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Application of Biosurfactants and Biopolymers in Sustainable Cosmetic Formulation Design

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Synopsis

Increased public awareness regarding the ingredients that make up cosmetic and personal care formulations coupled with the growing concern about the dwindling nonrenewable sources from which most cosmetic ingredients like surfactants and polymers are obtained from has led to a strong need to achieve sustainability within the cosmetic industry. It has become the need of the hour to incorporate sustainability at each and every point of the product life cycle. This review focuses on the sustainable sourcing and formulation design of two key cosmetic ingredients—polymers and surfactants. To be able to completely replace their synthetic counterparts, it is crucial that these green products exhibit an efficacy level at par or greater than that of the products already on the market. Hence, various studies that show the impact of these alternatives on various performance parameters such as film formation and rheology have also been discussed. Being a heavily consumer-driven industry, some of the decisive future trends and challenges that the cosmetic industry needs to address have also been explored in this review.

INTRODUCTION

Most companies and individuals today are focused on the sustainability of their processes and products. The UN World Commission on Environment and Development defines sustainability as "the ability to meet the needs of the present without compromising the ability of future generations to meet their own needs." As a result, industries are trying to incorporate sustainability in every aspect of product development. Furthermore, Dimitrova et al. (1) reported that consumers are becoming more environmentally aware and that this growing awareness was changing their buying patterns. They are shifting gears to a more healthy lifestyle for both themselves as well the planet.

Chemical processes and products are typically evaluated on the basis of their performance. However, at present, this "performance" solely depends on the primary function of the process or product and does not take into account the dire consequences of the same on the ecological system. Zimmerman et al. (2) in their study call attention to the need for

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redefining the term performance to include sustainability. Most organizations have attempted to tackle this issue by taking on a reductionist approach wherein the entire product life cycle is broken down into different components and trying to incorporate the concept of green chemistry and engineering into each phase individually. Zimmerman et al. state that this approach is faulty and works by transferring the adverse impacts of a particular phase of the product life cycle to another phase. They emphasize that the hazards and wastes must be eliminated from the system, and this can only be achieved by taking a holistic approach to sustainability—right from ingredient sourcing and production to waste disposal (2).

The cosmetic industry too has a major role to play in this context. Valued at nearly $532 billion, the cosmetic industry is rapidly expanding and has become a vital part of the consumers' life. The beauty and personal care industry is very heavily driven by the consumers, making it essential for cosmetic companies to adopt sustainable practices. Green chemistry can help cosmetic scientists and engineers to use sustainable practices while creating new products and processes. The 12 Principles of Green Chemistry, first introduced by Anastas and Warner (4), comprise a comprehensive construct for the design of new products and processes. These principles are applicable throughout the product life cycle and address the toxicity and biodegradability of the entire process. Therefore, it is crucial that beauty and personal care organizations achieve complete sustainability by adhering to green chemistry principles so as to reduce their ecological footprint and keep up with consumer demands.

The product life cycle of a cosmetic product with a sustainable approach is shown in Figure 1. The above figure shows that there are several factors that determine the sustainability of any industry. The decisions taken at the design stage have the potential to affect the processes and routes chosen for the final production. Hence, all decisions must be made keeping sustainability in mind. During the sourcing and extraction of raw materials, it is vital to ensure that the ingredients are obtained from green, biodegradable sources and that

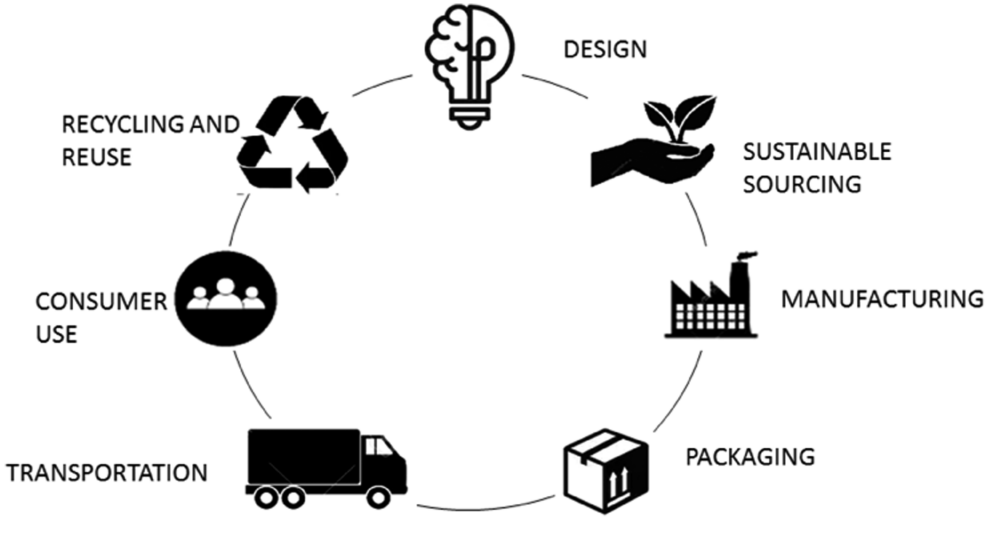

Figure 1. Sustainability in a product life cycle.

the extraction processes do not generate harmful residues. Sustainable ingredient sourcing has become an important area of research, and more and more companies are shifting to agricultural and microbial sources for their raw materials (5–10). Most of the beauty and personal care products are emulsions, and cold emulsification is a good alternative to the conventional emulsification processes. This eliminates the separate heating and cooling phases, thus reducing energy requirements during the production phase of the product life cycle. This process also makes it easier to control the emulsion, resulting in reduced production time (11). With regard to the final phase, companies are using recycled paper to make cardboard for packaging. Some are turning to biopolymers as sustainable alternatives for packaging (12). Another approach taken by companies involves long-lasting, reusable packaging which can be refilled (13). Although it is important to incorporate sustainability in every aspect of an industry, ingredient sourcing has a significant role in ensuring sustainability within the cosmetic industry.

The key ingredients used in the beauty and personal care products include surfactants, polymers, and emulsifiers, among others. The demand for green products and the dwindling resources has forced the cosmetic industry to explore various alternatives for conventionally derived cosmetic ingredients. Among these, biopolymers and biosurfactants have gained a lot of traction as viable alternatives to the chemically synthesized polymers and surfactants because of their biocompatibility and biodegradability (14–17). Biosurfactants have numerous advantages in terms of low toxicity and their effectiveness over wide pH and temperature ranges (18). The notable film-forming properties of biopolymers such as chitosan and carboxymethyl cellulose and the potential to be used as effective thickeners (19) make them suitable for applications in diverse industries such as beauty and personal care, food, packaging (20), and textile (21).

This article presents a review on sustainability in formulation design specific to the cosmetic industry as well as the effect of the green alternatives on the rheological properties and performance parameters of the formulations.

SUSTAINABLE SOURCING OF RAW MATERIALS

The first and foremost environmental responsibility of cosmetic corporations is raw material sourcing and its degree of sustainability. These responsibilities can be fulfilled by switching to bioalternatives for surfactants and polymers and also by the utilization of by-products from industrial wastes. A good way to do this is to use biosurfactants instead of synthetic surfactants for cosmetic applications. To extend the value of sustainability, biosurfactants can be obtained, for example, from fat- or carbohydrate-rich effluents produced by food or agricultural industries (5). There have been several studies where olive oil mill effluents, waste frying oils, animal fats, molasses, *etc.* are proven to be useful substrates for the production of glycolipid-producing microorganisms (6,7,22–24). There also exist similar studies in the case of biopolymer sourcing (8–10). Apart from being responsibly sourced, bio alternatives are also lower in toxicity and are biodegradable in nature (25–30). Because polymers and surfactants comprise a major portion of cosmetic and personal care formulations and often accumulate in the environment over time, it is important to study the aspect of their biodegradability.

The following sections expand further on the aforementioned concept of sustainable raw material sourcing and biodegradability.

BIOSURFACTANTS

Surfactants are an integral part of cosmetic and personal care applications. So far, the industry has primarily incorporated synthetic surfactants to serve the purposes of cleaning, wetting, dispersing, emulsifying, foaming, *etc*. This extensive use of synthetic surfactants, however, does not come without negative environmental consequences. A high concentration of synthetic surfactants has adverse effects on aquatic flora and fauna, leads to toxic accumulation in the human body, and depletes water quality when discharged (31,32). Biosurfactants have been subjected to toxicity tests against synthetic surfactants. One such study conducted by Kanga et al. (25) observed the solubilization of naphthalene from crude oil using glycolipids produced by the *Rhodococcus* species. This was compared with the synthetic surfactant Tween-80 or polyoxyethylene sorbitan monooleate. The study of toxicity per mass revealed that the glycolipid was 50% less toxic than the Tween-80 surfactant. The biosurfactant also exhibited a higher EC_{50} (effective concentrations at which 50% of the test organisms die) value which means that it poses a low toxicity to aquatic life.

Another such study conducted by Kumano et al. (26) observed the toxicity and surface activity of sophorolipids (SL) from *Starmerella bombicola*. Marine life was exposed to different concentrations of SL, and its growth was observed. Even with 72 h of exposure to the highest concentration of SL, the growth inhibition remained less than 50%. This EC_{50} is higher than those reported on the growth inhibition of microalga by chemical surfactants (27). The EC_{50} of SL was significantly higher than that of sodium dodecyl sulfate and linear alkylbenzene sulfonate, which proved SL to be of low toxicity. This highlights the necessity of transitioning to biological surfactants. A challenge faced here is the tedious and expensive process of obtaining these biosurfactants for complete commercial and large-scale utilization. The key to combating this issue is to promote biosynthetic methods of propagation while minimizing waste and maximizing yield. This would involve the microbial action of various types of yeasts, bacteria, and fungi (30). Even though the degree of toxicity of biosurfactants is without question far lower than that of synthetic surfactants, Munstermann et al. (33) found that the toxicity levels of biosurfactants can also vary depending on the source, strain, and synthesis.

However, synthetic surfactants are grouped according to their charge affinity and biosurfactants, and, on the other hand, can be classified according to raw material of sourcing, chemical constitution, and molecular weight. They are most often categorized according to their raw material of sourcing as follows—glycolipids, lipopeptides, fatty acids, phospholipids, neutral acids, and polymeric biosurfactants (34,35). Glycolipids and lipopeptides are low molecular weight biosurfactants. Higher molecular weight structures can be more easily classified as bioemulsifiers rather than as biosurfactants, and examples of these are polymeric saccharides, lipoproteins, *etc* (36,37).

GLYCOLIPIDS

Glycolipids, a well-studied classification of biosurfactants, are lipid molecules linked covalently to carbohydrate molecules. Glycolipids are further classified as rhamnolipids (RLs), SLs, and trehalose lipids based on their individual head group polarities (38).

RLs, which are synthesized by the genus *Pseudomonas* (particularly the strain, *Pseudomonas aeruginosa*), contain a mono/di rhamnose head group(s) linked by β-glycosidic bonds to a fatty acid tail group with a hydroxy functional group present in the third position (39).

The chemical bases of RL production are deoxythymidine diphosphate-*L*-rhamnose sugar—derived from *D*-glucose and 3-(3-hydroxy alkanoyl oxy) alkanoic acid—or HAA—derived by the fatty acid amalgamation of two-carbon units. The derivation of HAA is catalyzed by one of the key RL enzymes called RhlA; this is not found in the bacteria itself and makes up the hydrophobic end of RLs. There also exist other two enzymes which are key in the production, namely, RhlB and RhlC responsible for producing mono and di RLs, respectively (40).

Monorhamnolipid or Rha-C_{10}-C_{10} and di-rhamnolipid or Rha-Rha-C_{10}-C_{10} in chemical nomenclature are known as l-rhamnosyl-3-hydroxydecanoyl-3-hydroxydecanoate and l-rhamnosyl-l-rhamnosyl-3-hydroxydecanoyl-3-hydroxydecanoate, respectively (Figure 2) (41). The previously mentioned RhlA and RhlB are controlled by bacterial quorum sensing (QS). This is a method of signal transmittance by bacteria where the microbial cells produce an auto-inducer which is bonded to an environmental sensor that propagates the production of the functional QS system and begins a regulatory chain effect (42). The majority of the RL molecules are produced 20–36 h post-initiation or during the stationary phase where the rate of generation of new cells is equal to the rate of dissipation of the old cells. This is a yield-controlling factor that can be taken into consideration (43). The source of carbon for RL production can be obtained from more sustainable substrates such as xylose (food industry by-product) and glycerol (biodiesel) (44).

The second classification of glycolipids known as SLs is primarily biosynthesized from nonpathogenic yeast strains such as *Candida apicola* and *Starmerella bombicola* (45). SL consists of a sophorose- or glucose-derived disaccharide head and a fatty acid tail which can either be lactonic or acidic owing to the presence or absence of the ester linkage between the fatty acid tail and sophorose head, respectively (Figure 2) (46).

SLs can be biosynthesized from various glucose and fatty acid sources. The hydrophilic sugar sources undergo reduction, followed by glycosylation. The resultant compound acts as a catalyst for microbial growth. A part of glucose also reacts to become a glucose ester of

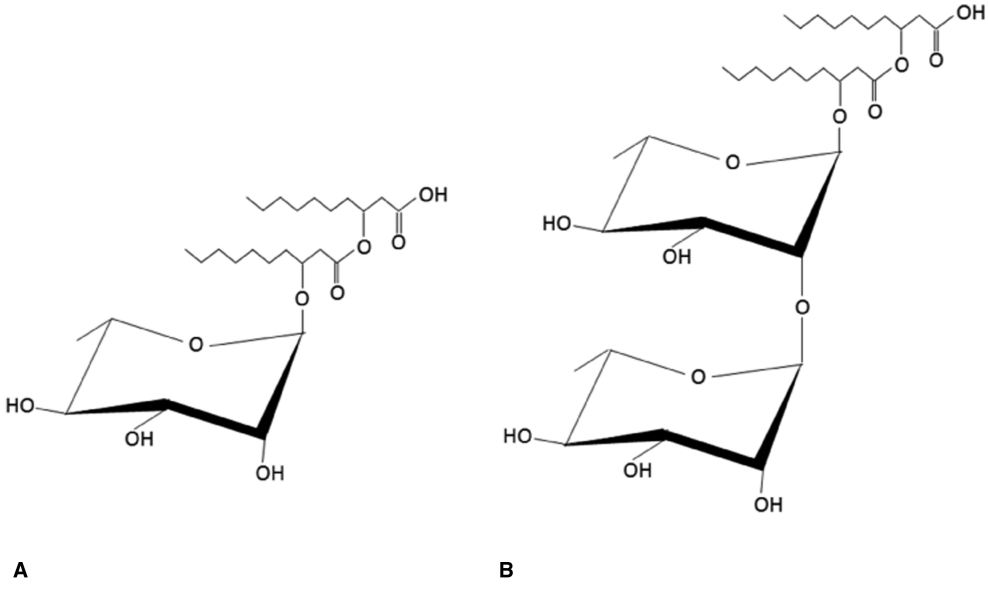

Figure 2. RL chemical structures. (A) Monorhamnolipid and (B) dirhamnolipid.

pyrophosphoric acid along with a nucleoside uridine and forms the predominant structure of SLs. The 16–18 carbon atom fatty acid is introduced into the microbial host through an aldehyde dehydrogenase enzyme, and consequently nonacetylated acidic SL is formed (47). Chemical alterations of this can produce acetylated SL and further be catalyzed to lactonic forms by lactone esterase (48). The sources of the sugars and fatty acids can be obtained from several renewable raw materials or as industrial by-products. Different combinations of the sugar and fatty acid sources vary the SL yield. For example, glucose with canola oil yielded a greater amount of SL (80%) than lactose with canola oil (only 45%). Several studies showed that glucose was the optimal sugar for highest SL conversion (49). Other industry by-products can also add to the long list of sugar alternatives such as sugarcane molasses medium. Renewable fatty acids such as plant and animal esters can be used for good SL production. One interesting proposition being studied is the production of SL using the waste oil of food industries; however, the methods have to undergo several modifications before being fully used, such as fed-batch culture and SSR or solid-state fermentation (50).

Finally, the third classification of glycolipids known as trehalose lipids or trehalolipids (TLs) meant for biosurfactant production is most commonly obtained from the species *Mycobacterium*, *Nocardia*, *Corynebacterium*, *Rhodococcus erythropolis*, and *Arthrobacter*. TL comprises a trehalose head group bound to an esterified fatty acid tail where the trehalose head group is two α glucose units linked by 1,1-glycosidic bonds (Figure 4) (51). The long-chain fatty acid tails are known as mycolic acids which have hydroxy functional groups in the α and β positions (52).

Similar to all amphiphilic biosurfactant biosynthesis, the mycolic tail is produced as a result of the hydrocarbon metabolic pathways, whereas the carbohydrate metabolic pathways lead to the formation of the trehalose head. The induction mechanism to synthesize TL involves the introduction of hydrocarbons to the bacterial propagation medium. In the past years, trehalose lipids have been found to be important for bioremedial applications, for example, solubilization and biodegradation of nonpolar molecules (53).

LIPOPEPTIDES

Cyclic lipopeptides, in particular surfactins, produced by the species *Bacillus subtilis*, are known for their powerful surfactancy (54). Surfactins are peptides bonded with a 14-carbon fatty acid chain, where the peptide comprises seven amino acids—GluOMe-Leu-Leu-Asp-Val-Leu-Leu (Figure 5). Similar to glycolipids, surfactin or subtilisin strains can also be produced by being grown on polyol compounds obtained from biodiesel manufacturing units. The initial strain

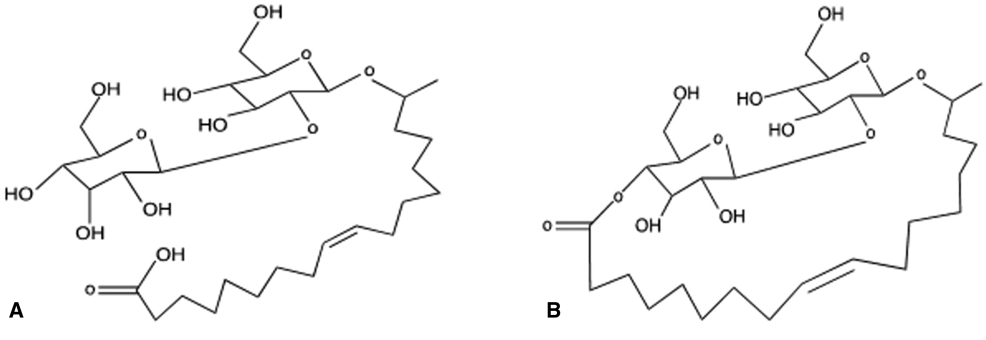

Figure 3. SL chemical structures. (A) Acidic form and (B) lactonic form.

obtained undergoes a comparative bacterial taxonomy and identification method known as 16S ribosomal deoxyribonucleic acid sequence analysis and fatty acid methyl ester profile analysis to determine the fatty acid methyl ester groups. The bacterium is then added to the glycerol medium. The surfactin produced is extracted from the foam produced in the fermentation process and purified before undergoing infrared analysis and nuclear magnetic resonance tests. The highest yield of the surfactin is obtained between 24 and 48 h into the fermentation process. This study concluded that renewable carbon sources could be used for surfactin production (55).

Another study showed that only molasses, glucose, and malt extracts were enough as a carbon source for surfactin production, which are also industrial by-products (56). Some studies added that the yield is dependent on the bioreactor's design, nitrogen origin, and, most importantly, the presence of inorganic salts or minerals (57).

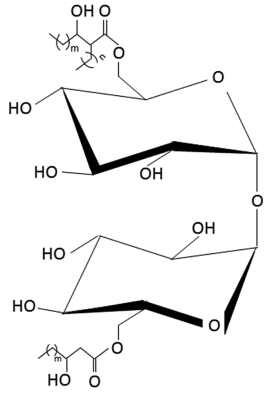

Figure 4. Trehalose lipid chemical structure.

FATTY ACIDS, PHOSPHOLIPIDS, AND NEUTRAL LIPIDS

Fatty acids, phospholipids, and neutral lipids that are microbially synthesized from hydrocarbons like alkanes classify as biosurfactants. The production of these biosurfactants occurs due to the growth of bacteria or fungi on these hydrocarbon surfaces which act as the carbon source. The bacteria can be of the *Acinetobacter* species and fungi of the *Aspergillus* species. These species also give rise to complex acids made of hydroxyl groups and alkyl branches like corino mycolic acids (58). According to the Chemical Entities of Biological Interest database, the complex is a 32-membered mycolic acid and a 3-hydroxy fatty acid. *Acinetobacter* species, when grown on hexadecane, produce phospholipids. Phospholipids have also been generated with the help of *Thiobacillus thiooxidans*. In yeast, neutral lipids are synthesized by the act of sequestration from intracellular fluid. These lipids have no charged molecules and are mostly simple lipids formed by fatty acids or triglycerides and a steryl ester (59).

POLYMERIC

Some common examples of this classification are emulsan, liposan, lipomannan, mannoprotein, and polysaccharide–protein complexes.

Emulsan is composed of *N*-acetyl-*D*-galactosamine, *N*-acetylgalactosamine uronic acid, and an amino sugar (Figure 6). It is linked *via* covalent molecular bonding to α and β hydroxydodecanoic chains through ester bonds (60). Emulsan is produced by the strain *Acinetobacter*

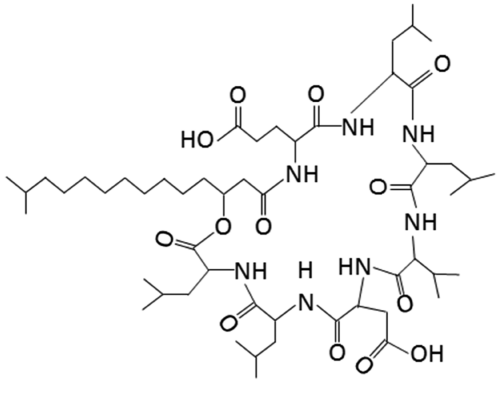

Figure 5. Chemical structure of surfactin.

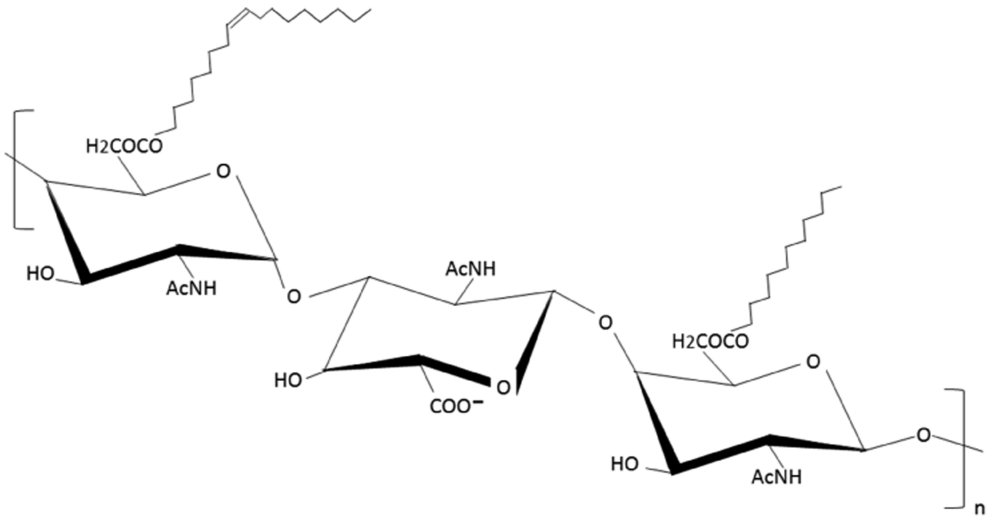

Figure 6. Chemical structure of emulsan.

calcoaceticus recombination-activating gene 1. They are produced with the aid of hydrocarbon 14 or ethanol 18 substrates (61). Emulsan culture production can be enhanced with varying ethanol or phosphate concentrations. Phosphate aids in the generation of emulsan by effects on cell metabolism. The hydrocarbon such as ethanol acts as the energy pool. The culture used is primarily batch fermentation followed by fed-batch fermentation so as to vary the carbon and phosphate feeding from controlled to continuous. An appropriate kinetic model has to be modeled around the emulsan culture process (62).

Liposan is obtained from *Candida lipolytica*. It comprises 83% carbohydrate and 17% protein (63). The carbohydrate is a heteroglycan that consists of glucose, galactose, galactosamine, and galacturonic acid, whereas the protein is most likely a glycoprotein (64). One study cultivated the yeast in soybean oil refinery residues and glutamic acid. The maximum yeast excreted the biosurfactant into the substrate, which is a hydrocarbon largely during the stationary fermentation phase (65). The *Candida* species can also be synthesized in selected food-grade waste such as canola oil and glucose substrate (66,67). Similar production of biosurfactant can be achieved through the culture of *Yarrowia lipolytica* in the presence of crude oils and hydrocarbon lipid substrates (68).

Mannoproteins are derived from the yeast *Saccharomyces cerevisiae*. It is the most common fermentation microorganism that can be obtained from fruit fermentation processes in the industry. Mannoproteins are glycoproteins that contain 15–90% mannose (69). However, according to Cameron et al. (70), there exists a second class of mannoproteins with 50–70% mannose and 30–50% protein. The National Center for Biotechnology Information states that the compound mannose is a sugar of the aldohexose carbohydrate. Mannoproteins are commonly extracted for the role of bioemulsifiers. These emulsifiers can be extracted *via* two methods, namely, autoclaving in a neutral buffer and the treatment of bakers' yeast with Zymolyase enzyme. The final filtered emulsifier obtained from the first method contains approximately 44% carbohydrate and 17% protein (70).

Lipomannan is a glycolipid that makes up the cell wall of *Mycobacterium* that contains a long mannose polymer. It carries an α-linked sugar mannose polysaccharide which

involves the addition of mannopyranosyl residues to phosphatidylinositol (71). Alasan is an anionic alanine comprising bioemulsifier obtained from *Acinetobacter radioresistens*, a species of bacteria which has a resistance toward radiation (72). Alasan is a complex of the α-amino acid alanine, polysaccharides, and proteins (73).

BIODEGRADABILITY

Biosurfactants have been long used to treat contaminated media such as water and soil. The amphiphilic nature of biosurfactants enables hydrophobic compatibility, where pollutant substrates such as hydrocarbons easily associate into the microbial cells. The mechanism of biodegradation was studied by Urum and Pekdemir (74), where it was discussed that biosurfactants followed different biodegradation mechanisms depending on their molecular masses. Biosurfactants containing lower molecular mass act in two ways, namely, (i) mobilization and (ii) solubilization (75). Mobilization takes place when the biosurfactant's concentration is lower than the critical micelle concentration (CMC). In this mechanism, biosurfactants act on the interface between the hydrophobic pollutant and surface by reducing interfacial tension which allows for easier removal of the pollutant. Solubilization occurs for concentrations that are greater than the critical micellar concentration. This mechanism involves the formation of thermodynamically stable micellar structures which encompass the hydrophobic pollutants. Biosurfactants of higher molecular masses carry out biodegradation by emulsification of pollutants (76).

Cameotra and Singh (77) outlined the uptake of hexadecane by RLs. RLs increased the surface area of the pollutant by breaking it down into smaller particles of 0.22 μm. The microbe engulfed the droplets and slowly began to render the hydrocarbon into its cellular phase by breaking it down metabolically. In addition to RLs, trehalose lipids have been important for soil bioremediation, and it has been proposed that they could also be useful in the treatment of wastewater through micelle formation (78). SLs have been used to degrade open and closed chain hydrocarbons in controlled conditions; this was tested in particular for soil bioremediation. It exhibited superior biodegradation capabilities for pollutants such as n-hexadecane, 2-methylnaphthalene, diesel, gasoline, and kerosene (79). There have been several studies of the effect of biosurfactants on *n*-alkanes such as octadecanes, polyaromatic hydrocarbons, oils, and hydrocarbon residues; however, studies on complex hydrocarbon mixtures are scarce. To study the effect on unresolved complex mixtures, Nievas et al. (75) collected marine ship waste known as oily bilge waste, which is a mixture of seawater and hydrocarbon residues, and studied the effect of a symbiotic microbial system on its degradation by emulsification. The positive effect of reduction on the complex mixture was around 58%.

Apart from their key roles in biodegradation of pollutants, biosurfactants are themselves easily biodegradable. Mohan et al. (80) investigated the biodegradability of RLs under aerobic, anaerobic, and nitrate- and sulfate-reducing conditions. The study revealed that RL was biodegradable against all four conditions with a soluble chemical oxygen demand efficiency percentage of 74 under aerobic conditions, 47.2 under anaerobic conditions, 34.2 under sulfate-reducing conditions, and 24.6 under nitrate-reducing conditions. Biosurfactants are also low in toxicity when compared with synthetic surfactants. Within biosurfactant classifications, environmental toxicity can vary with the type of strain that they are sourced from, for example, glycolipids synthesized from *Rhodococcus* ruber exhibits a

toxicity 10 times lower than that of TL (synthesized from *R. erythropolis*) and 13 times lower when compared with RLs (synthesized from *Pseudomonas aeruginosa*) (79).

The aforementioned evidence concludes that biosurfactants display several environmentally positive functionalities. There is a strong need for process optimization and feasible production of biosurfactants to commercially adapt them.

BIOPOLYMERS

Polymers find widespread use in beauty and personal care products, and a majority of these polymers are synthetic and nonbiodegradable. As a result of its widespread use across the industry, an alarming amount of polymer waste is being generated (81). In response to this increased awareness regarding the toxic effects of certain polymers, various biopolymers such as chitosan, alginate, and xanthan gum, and several other polysaccharides have been extensively explored as potential alternatives to the traditionally derived polymers (82–85).

Biopolymers are polymeric biomolecules derived from plants and microorganisms (86). They can be produced or sourced in different ways. Most biopolymers are found in abundance in nature and are extracted from plants, algae, or other microorganisms. Examples of such biopolymers include alginate and chitosan. Other methods of production are *in vitro* synthesis of biopolymers with isolated enzymes and through fermentation (87). Polysaccharides, also known as carbohydrates, are agro-based polymers. Some of the most common polysaccharides include cellulose, chitin, alginate, xanthan gum, and pectin.

CHITIN AND CHITOSAN

Chitin or poly(β-(1→4)-*N*-acetyl-*D*-glucosamine) is one of the most abundant polysaccharides present in nature second to only cellulose. Chitin is primarily extracted from the outer shells of crustaceans such as shrimps, crabs, and squids or the cell wall of fungi and yeast (88). However, at present, chitin is primarily sourced from the outer shells of crabs and shrimps. Thus, this biopolymer is essentially produced by recycling or processing biowastes from marine food industries (89). Chitosan is one of the most significant derivatives of chitin obtained by the deacetylation of chitin. On deacetylation, the acetyl groups of chitin are substituted by primary amino groups, resulting in the formation of chitosan (Figure 7) (90). Although chitin is found in abundance in nature, the main natural source of chitosan is limited to certain fungi such as Mucoraceae (91).

Pazo et al. (92) reported that crustaceans make up nearly 7% of the marine waste in oceans. Thus, discarded marine biomass has great potential for the production of chitin and chitosan. The waste shells consist of chitin along with various proteins and inorganic salts. As a result, the extraction of chitin from marine waste includes two steps—mainly deproteinization and demineralization. These processes may be achieved by many methods. The most common and conventional method involves chemical treatment. However, this route requires strong alkali and acids at extreme temperatures in addition to high energy consumption and effluent production (93–96). Furthermore, the extraction of chitin by chemical means only results in a 10% recovery of the raw material (97). This has led to a desire for the optimization of chitin production and the efficient use of shell waste by

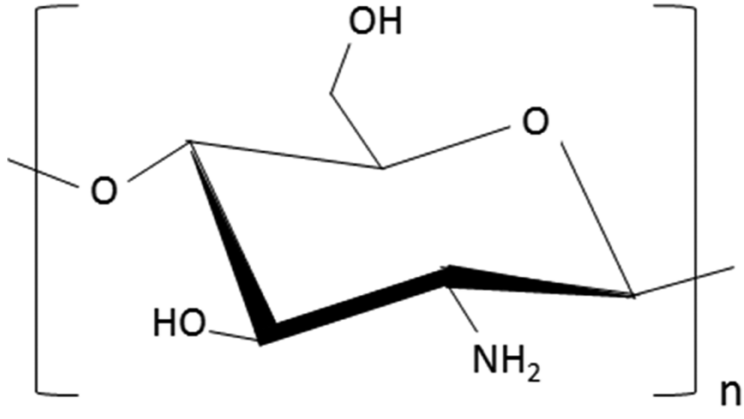

Figure 7. Chemical structure of chitosan.

exploring sustainable extraction processes involving microbial or enzymatic treatment (8,98–103). The substitution of strong alkaline treatments by enzymatic treatment resulted in reduced energy and water consumption, whereas microbial treatment for the deproteinization step recorded enhanced chitin recovery (99). Khanafari et al. (8) compared and characterized the chitin obtained by chemical and biological extraction methods from shrimp shells. Their studies revealed that microbial extraction resulted in enhanced preservation of chitin structure compared with the chemical method.

ALGINATE

Alginates are another group of natural linear polysaccharides that have garnered a lot of scientific interest in recent years because of their application in the cosmetic, food, textile, and pharmaceutical industries as a stabilizer, thickener, or film-forming agent. They mainly consist of varying ratios of β-*D*-mannuronate (M) and α-*L*-guluronate (G) (Figure 8) which are linked through 1-4 glycosidic bonds. The amount of M and G units depends on the biopolymer source (9). Currently, commercial alginate is sourced from marine brown algae (seaweed). This biopolymer is naturally present in the cell wall of these marine macroalgae. In particular, alginate is primarily sourced from a group of seaweed called kelp (103,104).

Alginate salts found in the algal cell walls are transformed to insoluble alginic acid by acidification. Sodium alginate is then extracted by treating with sodium hydroxide solution.

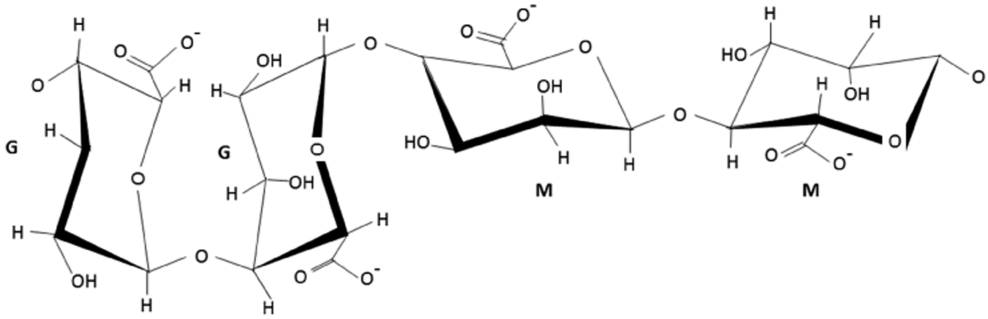

Figure 8. Chemical structure of alginate.

Seaweed residue is separated from this solution by filtration, and finally, sodium alginate is precipitated by the acidification of sodium alginate solution using dilute hydrochloric acid (105). The filtration step of alginate extraction requires large quantities of water, making the need for a more sustainable process or source for alginate production a necessity (104). In addition, as the demand for alginate increases, the macroalgal community, which is the main resource for alginate, is fast declining. This in turn has a negative impact on marine biodiversity in addition to other ecological and economic consequences (9,103). This growing concern over the harmful effects of excessive seaweed harvesting has paved the way for research on certain bacterial species such as *Azotobacter* and *Pseudomonas* as alternative sources for alginate production. The mutant strain of *Azotobacter vinelandii* has been extensively explored as it has the ability to produce greater quantities of the biopolymer (84,106,107). Furthermore, the excellent mechanical stability and wider pore size distribution of alginate produced by bacterial fermentation have made bacterial sources all the more favorable. Bacterial alginate also showcased better rheological properties, making it ideal for the cosmetic industry (84,106,107).

PECTIN

Pectin is a polysaccharide found in abundance in the cell wall and middle lamellae of many plants. It is a complex molecule and has *D*-galacturonic acid as its main monomeric unit linked by α-1→4 glucuronosyl links (Figure 9). These linkages may be interspersed with *L*-rhamnose units (108,109). This biopolymer has found itself a market within the beauty industry as a texturizer. A major portion of commercial pectin is derived from citrus peels and apple pomace (110).

The processes involved in extracting pectin from plant material can be broadly classified into raw material pretreatment, extraction, and post-extraction. The extraction stage involves an acid hydrolytic process at high temperatures which generates large amounts of acid wastewater. This process also consumes a lot of energy as it requires heating for extended time periods, further resulting in long extraction times (10,111). Researchers have been studying various alternative approaches for extracting pectin that would help provide better yield with low solvent and energy consumption. One popular method is the enzyme-assisted extraction where certain enzymes such as cellulases and proteases, which can degrade the various constituents of the cell wall, catalyze the reactions, thus reducing the amount of solvent required while

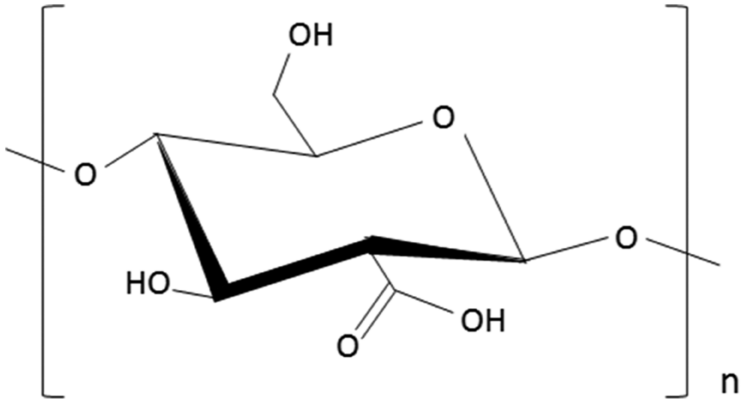

Figure 9. Chemical structure of pectin.

increasing the extraction yield (112). Other extraction approaches that are being explored include subcritical water extraction and ultrasound-assisted extraction, both of which optimize the process of pectin isolation from plant material (111,113,114).

XANTHAN GUM

Xanthan gum is a branched polysaccharide where the repeating units are composed of pentasaccharide units that include two glucose units, two mannose units, and one glucuronic acid unit (Figure 10). It is primarily produced by the bacterial fermentation of a plant pathogenic bacterium *Xanthomonas campestris* (115). Polysaccharides such as xanthan which are obtained from bacterial sources are promising alternatives to plant-based polysaccharides.

Commercial xanthan is obtained by batch fermentation and thermal treatment followed by recovery of the product using alcohol. The efficiency of the production process and the quality of the final product are heavily dependent on various process conditions like the microorganism used as well as the nutrients such as carbon and nitrogen supplied for culture growth. Because the production solely depends on glucose or saccharose as the main carbon source, it is quite expensive (116). There are many studies that explore alternative sources of carbon that can help in reducing the production costs of this biopolymer (117–119). Several food- and agro-based industries generate large amounts of agricultural waste. If not discarded properly, they can harm the soil and water bodies. Numerous studies have suggested the potential use of these wastes as a carbon and nitrogen source for various biotech processes. Woiciechowski et al. (117) showed that residues like cassava bagasse can be hydrolyzed and used as a carbon source for xanthan production with high yields.

CARBOXYMETHYL CELLULOSE

Carboxymethyl cellulose is a natural polymer derived from cellulose. Plant cell walls are the primary source of cellulose. It is made up of monomeric units of anhydroglucose

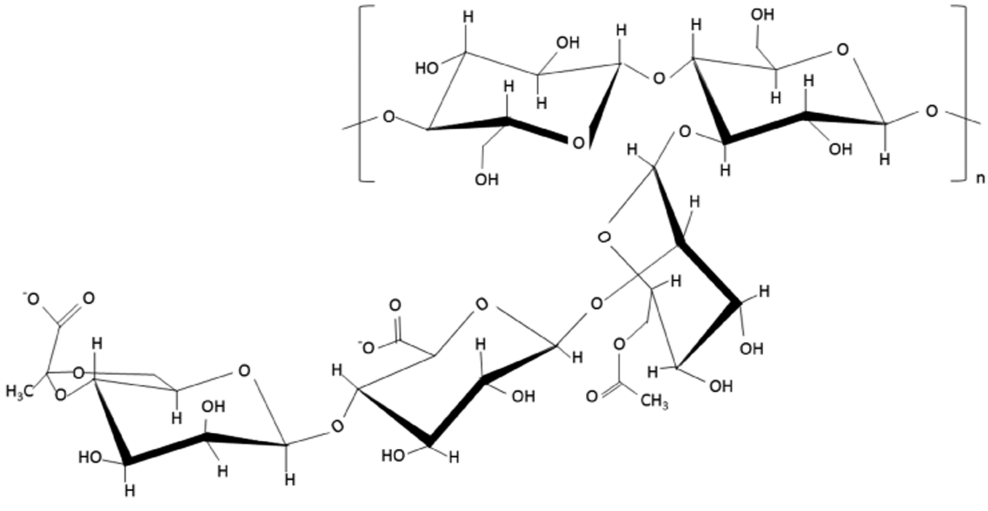

Figure 10. Chemical structure of xanthan gum.

where the glucose units are bound through β-1,4-glycosidic bonds (Figure 11). The varied chemical properties of this polysaccharide are attributed to the three reactive hydroxyl groups present in cellulose (120, 121). When cellulose is treated with an alkali and the hydroxyl groups are made to react with carboxymethyl in the presence of an organic solvent like sodium monochloroacetate, an ether is formed. This etherification reaction leads to the formation of carboxymethyl cellulose (120).

Cellulose is primarily extracted from agricultural or domestic wastes. A significant amount of waste is generated from agricultural industries and practices across the world (120–122). These residues are usually burnt, resulting in adverse environmental and other health issues (121). Huang et al. (121) explored the possibility of effective utilization of these agricultural by-products to produce cellulose and finally carboymethyl cellulose. They synthesized and characterized carboymethyl cellulose from various agro-wastes such as sugarcane bagasse and spent tea leaves obtained from different agro-based industries. They found that the physicochemical properties of carboymethyl cellulose produced from these residues were comparable to those of commercial carboymethyl cellulose.

BIODEGRADABILITY

A large number of "rinse off" cosmetic and personal care products such as shampoos, conditioners, soap, and toothpaste make use of polymers as film formers, viscosity modifiers, and stabilizers. These polymers are sometimes present in the form of microplastics. Microplastics are synthetic, nondegradable polymers with a size less than 5 mm (123). These polymers along with several other synthetic ingredients often end up in wastewater streams. Extensive studies have shown that wastewater treatment plants do not successfully remove these synthetic ingredients, and instead, a portion of the microplastics is emitted to water bodies (124,125). Oftentimes, sludge from treatment plants are used as fertilizers for crops. Microplastics also tend to accumulate in the sludge during the treatment process and thus start building up in the environment as well as at higher levels of the food chain (125).

Whereas biopolymers are completely biodegradable, the rate of degradation can range from a few hours to years according to the functional group present. Biopolymers usually

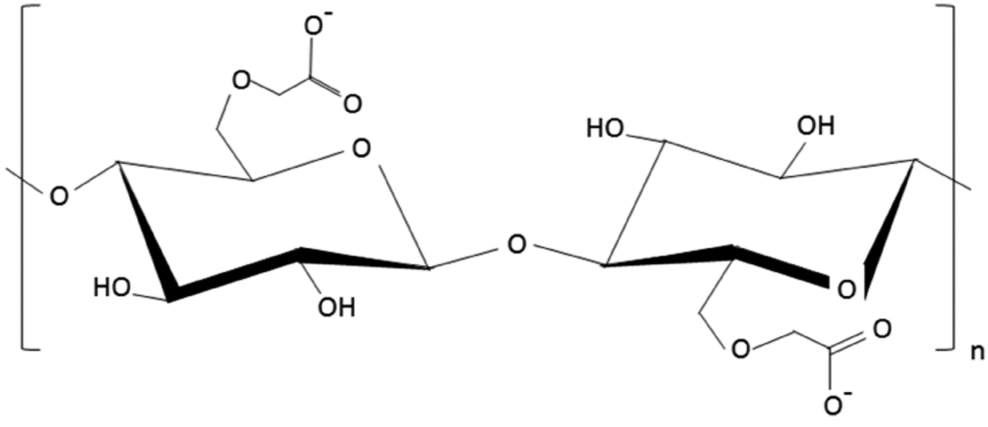

Figure 11. Chemical structure of carboxymethyl cellulose.

undergo enzymatic or microbial degradation (28). Biodegradability studies on chitosan show that this biopolymer degrades by enzymatic degradation into nontoxic oligosaccharides. The rate of degradation depends on the molecular weight as well as the degree of deacetylation of chitosan. This biopolymer is also biocompatible to some extent within the human body, making it suitable for application in cosmoceuticals as well (29). Xanthan gum, although completely biodegradable, is an extremely stable biopolymer, and only a few strains of xanthan degrading enzymes have been reported in microbes. As a result, it finds widespread use in areas that involve high enzymatic activity as a stabilizer or thickener (30).

Biopolymers have been shown to increase the susceptibility of nondegradable polymers to biodegradation by photo oxidation. Albertsson et al. (126) demonstrated that granular starch could improve the degradation rate of polyethylene by 10 times when compared with pure polyethylene.

FORMULATION CONSIDERATIONS

Cosmetic formulations should be able to satisfy not just the functional benefits but the aesthetic benefits required by the consumers as well. They need to achieve their main purpose which can be anything from forming a protective barrier on hair or skin to delivering certain active ingredients. However, the product also needs to appeal to the consumer on application. It should have an ideal consistency (rheology). The cosmetic industry makes use of emulsions, especially oil-in-water emulsions, to formulate products with desirable sensory properties (127). Furthermore, the droplets in the emulsion work as a delivery agent for various antimicrobials, moisturizing agents, or fragrance which are usually entrapped within the emulsion droplets (128,129).

Cosmetic products with a long shelf life and good physicochemical and functional properties require the oil-in-water emulsions to be stable. Because of their inherent thermodynamic instability, they require additional emulsifiers and stabilizers (130). Thus, while formulating cosmetic products, it is vital to take into account the stability and rheology of the final product.

FILM FORMATION

For a wide range of cosmetic and personal care products such as mascara, lipstick, and hair fixatives, the ability to form a continuous and flexible film on the required substrate forms an important criterion for adequate performance and functioning of the product. Polymers constitute the main group of film formers in the cosmetic industry. On the application of the polymer solution onto the substrate, the solvent begins to evaporate. As the solvent evaporates, the polymer chains slowly start to entangle and interpenetrate to form a film over the substrate (131). Because of the environmental and health hazards of the synthetic polymers used in cosmetic formulations, there have been many studies on the potential application of biopolymers as film-forming agents in cosmetic products (132–136).

Although biopolymers have excellent film-forming properties, the mechanical properties of these films are inferior to that of the synthetic, petroleum derived polymer films (134). Thus, to completely substitute the conventional polymeric film-forming agents used in the cosmetic industry, it is necessary to modify the properties of the bio-based film formers. Blending various biopolymers is a good way of creating new materials with improved

film properties based on the molecular interactions between the biopolymers (133). Several researchers have tried to characterize and determine the properties of the films formed by biopolymers such as chitosan, xanthan gum, alginate, and carboxymethyl cellulose for use in the cosmetic industry (132–134). The film-forming properties of chitosan have been an important area of research (133–137). Chitosan films were found to lack resistance to water transmission and have poor structural integrity (135). However, Miranda et al. (137) demonstrated that the incorporation of lipids and plasticizers enhanced the hydrophobic character and mechanical strength of the film. Sionkowska et al. (136) reported that it was possible to engineer the mechanical parameters of the biopolymer films by blending two or more polymers. The addition of up to 1 wt% of hyaluronic acid to a mixture of chitosan and collagen led to increased mechanical resistance of the film. Furthermore, the application of this three-component polymer blend on hair tresses showed an improvement in the mechanical properties of hair by forming a film on the hair fibers. Thus, this system shows great potential for use in hair care formulations.

The addition of xanthan gum can improve the mechanical parameters like the tensile strength of starch-based films. These enhanced film properties emerge as a result of the development of hydrogen bonds between the starch and gum polymer chains. Xanthan gum easily dissolves in cold or hot water without significant effect on its viscosity because of temperature or pH, which is ideal for film formation (132). Another study reported that the addition of 5 wt% cellulose nanocrystals increased the elastic modulus and tensile strength of a mixture of carboxymethyl cellulose and starch by 94.77% and 65.86%, respectively, due to strong interfacial interactions resulting from the formation of hydrogen bonds between the three components (133).

It is clear that although biopolymers have great potential as film formers in the cosmetic and personal care industry, further research needs to be conducted to optimize the mechanical properties of these substances.

STABILITY

Currently, the emulsifiers used to stabilize oil-in-water systems include petroleum-derived surfactants or animal-based polysaccharides (138). Manufacturers are however shifting to biosurfactants and plant-derived or microbial biopolymers to decrease the harsh ecological impact of chemically synthesized ingredients.

Biopolymers such as xanthan gum and carboxymethyl cellulose have found widespread uses as emulsion stabilizers in the beauty and personal care industry (83). Most biopolymers act as emulsion stabilizers, and they are not good emulsifiers as this requires them to be surface active. They are typically used in conjunction with biosurfactants to impart stability to systems on a long-term basis (139). They increase emulsion stability by means of electrostatic interactions or steric hindrance. The biopolymer molecules adsorb onto the droplets and steric stabilizes the emulsion by forming a layer around the droplets (139). However, certain biopolymers like chitosan are hydrophobically modified to make them good emulsifiers. Desbrieres and Babak (140) showed that the attachment of hydrophobic moieties like alkyl chains to the polymer backbone makes it amphiphilic, thus enhancing its interfacial properties. Another widely used biopolymer in emulsions is xanthan gum. It stabilizes oil-in-water systems through rheology modification. Xanthan gum improves the viscosity of the aqueous phases, thus stopping or decreasing the rate of creaming of the droplets (141).

Biosurfactants are made of a head which is a hydrophile and a tail which is a hydrophobe. The degree of each of these determines the hydrophilic–lipophilic balance which contributes to the biosurfactant's properties.

The physicochemical attributes of biosurfactants can be modified based on application. These properties include surface tension, surface rheology, and interfacial tension. Another important aspect would be to identify the critical micellar concentration values of biosurfactants which helps to study the biosurfactant efficiency in terms of foaming and cleansing.

Biosurfactants arrange themselves into thermodynamically favorable formations at the surfaces or interfaces of liquids. At CMC, they begin to make up structures known as micelles, bilayers, and vesicles. Thermodynamic arrangements of biosurfactant molecules decrease surface and interfacial tension of liquids that are not miscible, and allow for enhanced solubility. Lowering of surface tension also improves foaming and cleaning capabilities (142,143).

It is necessary to recognize that low molecular weight biosurfactants are still classified as biosurfactants because of their surface activity; however, higher molecular weight structures will fall into the category of bioemulsifiers and not biosurfactants. These are surface inactive agents which aid in emulsification (36,37).

The biosurfactant effects on surface activity have been showcased in various studies. For instance, in the glycolipids groups, RLs can reduce the surface tension of water from 70 mN/m to a lower limit value of 25 mN/m and the interfacial tension of the water/n-hexadecane system to less than 1 mN/m. The CMC of RLs ranges from 10 to 30 mg/L, which ensures easier foaming than synthetic surfactants with higher CMC values. Zhu et al. (144) found that in the binary system of RL/cocamidopropyl betaine and ternary system of RL/CAPB/SL, where CAPB is a common zwitterionic synthetic surfactant, RLs dominated at both interfaces. In case of SLs, both acidic and lactonic variants of the biosurfactant can decrease the surface tension of water in a similar fashion—from 72 mN/m to 30 mN/m and the interfacial tension of water/n-hexadecane and water/vegetable oil systems to 1–5 mN/m (145). The low CMC and molecular weight of SL increase the solubility of the oil by micelle formation (146). The surface activity properties were found to be functions of the hydrophobic chain length. If the alkyl ester chain length of the SL increased by the addition of one carbon unit, the CMC decreased by half (147). Similarly, trehalose lipids lower the surface tension to a range between 25 and 40 mN/m, and interfacial tension of the same oil/water system to 1–17 mN/m. The CMC of TL is as low as 2 mg/L. Lipopeptide surfactins have a CMC range of 25–50 mg/L. They reduce the surface tension of water to 27 mN/m and the interfacial tension of oil/water to 1 mN/m (145,147). In lipopeptide groups, surfactin is the most surface active agent (148). The surface properties are proportional to the hydrophobicity and amino acids present (149). Surfactins compared with sodium dodecyl sulfate and BAS have better foaming capabilities because of their low CMC values (150).

Bioemulsifiers bind tightly to hydrocarbons or oils in an emulsion and prevent them from de-stabilizing an emulsion by coalescing/flocculation/*etc*. This is performed by increasing their kinetic stability, and an important contributing factor is their chemistry (151,152). The combination of fatty acids, proteins, and occasionally sugar polymers contributes to their stabilizing nature. Emulsan, for example, can emulsify oils even when present in minute weight percentages because of the lipophilic sites of the fatty acids. In case a protein is present, that acts as the hydrophobic site. Uzoigwe et al. (73) have extensively studied and described the different stabilizing mechanisms of emulsan, alasan, mannoproteins, *etc*.

RHEOLOGY

Rheology is an important parameter when it comes to cosmetic formulations. The viscosity of a formulation is often used as a control parameter. Beauty and personal care products are often exposed to a varied range of shear rates during processing, packaging, and finally when used by the consumer. This makes it vital to control the rheological properties of a cosmetic product across the shear rate range. In addition to their functional properties like film formation, biopolymers are often added as viscosity modifiers in cosmetic formulations (153–155).

The viscoelastic properties of chitosan have been widely studied (156–158). Hwang and Shin (156) explored the effect of polymer concentration on the rheological response of chitosan solutions. They recorded an increase in the bulk viscosity as the concentration of chitosan was increased. Furthermore, they also reported that the chitosan solution exhibited greater shear thinning flow at greater chitosan concentrations. They attributed this to the fact that at increased polymer concentrations, the movement of the individual polymer chains becomes more restricted. Thus, the time taken to create new entanglements to replace the ones initially deformed increases, making it more pseudoplastic (156).

In another study, Chen and Heh (153) observed the impact of the molecular weight of chitosan on the rheological properties of moisture creams. The bulk viscosity of the creams increased when chitosan of greater molecular weight was added to the formulation. Also, the viscosity of the moisture cream with 0.5 wt% chitosan was found to be greater than that of the same moisture cream formulation with 2 wt% of a traditional viscosity modifier like glycerol monostearate.

The bulk rheological properties of xanthan gum depend on the average molecular weight as well as the acetate and pyruvate contents which in turn vary depending on the operational conditions during processing. Casas et al. (154) determined the effect of temperature and other parameters like fermentation time on the molecular structure of xanthan gum produced as well as their rheological properties. At low temperatures, the synthesized xanthan gum had high molecular weight, and thus exhibited high viscosity. On the other hand, high processing temperatures (34°C) resulted in low viscosity polymers. At a concentration greater than 0.3 wt%, the viscosity of xanthan solution is independent of salt, making it excellent for viscosity building in ion-containing solutions (159).

Xu et al. (160) studied the shear thinning properties of xanthan gum in aqueous solutions which was due to the disruption of the polysaccharide aggregates at high shear rates. An increase in the apparent viscosity of the polymer solution was observed with increasing polymer concentrations. Xanthan gum solutions of high concentrations have a yield stress which makes it ideal as a suspending agent in various cosmetic formulations. This yield stress arises from the numerous hydrogen bonds present in the helix structure of the biopolymer. Xanthan solutions have a dominant elastic flow behavior which makes them ideal rheology modifiers (85).

Carboxymethyl cellulose is another polysaccharide that is extensively used to modify rheological properties in cosmetic applications in various creams, lotions, or toothpastes (155). Carboxymethyl cellulose exhibits shear thinning behavior through a mechanism similar to those mentioned previously in this section. Edali et al. (161) generated hysteresis loops of the shearing cycles by first increasing the shear stress to a fixed value, and then holding the stress constant at the maximum value, followed by reducing the shear

stress to evaluate the thixotropic properties of carboxymethyl cellulose. Carboxymethyl cellulose solutions showed excellent thixotropic behavior. Furthermore, this time dependence of viscosity increased at greater carboxymethyl cellulose concentrations. This was explained by the different rates of disentanglement and re-entanglement of the polymer chains when a shear is applied (162). Because of its thixotropic behavior, carboxymethyl cellulose has found widespread use in cosmetic products such as nail polish.

Studies on the rheological effects of biosurfactants are few. One study carried out by Abbas et al. (163) discussed the rheology of the biosurfactant synthesized by *Pseudomonas aeruginosa*—in other words, RLs from food industry by-products. Rheological measurements were carried out using viscosity-shear, strain, and frequency sweep tests. The biosurfactant displayed a linear viscoelastic region of less than 1% on carrying out the strain sweep test. The viscosity tests revealed shear thinning behavior, and the frequency sweeps revealed a dominant storage (G′) modulus throughout the range, where the modulus was frequency dependent. When the sample was subjected to a constant shear rate, it displayed thixotropic behavior with respect to time.

Another study by Jain et al. (164) studied the rheology of biosurfactant produced by an alkaline environment preferring bacterium *Cronobacter sakazakii* which was extracted from wastewater polluted by oil. This biosurfactant is a heteropolysaccharide–protein complex which is also emulsifying in nature. Viscosity measurements were carried out for the sample. The flow sweep revealed that the biosurfactant was a pseudoplastic, or, in other words, it was shear thinning in nature. The viscosity was 0.429 Pa/s at 0.01 1/s shear rate and decreased from there onward with an elevation in the shear rate. Another biological emulsifier produced from *Halomonas eurihalina* also displayed similar pseudoplastic behavior (165).

Finally, Xu and Amin (15) carried out mechanical rheometry to study the effect of RLs on sodium lauryl ether sulfate and CAPB—which are common synthetic surfactants. The addition of RLs to the SLES/CAPB system lowered the viscosity at low shear rates. The viscoelastic behavior was Maxwellian—where before crossover, the loss modulus (G″) was dominant. As more RLs were added, the crossover shifted to shorter relaxation times, which is always inversely proportional to the frequency. Micro rheological tests were also performed to understand the rheological properties of the ternary system at higher frequencies. From the tests, one could construe that with the addition of RLs, the long micelles broke into shorter micelles because of weaker entanglements. This explained the reduction in viscosity.

Further research on biosurfactant and bioemulsifier effects on rheology would make for an interesting long-term study on the development of novel rheological textures in cosmetics and cosmeceuticals.

FUTURE TRENDS AND CHALLENGES

Shifting into the realm of sustainability has become a necessity for the sustenance of cosmetic companies. This transition, although advantageous in terms of environmental considerations, comes with its own challenges. The most consequential challenge that is faced in today's market scenario is the existence of a supply–demand paradox, where low demand has led to difficulty in quelling market prices of green cosmetic commodities. This can be addressed by systematically increasing the percentage of sustainable ingredients in cosmetic formulations and continually funneling these into the market for consumer accep-

tance. Growth in consumer acceptance is also heavily dependent on the performance properties of green cosmetics. Their performance can be engineered by exploring interactions between traditional surfactants and polymers, and their bio-based alternatives which have been discussed extensively in this article. Furthermore, biosurfactants and biopolymers can be rheologically modified and explored as discussed by Xu and Amin (15). This is a scarcely investigated area which presents researchers with a plethora of opportunities.

Today, there is a highly anticipated evolution transpiring across the entire product life cycle of the cosmetics industry—right from sourcing raw materials for commercial-scale production—all the way up to final market appeal. From a scientific standpoint, the design stage of cosmetics is a key factor in incorporating sustainability into the product life cycle. The design stage should address the principles of green chemistry and green engineering, which calls for studying fundamental molecular properties and transformations. On the consumer end, with evolving demands and industry regulations, there is a need for high-throughput and high-output research in the formulation space. This can be achieved by introducing automation platforms to the formulation process. Automation can meet the large volume requirement for customization techniques and can provide companies with flexibility in formulation without time and cost constraints, and can hence enable more iterative investigation into structure, property, and performance.

In the coming years, it is inevitable that with research in this field picking up pace, there will be a complete metamorphosis of the cosmetics industry into a model that is highly sustainable and automized.

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