough and uneven

Dryness of the skin further accumulates into a reduction of elasticity and wrinkles of the skin consequently as evidenced by biomechanical properties of the skin (Choi et al. 2013a). Therefore, application of skin hydrating cosmetics is not only to hydrate the skin, but their pleiotropic skin benefits ultimately enhance aesthetic preference of the skin (Rawlings et al. 2012). That is recently known as corneotherapy (Klingman 2011).

Moisturizers can immediately prevent excessive water loss from the skin, principally via their occlusive elements. The stratum corneum's barrier function prevents entry of foreign substances and the loss of internal substances, including water. The water content of the stratum corneum (SC) should be greater than 10 % in the skin having a normal appearance and not feeling rough, scaly, or dry. Ideally, SC should have 20–35 % water content. Moisturizers serve to return water content to the skin with the humectants and occlusive ingredients preventing transepidermal water loss (TEWL) (Flynn et al. 2001). Skin hydration is regulated by the SC components in particular corneocytes and natural moisturizing factor (NMF) and intercellular lipid bilayer matrix. NMF is a combination of several compounds created in the skin and comprising approximately 20–25 % of the keratinous layer



in which it retained the water content (Shai et al. 2009). A defective skin barrier function causes inflammation of the skin in addition to impairment of filaggrin initiating atopic dermatitis resulting in skin dryness. Filaggrin forms NMF in SC and is essential during formation of the cornified enveloped corneocytes (Rawlings and Harding 2004) that links between the adjacent corneocytes by corneodesmosomes. Filaggrin deficiency, therefore, abnormalizes the skin barrier in turn and severely enhances skin dryness causing atopic dermatitis accordingly (Wolf and Wolf 2012). In addition to protease degrading filaggrin, corneodesmosome degradation by proteolytic enzymes also enhances skin dryness causing desquamation that is visually noticed as skin flakes (Harding et al. 2000). Protection from excessive water and electrolyte loss from the skin is regulated by SC intercellular lipid. The occlusive oily layer therefore effectively suppresses TEWL by hydrogen bonding with water at the polar head lipids that are in orthorhombic (solid) and hexagonal (gel) packing.

Moisturizers can be considered safe in comparison with traditional drug used by dermatologists. However, inconvenient skin reactions from topical preparation may be encountered. Therefore, moisturizers that are usually free from irritating substances are highly in demand (Lodén 2004) particularly natural moisturizer. Thus, this chapter is exclusively devoted for skin hydrating biopolysaccharides.

### 3.1 Mechanism of Moisturizer

Moisturizing product is formulated and expected to suppress TEWL and retain or increase the content of water in SC in order to maintain the skin barrier. Although function mechanism of this active cosmetic category is complicated, simple classification on the basis of the actions would be by:

1. Occlusive effect: TEWL in SC which physically blocks thereafter the percolation of water from the inner viable epidermis is protected. In addition, emollience or lubricance that smoothens the skin by filling up the spaces between skin flakes is enhanced to retain the skin hydration. Occlusive ingredients generally used in personal care products are petrolatum, mineral oil, paraffin, and squalene including vegetable and animal fats.
2. Humectant effect: skin hydration in SC is improved by an attraction of water from viable skin tissues re-moisturizing the skin from the inside out. Commonly used humectants in cosmetics are glycerin, propylene glycol, urea, sodium lactate, sorbitol, and pyrrolidone carboxylic acid (PCA).

Skin hydrating cosmetics usually combine the moisturizing effects from occlusants and humectants. Synergistic effects by water retaining in the skin and the prevention of TEWL compulsively sustain the skin barrier, therefore largely contributing to hydrating efficacy. Although skin moisturizing efficacy could be monitored by sensory evaluation, instrumental analysis would accurately reflect the efficacy with the practical validation between different studies.

## 3.2 Evaluation of Skin Hydrating Efficacy *In Vivo*

Skin barrier is a physical property referring to water content in the skin that can be assessed by several techniques. This chapter will be devoted to those of noninvasive methods that are the agreed standardized methods used in clinical evaluation of skin hydrating or moisturizing products which are TEWL, skin hydration, and skin image. The devices based on spectroscopic and microwave principles are not included.

### 3.2.1 TEWL

Transepidermal water loss is the outward permeation of condensed water through SC by diffusion, of which perspiration including other forms of water loss is excluded from TEWL. This transcutaneous water loss is generally measured by open and closed chamber methods that are commercially available. The open chamber type relies on Fick's diffusion law indicating the quantity being transported per specific area and time. TEWL is thereafter processed and shown in  $\text{g/m}^2/\text{h}$ . Although this method allows continuous measuring of TEWL, opening of the probe to the surrounding atmosphere turbulences the result. The closed chamber devices determining skin water flux density are therefore developed to limit the atmosphere influence, which are the condenser chamber and unventilated chamber. The unventilated closed chamber can occlude the skin and might be improper for continuous measurement as the normal evaporation of the skin is blocked. Therefore, the ventilated ones are implied by using dry or moistened carrier gas for continuous determination of TEWL.

TEWL conferring skin barrier function is routinely tracked by Tewameter<sup>®</sup> (Courage + Khazaka, Germany), the open chamber type, and unventilated closed chamber type, that is, VapoMeter<sup>®</sup> (Delfin, Finland) including the condenser closed chamber, AquaFlux<sup>®</sup> (Biox, UK). In addition, DermaLab<sup>®</sup> (Cortex, Denmark) and Evaporimeter<sup>®</sup> (ServoMed, Sweden) sharing the same principle with Tewameter<sup>®</sup> are also used. In the meantime AS-CT1<sup>®</sup> (Asahi, Japan) that is an unventilated closed chamber type is additionally used besides VapoMeter<sup>®</sup>.

In addition to direct measurement of skin water loss rate, SC water content or skin hydration can be determined indirectly by means of electrical properties of the skin.

### 3.2.2 Skin Hydration

The skin water content in terms of SC hydration reflecting skin barrier is measured on the basis of electrical capacitance, conductance, or impedance. These fundamentals rely on the dielectric medium nature of SC. The instrument is therefore developed on the basis of this electrical concept of the skin. Measurement of skin permeability to alternating electric current (impedance) reflects electromagnetic interaction with skin dipoles and electrolytes (Kajs and Gartstein 1991). A low resistance but high impedance correlates with a greater skin hydration (water content). Skicon<sup>®</sup> (IBS, Japan) operates at 3.5 MHz with the result expressed in microsiemens ( $\mu\text{s}$ ) ranging from 0 to 1,999  $\mu\text{s}$ . This conductance instrument consists of the concentric interdigital electrodes liberating a direct galvanic contact between the probe and skin surface. The noninvasive capacitance-based devices are based on the difference

of the dielectric constant of water and other substances brought in the electrical measurement field using low operating frequency (up to 1 MHz) (Darlenski et al. 2009). Examples of the capacitance principal are Corneometer<sup>®</sup> (Courage + Khazaka) and Nova<sup>®</sup> dermal phase meter or DPM (Nova, USA). The measurements are shown in arbitrary unit (AU). Corneometer<sup>®</sup> contains an interdigital grid of gold electrodes covered with a low dielectric vitrified material. The frequency shift of the oscillating system is detected referring to skin capacitance that is in contact with the probe ranging from 0 to 120 AU. Nova<sup>®</sup> DPM has two concentric brass ring electrodes separated by an isolator with a distance between the inner and outer probes of 1 mm and readout measurement ranging from 90 to 999 AU. In addition, Moist Sense<sup>®</sup> (Moritex, Japan) is also used to assess the relative skin moisture value with 0 to 99 AU. Furthermore, other devices measuring skin conductance, ASA-M2<sup>®</sup> (Asahi) in addition to Skicon<sup>®</sup>, are also used. In the meantime, Moisture Meter SC<sup>®</sup> (Delfin, Finland) exterminating SC hydration by means of skin capacitance and DermaLab Moisture Unit<sup>®</sup> (Cortex) sharing the same principle with Nova<sup>®</sup> DPM are also used to verify skin hydrating efficacy of topical products.

Skin hydration measurement is therefore assessable by capacitance- and conductance-based device regarding to their correlation. In addition, there are validations of different instruments that are developed by different manufacturers. For instance, Corneometer<sup>®</sup> and Skicon<sup>®</sup> are strongly correlated as examined *in vivo* ( $r = 0.97$ ). However, conductance method is influenced by electrolytes with a lack of sensitivity at low hydration. In contrary, the sensitivity of the capacitance instrument is limited at high hydration values (Clarys et al. 2012).

Capacitance imaging (CI) of the skin surface is developed on the basis of silicon image sensor (SIS) technology that is previously developed for security reasons by fingerprint recoding. The resulting capacitance map is interpreted in terms of skin hydration/dryness. This skin recoding called SkinChip<sup>®</sup> (L'Oréal, France) composed of 92,160 microcapacitors on a  $1.8 \times 1.28$  cm plate plugged directly to the USB port is recently proposed to determine skin hydration *in vivo* (Lévêque et al. 2006).

### 3.2.3 Skin Image

In addition to the above noninvasive techniques that determine skin condition relevant to cutaneous moisture, skin flakes resulting from desquamation are collected and analyzed by D-Squame<sup>®</sup> (CuDerm, USA). It is the test kit that validated with the above instruments' applicability for clinical efficacy evaluation of skin moisturizing products. Skin dryness resulting from desquamation is visually scaled following the application of the D-Squame<sup>®</sup> tape onto the skin with a moderate pressure using the thumb or fingertips. Scaliness of the skin is divided into a 1–5 score referring normal to very dry skin. The desquamated corneocytes collected by the stripping tape can be additionally analyzed using an image analyzer (Black et al. 2006; Gasser et al. 2004). Furthermore, the skin image that is directly taken from the volunteer's skin by Visioscan<sup>®</sup> (Courage + Khazaka) on SESc recording parameter alternatively used scaliness to assess skin hydrating efficacy of the cosmetic product. In addition, skin replica is also analyzed upon scaliness of the skin by Visiometer<sup>®</sup> (Courage + Khazaka).

### 3.2.4 *In Vivo* Assessment of TEWL, Skin Hydration, and Skin Image

Although there might be some differences resulting from the different instruments used, standard guidelines by EEMCO (European Group for Efficacy Measurements on Cosmetics and Other Topical Products) recommendation are adopted worldwide that make the results able to be validated in different analytical conditions. In addition, the measuring instruments should be calibrated routinely on the basis of the manufacturer guideline. Furthermore, TEWL is related with SC hydration. These determination concepts are therefore used interchangeably. However, clinical evaluation strictly relies on the same practice.

Prior to starting the measurement, the volunteer or the participant must be acclimatized in the temperature- and humidity-controlled environment to suppress turbulent effect from sweating that alters water evaporation rate of the skin. This volunteer preparation will take 15–30 min at 20–22 °C and relative humidity of 40–60 %. The measurement will be taken in the same climatized room without external air convection turbulence (du Plessis et al. 2013).

Clinical evaluation of skin hydrating efficacy is equivalently measured on the face or volar forearm. Therefore, the volar forearm is generally chosen in skin biomechanical property assessment with a minimal discomfort to the volunteer (Bazin and Fanchon 2006).

## 3.3 *In Vitro* Hydration Property

Hydration property of polysaccharide is determined by means of water absorption, water-holding capacity, and swelling properties. These parameters confer skin hydrating potential of the polysaccharides that should be conducted prior to clinical evaluation *in vivo* in terms of TEWL and/or SC water content.

Absorption of water refers to the structural network of polymer specifically the volume. Baumann apparatus is generally used to measure water absorption, that is, the kinetics of water uptake. However, measurement of water absorption capacity is routinely calculated as the percentage of weight increases of the sample dried over P<sub>2</sub>O<sub>5</sub> *in vacuo* for 24 h by

$$\text{Water absorption capacity (\%)} = 100 \times \frac{(W_n - W_o)}{W_o}$$

where  $W_n$  and  $W_o$  are the weights of the sample before and after putting the saturated (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> desiccator (81 % RH) and the saturated K<sub>2</sub>CO<sub>3</sub> desiccator (43 % RH) at 20 °C after 48 h of the test.

Water-holding capacity is the amount of water that is retained by the polymer at the specific weight commonly 1 g and determined under a specific temperature, humidity, time, and speed of centrifugation. This parameter sometimes is known as water-retaining capacity. However, centrifugation measurement is generally higher than the determination by Baumann apparatus. The standardized protocol determination is studied by hydrating a known polysaccharide weight in a centrifuge tube for 18 h

before pelleting the insoluble residue by centrifugation (3,000 g; 20 min). Following removal of the excess supernatant and/or soluble material, the hydrated polysaccharide residue is weighted prior to repeating the residue weight in the dry form. Consequently, the water retention capacity is calculated using the following equation:

$$\text{Water retention capacity}(g/g) = \frac{\text{Residue fresh weight} - \text{Residue dry weight}}{\text{Residue dry weight}}$$

In addition, the moisture-retention ability of polysaccharide can be calculated as the percentage of residual water of wet sample prepared by adding 10 % water to the sample dried over P<sub>2</sub>O<sub>5</sub> *in vacuo* for 24 h by using the equation

$$\text{Water retention capacity}(\%) = 100 \times \frac{W_n}{W_o}$$

where W<sub>n</sub> and W<sub>o</sub> are the weights of the sample before and after putting the saturated K<sub>2</sub>CO<sub>3</sub> desiccator (43 % RH) and the silica gel at 20 °C after 48 h of the test.

Swelling property is assessed by the bed volume technique by swelling the polysaccharides in water overnight using a volumetric cylinder. Generally a known weight of polymer (100–200 mg) hydrated with water in a graduated cylinder (10 ml) is dispersed with gentle stirring, covered, and left for saturation for 18 h at room temperature. Thereafter, the settled volume occupied by polysaccharide is recorded and swelling is calculated by the equation as shown below:

$$\text{Swelling} = \frac{\text{Volume occupied}}{\text{Polysaccharide dry weight}}$$

In addition to the above physicochemical properties that indirectly confer skin hydration potential of the polysaccharides, total polysaccharide content, the sugar constituents, molecular weight, porosity, and particle size also contribute to the moisturizing property.

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## 4 Skin Hydrating Effect of Polysaccharides

Regarding the above classification of moisturizing polysaccharides, those of commercial available skin moisturizing polysaccharides are summarized as shown in Table 4 with the recommended concentrations and useable preparation as available. CAS (Chemical Abstracts Service) number and INCI (International Nomenclature of Cosmetic Ingredients) name are included for further reference.

In addition to the currently used commercialized moisturizing polysaccharides, candidate biopolysaccharide from different sources potential for skin hydrating cosmetics is also included. Those with *in vitro* (water-retaining and water absorption capacities and total polysaccharide content) and *in vivo* (human volunteers or animal model) results from accredited journal and patents are exclusively summarized and alphabetically listed. However, those of mushroom-derived polysaccharides are excluded from this article.

**Table 4** Commercialized moisturizing polysaccharides in cosmetics

Name <sup>a</sup>	Supplier	CAS number	INCI name/ composition	Dose (%)
ABS aloe beta-glucan	Active Concepts		<i>Aloe barbadensis</i> Yeast $\beta$ -glucan	1–5
Actiglow <sup>®</sup> C	Active Organics		Hydrolyzed GAGs	1–35
Actimoist <sup>®</sup> Bio		7732-18-5, 9067-332-7	Sodium HA	1–10
Actiphyte <sup>®</sup> Acacia			Acacia gum	5–10
Actiphyte <sup>®</sup> Algae		92128-82-0	Algae	
Actiphyte <sup>®</sup> Aloe vera 10-fold		85507-69-3	<i>Aloe barbadensis</i>	
Actiphyte <sup>®</sup> <i>Spirulina</i>			<i>Spirulina maxima</i>	
Actisea <sup>®</sup> 100		Algae	1–10	
ROVI Sodium Hyaluronate	Air Products		Sodium HA	
Akomarine <sup>®</sup> Active Complex	Akott		Algae Carrageenan Algin	
Akomarine <sup>®</sup> Chlorella			<i>Chlorella vulgaris</i>	
Akomarine <sup>®</sup> Gum Complex			Algae	
Akomarine <sup>®</sup> Kelp			<i>Laminaria digitata</i>	
Akomarine <sup>®</sup> Sea Lettuce			<i>Ulva lactuca</i>	
Carboxymethyl yeast beta-glucan (CMG) C90	Angel Yeast Co., Ltd.	9050-93-5	Sodium carboxymethyl $\beta$ -glucan	5–10
Yeast polysaccharides M60		68876-77-7	Yeast polysaccharides	0.5- 3
Yeast mannoprotein M60				0.05-0.5
PatchH <sub>2</sub> O <sup>TM</sup> A00297	BASF		Algin Sodium HA Pullulan	1–3
Bio-Beta-Glucan	Bioland	160872-27-5	$\beta$ -Glucan	
Marin moist		92128-82-0	<i>Laminaria japonica</i>	
Fructan <sup>TM</sup>		9013-95-0	Fructan	
Nanomoist				
SC-Glucan		5965-23-6, 160872-27-5	$\beta$ -Glucan	
Ulmus			<i>Ulmus davidiana</i>	
Dermatein <sup>®</sup> Hyaluronic Acid	BioOrganic Concepts	9067-32-7	Sodium HA	
Dermatein <sup>®</sup> Power		9050-36-6, 9067-32-7	Sodium HA $\beta$ -Glucan <i>Aloe barbadensis</i> / Guar	

(continued)

**Table 4** (continued)

Name <sup>a</sup>	Supplier	CAS number	INCI name/ composition	Dose (%)	
Echinacea extract	Carruba	90028-20-9	<i>Echinacea purpurea</i>		
Wakame extract			<i>Undaria pinnatifida</i>		
Hygroplex <sup>TM</sup> HHG	Chemisches Laboratorium Dr. Kurt Richter GmbH			2–5	
Tinocare <sup>®</sup> GL <sup>b,c</sup>	Ciba	39464-87-4	Sclerotium gum		
Zenzivo <sup>TM</sup>	Clariant		Chitosan		
Pheohydrane <sup>®c</sup>	Codif		Hydrolyzed algin <i>Chlorella vulgaris</i>	0.5–1	
Pheofiltra <sup>®</sup> Undaria HG			<i>Undaria pinnatifida</i>	2–5	
SMW Hyaluronic acid	Contipro Biotech s.r.o.			0.005–0.06	
Cromoist HYA	Croda		Hydrolyzed collagen Hyaluronic acid		
Cromoist HWYA			70084-87-6, 9004- 61-9	Hydrolyzed wheat protein HA	
Cromoist CS				Hydrolyzed collagen Sodium chondroitin sulfate	
Phytessence Wakame		56-81-5, 7732-18- 5, 223751-81-3	<i>Undaria pinnatifida</i>	1–7	
Phyaluronate <sup>®J</sup>	DSM	9000-40-2	<i>Ceratonia siliqua</i> gum	1–5	
Hyasol BT			Sodium HA	3–5	
HA-Sol <sup>TM</sup>	Engelhard- BASF		Sodium HA		
ABIL <sup>®</sup> Filler CL <sup>b,c</sup>	Evonik Goldschmidt	7732-18-5, 22047- 49-0, 105524-32-1, 849230-52-0, 64248-79-9, 64-17-5	Sodium HA cross polymer	0.5–5	
HyaCare <sup>®</sup>			Hydrolyzed HA	0.01–0.2	
TEGO <sup>®</sup> Smooth			Hydrolyzed sclerotium gum	1–10	
MG-60	Hayashibara International				
Unicerin C-30	Induchem		Cellulose Hydroxypropyl methylcellulose		
Chitosan	Jeen International Corporation	9012-76-4			

(continued)

**Table 4** (continued)

Name <sup>a</sup>	Supplier	CAS number	INCI name/ composition	Dose (%)
Glucan $\beta$	Kaden Biochemicals GmbH	-		-
Collagen-Hyal	Kelisema		Soluble collagen Sodium HA	
Indinyl <sup>®</sup> CA LS 8998	Laboratories Serobiologiques		<i>Cassia angustifolia</i> polysaccharide	2.5–10
PA Reviviscence <sup>®</sup> LS 9562			<i>Tamarindus indica</i> polysaccharide	3–5
Active Powder <sup>®</sup> Moist LS 9696			<i>Cassia angustifolia</i> polysaccharide Gellan gum	3–7
Active Powder <sup>®</sup> Volu Lips LS 9773			<i>Pisum sativum</i> Algae <i>Cassia angustifolia</i> polysaccharide Gellan gum Xanthan gum	4–7
Lipo pearl <sup>™</sup>	Lipo Technologies	61789-91-1, 8042- 47-5, 9000-70-8, 12001-26-2, 13463-67-7	Gelatin Cellulose gum	
Phytohyaluronate	Lonza			1–10
Trimoist	Mibelle AG Biochemistry		Sodium carboxymethyl $\beta$ -glucan	
Chitosan MM 222	Michel Mercier		Chitosan	0.5–1
Chitanide <sup>™</sup> 222	M.M.P.		Chitosan succinamide	10
CD-58	Onlystar Biotechnology	1398-61-4	<i>N</i> -succinyl chitosan	
NMF-26		9012-76-4	Algae	
Astaxanthin	Oryza Oil & Fat Chemical Co., Ltd.		<i>Haematococcus</i> <i>pluvialis</i> Astaxanthin	
Seamollient <sup>®</sup>	Philip Rockley	7732-18-5, 68917- 51-2, 92128-52-0	Algae	10–50
Fructan	Presperse Incorporated	9013-95-0	Fructan	3
Ulmus Extract			<i>Ulmus davidiana</i>	
Phycol <sup>®</sup> FV		57-55-6, 7732-18- 5, 84696-13-9	<i>Fucus vesiculosus</i>	
Sea Silk		7732-18-5, 92128- 82-0	<i>Ulva compressa</i> <i>Himanthalia</i> <i>elongata</i>	3–5
Pheofiltrat <sup>®</sup> Undaria HG			<i>Undaria pinnatifida</i>	2–5
Hydrane <sup>®</sup> BG		<i>Gigartina stellata</i>	3–5	
Hydractin <sup>®</sup>	Rahn		<i>Carica papaya</i> Algin	2–8

(continued)



**Table 4** (continued)

Name <sup>a</sup>	Supplier	CAS number	INCI name/ composition	Dose (%)
Ritachitosan LV	RITA Corporation	9012-76-4	Chitosan	
Hydroil	Shanghai Leasun Chemical		HA	3–6
Sodium hyaluronate	Shandong Freda Biochem Co., Ltd.		HA	0.05-0.5
Chitoglycan	Sinerga	83512-85-0	Carboxymethyl chitosan	
Red Alga Gel		68917-51-1, 9000-07-1	Algae	
Fucogel 1000 <sup>®</sup>	Solabia	–	Biosaccharidegum-1	5
Fucogel <sup>®</sup>		–		1–20
Hyaluronic acid BT		–	Sodium HA	–
Bashyal	Soliance	–	Sodium HA	–
Cristalhyal		–	–	–
Soligel		–	Rhizobian gum	–

<sup>a</sup>All of the listed polysaccharides are used for baby care, cleansing, body care, facial care

<sup>b</sup>Additionally used in makeup cosmetics

<sup>c</sup>Additionally used in sun care

## 4.1 Animal Polysaccharides

Hyaluronic acid (HA) is the predominant mucopolysaccharide of the skin acting as the key molecule that regulates skin hydration. It is therefore popularly formulated in moisturizing products at a concentration varying from 0.025 to 0.050 %, serving as skin hydrating agent (Stern and Maibach 2008). In addition to the common application of HA in the forms of dermal fillers (e.g., Hylaform<sup>®</sup>, Restylane<sup>®</sup>, and Dermalive<sup>®</sup>), it is topically applied to maintain SC function restoring skin barrier.

Comparative clinical evaluation of skin hydrating effect of HA (anionic polysaccharide) and ceramide in foam and emulsion cream was conducted by a randomized double-blind split body study in 20 female volunteers. The appearances relevant to skin dryness including moisturizing effect were significantly improved ( $p < 0.05$ ) following 2 weeks as rated by the investigator. The improvement was enhanced at the end of the evaluation for 4 weeks ( $p < 0.001$ ), although that of HA foam was more superior over the ceramide cream (1.5-fold at 2 weeks and 1.3-fold at 4 weeks) (Draeos 2011). However, concentrations of moisturizing agents were not addressed. In addition, formulation using the same dosage form including instrumental evaluation would additionally support the outcome of these moisturizers.

Moisturizers containing ceramide are included. Impruv<sup>®</sup>, Cetaphil RestoraDerm<sup>™</sup>, CeraVe<sup>™</sup>, Triceram<sup>®</sup>, EpiCeram<sup>®</sup>, Atopiclair<sup>®</sup>, and MimyX<sup>®</sup>

are commonly commercialized over-the-counter (OTC) products. GAGs with the molecular weight of  $10^3$ – $10^7$  Da at the concentration of 0.05–5 % were patented into skin hydrating cosmetics (Bosco et al. 2013).

In addition to the above animal-derived skin hydrating polysaccharide, chitosan modified from shrimp (*Solemoscera prominentis*) chitin with the degree of substitution of 83.2 % and molecular weight of 2,420 KDa was formulated in the moisturizing mask. Skin water-holding capacity of the mask was examined in seven volunteers in a comparison with the control mask containing methylcellulose at the same concentration (2 %). Skin capacitance (Corneometer<sup>®</sup>) of the shrimp chitosan was better than that of methylcellulose (Chen and Hen 2000). Those of commercialized glycosaminoglycans (GAGs) including HA for skin hydration are included in Table 4.

## 4.2 Botanical Polysaccharides

### 4.2.1 *Abelmoschus esculentus*

Okra is regarded as the important source of polysaccharide according to its high content of the fruit mucilage. Its polysaccharides with physicochemical properties found more applications in cosmetics (Camciuc et al. 1998; Sengkhamparn et al. 2010). Moisturizing alcohol-based hand rub containing okra polysaccharide was formulated. This moisturizing product with 0.105 % polysaccharide maintained skin hydration significantly better than the placebo as instrumentally monitored (Moist Sense<sup>®</sup>) in 20 volunteers who are health-care workers in the hospital. Skin hydration was retained for 210 min of application. Therefore, it was recommended for application encouraging hand hygiene with antiseptic properties (Kanlayavattanakul et al. 2012).

### 4.2.2 *Aesculus hippocastanum*

Horse chestnut that is adopted in traditional German medicine is one of the important sources of polysaccharides including oligosaccharides that composed more than 50 % in the herb (Thornfeldt 2005). Thus, it is the candidate botanical source of skin hydrating polymers applicable for cosmetics. However, none of horse chestnut polysaccharide moisturizer is presented yet, including the skin hydrating efficacy. Thus, this botanical polysaccharide is worthy to be formulated and challenged for clinical evaluation.

### 4.2.3 *Aloe vera*

The leaf enriched with polysaccharides is largely implied in skin preparation and popularly sold over the counter (OTC) for skin nourishing effect. Aloe polysaccharide in topical product (0.1, 0.25, and 0.5 %) significantly increased skin capacitance (Corneometer<sup>®</sup>), although TEWL (Tewameter<sup>®</sup>) was insignificantly suppressed as examined in 20 volunteers monitored after 1 and 2 weeks of application (Dal' Belo et al. 2006). Aloe polysaccharide is therefore widely commercialized in several trade names as shown in Table 4.

#### 4.2.4 *Aztec chia*

Chia native to Mexico was a polysaccharide gel isolated from the seed. Low molecular weight chia polysaccharide (150–250 KDa) exhibited moisturizing effect. It was therefore formulated with glucan (700–1,300 KDa) and HA (800–1,500 KDa) claiming as skin hydrating cosmetics at 0.5–3 % (Choi et al. 2010).

#### 4.2.5 *Camellia sinensis*

Tea polysaccharide containing 64.27 % of neutral sugar and 27.95 % of uronic acid was shown to be a good moisturizer as it is able to retain water (*in vitro* test) comparable to glycerol at the same tested concentration. It is therefore highlighted as another important bioactives derived from tea in addition to phenolics that are widely formulated in aesthetic products (Wei et al. 2009). Tea polysaccharide with molecular weight range between 100 and 300 KDa was prepared and formulated (0.1–20 %) into moisturizing cosmetics as patented by the Korean cosmetic firm (Kwon et al. 2010).

#### 4.2.6 *Carica papaya*

Papaya fruit is one of the important skin hydrating polysaccharides. Papaya polysaccharide with a molecular weight of 2,540 KDa having 76.9 % of total sugar and 10.92 % of uronic acid was characterized. Galactose (52 mol ratio) and arabinose (21.6 mol ratio) were found as the main monosaccharides followed by glucose, rhamnose, and xylose (11.0, 10.2, and <0.1 mol ratio). This antioxidant polysaccharide absorbed and retained moisture content (*in vitro*) comparable to HA and glycerol at the same tested concentration (100 mg) (Zhang et al. 2012). Papaya polysaccharide is commercialized by Rahn in Hydractin<sup>®</sup> (Table 4).

#### 4.2.7 *Durio zibethinus*

Durian is one of the important tropical fruits that is enriched with polysaccharides in the hull. Durian polysaccharide consists of polygalacturonan branched with galactose, glucose, rhamnose, fructose, and arabinose with molecular weight approximately 500–1,400 Da (Hokputsa et al. 2004). The polysaccharide was therefore formulated into gel (10 %) and assessed on its skin hydrating activity in 18 volunteers for 8 weeks. A randomized single-blind split-face placebo-controlled study was directed to apply 0.139 % polysaccharide gel formulation or 0.3 g of product twice daily (morning and evening). Skin water content (Corneometer<sup>®</sup>) was significantly increased at the first examination following treatment of 4 weeks ( $p = 0.024$ ) and largely achieved ( $p = 0.003$ ) at the end of the study. The results additionally revealed that the efficacy in female volunteers was more superior over male. In addition, the product imparted excellent enhancement of skin hydration in the subjects who are younger than 30 years old than the older (Futrakul et al. 2010).

#### 4.2.8 *Echinacea purpurea*

The root of the herb has polysaccharides which are isolated and characterized. Polysaccharides (xylan and galactan) with molecular weight approximately 35 and

450 KDa were obtained. This polysaccharide with biological activity was suggested to be incorporated in health benefit preparations (Dalby-Brown et al. 2005). The polysaccharide extract was further commercialized and claimed as skin moisturizer as shown in Table 4 by Carruba.

#### **4.2.9 *Malva sylvestris***

Malva nut is widely applied in dermatological use due to its therapeutic effects relevant to the skin (Pieroni et al. 2004). The herb's potential in skin hydration is governed by its abundant mucilage. Polysaccharides in this herb consisted of glucuronic acid, galacturonic acid, rhamnose, galactose, fructose, glucose, sucrose, and trehalose with the minor constituents of uronic acid, arabinose, mannose, xylose, fucose, raffinose, and xylotriose (Barros et al. 2010; Classen and Blaschek 1998). Therefore, Malva mucilage was formulated into skin hydration products (Cauchard et al. 2010; Choi et al. 2005).

#### **4.2.10 *Myrosma cannifolia***

Guapo, native tuber plant of Venezuela, is examined for its potential starch of cosmetic application. Its amylase and amylopectin ratio is corn resembling with optimal physicochemical properties for cosmetics in addition to safety and compatibility in cosmetic base. Its water absorption capacity is adequate and challenge to be verified on its skin hydrating efficacy (Rincón et al. 2005).

#### **4.2.11 *Orchidaceae* sp.**

Orchid, a plant of the genus *Odontoglossum* of the family *Orchidaceae* and/or a plant derived from a hybrid plant of the genus *Odontoglossum* and the genus *Cochlioda*, constituted 60–70 % polysaccharide in which mannose is the main neutral sugar (90 %) prepared. Cosmetics with moisturizing efficacy were formulated and claimed at the extract concentration of 0.1–15 % (Sasaki et al. 2013).

#### **4.2.12 *Piptadenia colubrina***

A native leguminous tree of South American rain forest has isolated skin beneficial polysaccharide with the extractive yield of 0.05–0.25 %. The extracted polysaccharide was further formulated into a gel-cream product (5 %). Clinical evaluation on the basis of skin capacitance was examined by randomized single-blind placebo-controlled study in 15 volunteers for 14 days and tracked by Corneometer<sup>®</sup>. Skin capacitance was significantly achieved. Cellular skin hydrating effect was evidenced by expression of filaggrin enhanced by the polysaccharide in human skin explants (Pereda et al. 2010).

#### **4.2.13 *Tamarindus indica***

Polysaccharide tamarind seed (65–73 % of the kernel) with the molecular weight of 600–750 KDa was formulated into cosmetics (0.1–1 %) with skin hydration activity claimed (Cocchi and Sanso 2010). Tamarind polysaccharide claiming skin moisturizing activity is commercialized with the trade name of PA Reviviscence<sup>®</sup> LS 9562 by Laboratoires Serobiologiques (Table 4).

#### 4.2.14 *Ulmus davidiana*

The root of *U. davidiana* var. *japonica* that has been used traditionally in Oriental medicine was examined on its skin benefits. The polysaccharide derived from the plant root with molecular weight of 20 KDa consisting mainly of rhamnose (57.37 %) was preliminary water retaining *in vitro* including its safety and activity in human skin fibroblast. The noncytotoxic polysaccharide with water-holding capacity additionally suppressed inflammatory mediators as evidenced by the reduction of PEG2, IL-6, and IL-8 in the cultured cells. Moisturizing activity of the polysaccharide was further assessed in 10 female volunteers. Skin hydrating effect monitored by Corneometer<sup>®</sup> and VapoMeter<sup>®</sup> was almost the same as HA that was used as the positive control (Eom et al. 2006). This skin hydrating polysaccharide is further commercialized by Bioland and Presperse Incorporated as shown in Table 4.

### 4.3 Microbial Polysaccharides

#### 4.3.1 *Aspergillus niger*

The mycelium was biotechnologically controlled to produce chitin-glucan with the ratio of these two polysaccharides between 30:70 and 50:50. The obtaining composite of biopolymer was formulated into oil in water emulsion at 0.5–2.0 % and clinically evaluated in 13 female volunteers for 6 weeks. That of 1.5 % polysaccharide significantly improved skin hydration by the suppression of TEWL (Tewameter<sup>®</sup>) with no erythema. Confirmatory skin moisturizing effect of the 1.5 % chitin-glucan formulation was further conducted in 20 male volunteers for 16 weeks. This natural polysaccharide significantly improved skin barrier by water-holding capacity in SC with additional effect on skin rejuvenation as skin roughness was decreased (Gautier et al. 2008).

#### 4.3.2 *Aureobasidium pullulans*

$\beta$ -Glucan from *A. pullulans* was prepared and further incorporated into skin moisturizing cosmetics at the amount of 5–20 % that enhanced skin hydration evidenced in 5 female volunteers (Moriya et al. 2011).

#### 4.3.3 *Gluconacetobacter sacchari*

Bacterial cellulose produced from *Gluconacetobacter sacchari* composited with glycerin (1 %) showed a significant skin moisturizing effect as examined in 15 volunteers who contacted with the product for 24 h. TEWL was suppressed, whereas skin capacitance was increased as shown by Tewameter<sup>®</sup> and Corneometer<sup>®</sup> (Almeida et al. 2013).

#### 4.3.4 *Klebsiella pneumoniae*

Polysaccharide from a nonpathogenic strain was formulated (10 %, 40 kDa) and assessed on its skin hydrating efficacy in 40 female volunteers. The formulation

significantly enhanced skin water content following 15 and 30 days of study as evidenced by Corneometer<sup>®</sup> with an ability to suppress TEWL as shown by Tewameter<sup>®</sup> (de Cargo and Gaspar 2012).

#### **4.3.5 *Nostoc commune***

Cyanobacterium in *Nostoc* genus particularly *N. commune* largely synthesized the mucilaginous matrix. The polysaccharide plays an important role in the bacterium's defense mechanism, of which *Nostoc* polysaccharide is regarded as the biomedical potential natural product with a wide variety of therapeutic effects applied in traditional medicine of several countries. Furthermore, *Nostoc* polysaccharide showed a comparable in vitro moisture absorption and retention capacities to chitosan and urea studied at the same concentration. Consequently, its skin hydrating efficacy was confirmed in an animal model as the water content in mouse SC was improved (Li et al. 2011).

#### **4.3.6 *Saccharomyces cerevisiae***

Baker's yeast is one of the important sources of glucan, moisturizing polysaccharides in cosmetics (Kanlayavattanukul and Lourith 2008). Glucan derivatives are widely used in topical preparations particularly carboxymethyl glucan. It improved skin barrier function as evidenced in enhancement of skin hydration (Corneometer<sup>®</sup>) in 5 volunteers whom were directed to apply the product containing carboxymethyl glucan (0.04–0.4 %) twice daily for 2 weeks (Züllli et al. 1998). Modifiers of  $\beta$ -glucan enlarge applications suitable for various preparations including sodium carboxymethyl  $\beta$ -glucan. Nano-cosmetics for eye hydration were formulated in a form of liposome containing 0.1–5 % of the active polysaccharides (Mercuri 2008).

#### **4.3.7 *Zymomonas mobilis***

Levan, fructan polysaccharide, was prepared using *Z. mobilis*. The prepared polysaccharide with a molecular weight of 2,250 KDa was noncytotoxic in human skin cell cultures with the anti-inflammatory effects against IL-1 $\alpha$ . Skin moisturizing effect was further evaluated in a comparison with hyaluronan at the same concentration by means of TEWL using VapoMeter<sup>®</sup> and skin capacitance using Corneometer<sup>®</sup> in 10 female volunteers. Skin hydrating efficacy of *Z. mobilis* polysaccharide was comparative to that of HA (Kim et al. 2005). This microbial polysaccharide is commercialized by BASF and Bioland (Table 4).

### **4.4 Seaweed Polysaccharide**

In addition to the above skin hydrating polysaccharides from microbial source, the seaweed Rhodophyta (red algae) is an important source of sulfated galactans including carrageenans, whereas the brown seaweed (Phaeophyta) largely produces alginates. Carrageenan is exhibited as the excellent active polysaccharide.  $\kappa$ -Carrageenan was formulated (0.5–10 %) with starch (0.5–20 %) in skin mattifying cosmetics with

the moisturizing feeling (Cassin 2013). Furthermore, anionic polysaccharide with the average size of less than 500 KDa was prepared from cell culture of microalgae of the genus *Parachlorella* or *Chlorella* and commercialized by Codif (Table 4). The polysaccharide is composed of rhamnose, xylose, mannose, glucose, arabinose, and glucuronic acid at 15–55, 3–30, 1–25, 1–45, 0.5–10, 22, and 0.1–15 mol%. The polysaccharide (0.1 %) was formulated into a topical application product claiming safety and efficiency (Coragliotti et al. 2010).

#### 4.4.1 *Gigartina stellata*

This red seaweed with the synonym of *Mastocarpus stellatus* enriched with polysaccharide mainly composed of galactose was revealed as the potential source for skin hydrating product according to the *in vitro* water absorption with the swelling capacity of  $7.20 \pm 0.42$  ml/g and water retention capacity of  $5.42 \pm 0.06$  g/g (Gómez-Ordóñez et al. 2010). Presperse Incorporated is the company that produces red seaweed polysaccharide as shown in Table 4.

#### 4.4.2 *Himanthalia elongata*

Comparative *in vitro* water retention evaluation of edible seaweed of the Spanish coast was conducted. *H. elongata* was noted as the potential polysaccharide for skin moisturizing effect due to its water retention capacity of  $7.26 \pm 0.13$  g/g and swelling ability of  $10.97 \pm 0.62$  ml/g (Gómez-Ordóñez et al. 2010). Similar to *G. stellata* polysaccharide commercialization, *H. elongata* is commercialized by Presperse Incorporated (Table 4).

#### 4.4.3 *Laminaria* sp.

Hydrocolloids extracted from 12 edible seaweeds including *L. japonica* or kombu were comparatively evaluated on skin moisturizing activity. Skin capacitance (Corneometer<sup>®</sup>) in 10 female volunteers was superiorly enhanced by *L. japonica* over the others at the same tested concentration (5 %). This edible seaweed extract was further formulated into cosmetic cream at various concentrations (1–15 %). Skin moisturizing effect was found significant and superior with the 10 % hydrocolloid algae as it prolonged the suppression of TEWL (Tewameter<sup>®</sup>) for 8 h (Choi et al. 2013b). This commercialized polysaccharide (Akott) is included in Table 4. In addition, sweet kombu or *L. saccharina* is additionally highlighted as the suitable moisturizing polysaccharide due to its high water retention and swelling capacities ( $8.93 \pm 0.52$  g/g and  $10.20 \pm 0.37$  ml/g) (Gómez-Ordóñez et al. 2010).

#### 4.4.4 *Monostroma nitidum*

These edible green macroalgae called aonori in Japanese were extracted to give humectant mucilage. The mucilage was formulated into cosmetic product in the form of a mask in combination with hydroxyethylcellulose (HEC). The equivocal amount of the algal mucilage and HEC (total 2 %) was found superior over that containing 2 % methylcellulose in terms of moisturizing effect as assessed in 7 volunteers monitored by Corneometer<sup>®</sup>. In addition, the mucilage functioned as thickening agent (Chen and Chen 2003). It is therefore accountable as multifunctional ingredient.

In addition to the above edible seaweed, *Ulva* sp. producing water-soluble sulfated polysaccharides with (ulvan) 8–29 % of the algal dry weight consisted mainly of rhamnose and is also one of the important sources of moisturizing polysaccharide. *U. lactuca* polysaccharide with variety of health benefits is also commercialized as skin moisturizing agent, Akomarine<sup>®</sup> Sea Lettuce (Table 4). In addition to *U. lactuca*, *U. compressa* is also claimed as a skin moisturizing polysaccharide (Carruba, Codif, and Presperse Incorporated). Furthermore, *Undaria pinnatifida* or wakame is one of the edible seaweeds producing polysaccharides with SC benefits.

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## 5 Conclusion

Moisturizing or hydrating polysaccharides are derived from several natural sources of which botanical and edible hydrocolloids particularly botanical polysaccharides are largely meeting the consumers' preferences toward natural cosmetic products. In addition, advanced biotechnology preparation of skin hydrating polysaccharides affords those of economically feasible choices with animal and microbial polysaccharides. Furthermore, delivery system employing nanotechnology would enhance the skin hydrating efficacy. Those with *in vitro* water-retaining activity are encouraged for further clinical evaluation including those of candidate herbs or botanical sources enriched with polysaccharide content. Health benefits of this biopolymer in sufficiently suppressing dryness of the skin and potentially protects and/or treats wrinkles of skin acting as antiaging ingredients accordingly.

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