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REVIEW

Microbial Polysaccharide-Based Membranes: Current and Future Applications

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ABSTRACT: Microbial polysaccharides are characterized by high molecular structure variability which translates into a wide range of different properties offering interesting opportunities for application in many different areas, including membrane-based products and processes. Due to their new or improved properties, microbial polysaccharides can replace plant, algae, and animal products, either in their traditional or in new applications. The main constraint to their wider use is the production costs that are still higher than that of other natural and synthetic polymers. The current applications of microbial polysaccharide membranes in medical, food, and industrial processes are outlined. The limitations still faced by these membranes and the requirements for obtaining innovative products and processes are also addressed. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40047.

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INTRODUCTION

Microbial polysaccharides are renewable, biodegradable, and biocompatible biopolymers with commercially relevant material properties that are attractive for a wide range of applications, ranging from several chemical industries to biomedicine and cosmetics (Table I). Although they are mainly used as hydrocolloids, many microbial polysaccharides possess film-forming properties that render them suitable for the preparation of membranes with different characteristics (Table II).

Polysaccharide-based membranes have important uses in several medical, food, and industrial processes. To date, most polysaccharide-based membrane applications have been developed with polysaccharides extracted from plants (e.g. starch), algae (e.g. alginates), or animal sources (e.g. chitosan). However, microbial polysaccharides have new or improved properties that make them competitive with other natural polysaccharides, as well as with synthetic products (e.g. polyvinyl alcohol (PVA)).

The mechanical and barrier properties of a polysaccharide-based membrane depend on the structure, relative humidity, film composition, plasticizer additives, cross-linking agents, and the preparation procedure.[16] Polysaccharide membranes are considered effective barriers against gases (oxygen and carbon dioxide) due to their hydrogen-bonded dense polymer matrix. However, their hydrophilic nature restricts their moisture barrier properties, significantly limiting their applications. Moreover, their mechanical properties are not satisfying for all membrane applications. Hence, there have been many studies to improve the mechanical properties of polysaccharide-based membranes by making blends of different polymers or incorporating hydrophobic materials and plasticizers. In particular, synergistic properties have been reported for membranes prepared from blends of some microbial polysaccharides with other natural (e.g. gellan/gelatin,[17] pullulan/gelatin,[1] pullulan/bacterial cellulose,[2] chitosan/bacterial cellulose,[38,74] chitosan/hyaluronan[63]), or synthetic polymers (e.g. gellan/PVA,[18] pullulan/PVA[3]). Reaction with multivalent metal cations (e.g. Ca^{2+}) has been reported to improve the properties of gellan[16] and chitosan/pullulan[4] membranes. Plasticizers, such as glycerol or poly(ethylene glycol) are commonly used to improve membrane flexibility and processability, although they affect their hydrophilicity and usually increase their permeability to oxygen.[75] Lipids (e.g. sunflower oil) are also often included in the formulations to improve their water vapor and oxygen permeability.[75]

Microbial polysaccharides with film-forming capacity include: pullulan, gellan gum, levan, curdlan, hyaluronan, bacterial cellulose, and bacterial alginates (Table I; Figure 1). Some microbial polysaccharides (e.g. xanthan gum) are used in blends with other natural or synthetic polymers for the production of improved membranes.[76–78] Nevertheless, only a few commercial membrane applications based on microbial polysaccharides have

Table I. Properties and Membrane Applications of Microbial Polysaccharides

Polysaccharide	Main microbial producers	Composition		Charge	M_w[a]	Properties	Membrane applications	References
		Sugar monomers	Acyl substituents					
Pullulan	*Aureobasidium pullulans*	Glucose	-	Neutral	(2.0-5.0) $\times 10^5$	Water soluble, adhesive ability, forms fibers, Films: transparent, printable, heat sealable and impermeable to oxygen	Pharmaceutical industry. Nutraceutical capsules. Food	1-15
Gellan gum	*Sphingomonas paucimobilis*	Glucose, rhamnose, glucuronic acid	Acetate, glycerate	Anionic	5.0×10^5	Hydrocolloid; stability over wide pH range; Gelling capacity; thermoreversible gels. Film-forming	Edible coatings, encapsulation of flavors and bioactive ingredients in food systems	16-26
Levan	*Zymomonas mobilis, Halomonas smyrnensis, Bacillus subtilis*	Fructose	-	Neutral	(1.0-3.0) $\times 10^6$	Low viscosity. High water solubility. Biological activity. Adhesive strength. Film-forming capacity	Biomedical and tissue engineering: wound healing, surgical sealants,coating of solid oral dosage forms	27, 28
Curdlan	*Agrobacterium* sp.	Glucose	-	Neutral	5×10^4 - 2×10^6	Gel-forming ability. Water insolubility. Edible and nontoxic. Biological activity	Encapsulation and controlled drug release. Edible coating. Encapsulation of food ingredients	28-35, 119
Bacterial alginate	*Azotobacter vinelandii; Pseudomonas aeruginosa*	Guluronic acid, mannuronic acid	Acetate	Anionic	(0.3-1.3) $\times 10^6$	Water soluble. Hydrocolloid. Gelling capacity. Film-forming	Medicine: surgical dressings, wound management, controlled drug release	36,37
Bacterial cellulose	*Gluconacetobacter* sp.	Glucose	-	Neutral	$\sim 10^6$	High crystallinity. Insolubility in most solvents. High tensile strength. Moldability	Biomedical: wound healing, tissue engineered blood vessels.Audio speaker diaphragms	1, 2, 38-62
Hyaluronan	*Streptococcus* sp.	Glucuronic acid, acetylglucosmine	-	Anionic	(1.0-2.0) $\times 10^6$	Biological activity; highly hydrophilic	Tissue engineering, tympanic membrane, wound healing, drug delivery, ophthalmic contact lenses	46-48, 63-66
GalactoPol	*Pseudomonas oleovorans*	Galactose, mannose, glucose, rhamnose	Acetate, succinate, pyruvate	Anionic	(1.0-5.0) $\times 10^6$	Viscous pseudoplastic aqueous solutions, film-forming, emulsifying capacity, flocculating capacity	Coatings, packaging, solvent dehydration	67-72

[a] Indicative values.

Table II. Mechanical Properties of Microbial Polysaccharides and Blends

Materials	Plasticizer	Young modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	References
Bacterial cellulose	No	34	15	32	38
Bacterial celulose/chitosan	No	132	10	28	38
Pullulan	No	3000	70	4	74
	No	1700	31	4	71
Pullulan	Glycerol (15%)	n.a	48	1.3	14
	Glycerol (30%)	1	1	670	2
Pullulan/bacterial cellulose (40%)	No	46	61	2.5	2
	Glycerol (30%)	23	40	10	2
Pullulan/chitosan (40%)	No	3100	70	2.5	73
Pullulan/chitosan (33%)	Glycerol (15%)	NA	48	2.3	14
Pullulan/sodium alginate (40%)	No	2000	44	4	73
Curdlan	Glycerol (50%)	NA	5	48	31
Gellan gum	No	NA	30	34	16
	Glycerol (50%)	NA	59	16	17
Gellan gum/gelatin (40%)	Glycerol (50%)	NA	30	28	17
GalactoPol	No	1738	51	9.5	71

NA, data not available.

been developed and are currently being exploited. The main constraint to their wider use in membrane-based applications is the production costs that are still higher than that of other natural and synthetic polysaccharides.

On the other hand, as a result of the current extensive research on new polysaccharide-producing strains, polymers with novel molecular structures and functional properties are being proposed for use in membrane applications. An example of such polymers is GalactoPol, a recently reported exopolysaccharide (EPS) synthesized by the bacterium *Pseudomonas oleovorans* that possesses interesting functional properties[67–72] (Table I). This EPS is a high molecular weight negatively charged heteropolysaccharide, composed of neutral sugars (galactose, glucose, mannose, and rhamnose) and acyl group substituents (pyruvil, succynil, and acetyl).[68] It forms viscous aqueous solutions[70] and it is insoluble in organic solvents (e.g. ethanol, acetone and tetrahydrofuran). It has demonstrated the capacity of producing films (Figure 2) with promising characteristics (Table II).[68,71,72]

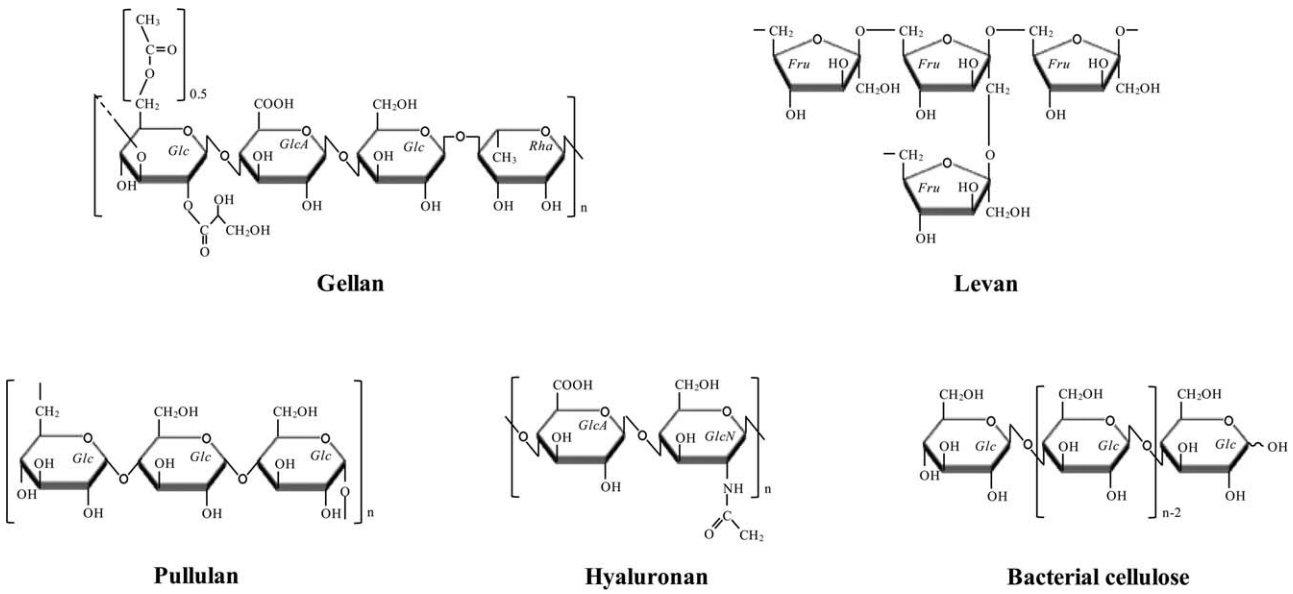

Figure 1. Chemical structures of some microbial polysaccharides.

Figure 2. Film prepared with the exopolysaccharide GalactoPol by solvent casting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This review outlines the main aspects of microbial polysaccharide based membranes, focusing on their production and their current and future applications in medical, food and industrial processes. The limitations still faced by these membranes and the requirements for obtaining innovative products and/or processes are also addressed.

BIOPRODUCTION AND DOWNSTREAM PROCESSING

Microorganisms are able to convert a wide range of carbon sources into a variety of polysaccharides with different chemical structures and material properties (Table I; Figure 1). Microbial polysaccharides are obtained through sustainable processes, based on renewable resources, under controlled cultivation conditions that assure the yield of products with known composition, unaffected by environmental factors. Most industrial bioprocesses for the production of microbial exopolysaccharides, like gellan, bacterial cellulose, or pullulan, rely on the use of carbohydrates as carbon sources because they allow for high productivities and yields.[5,19,29,39,79] Sucrose and glucose are the most common substrates. Xylose, galactose, and lactose are less frequently used substrates since many microorganisms are unable to use them or they result in reduced polymer productivities.[79]

Several agricultural and industrial wastes and byproducts (e.g. glycerol-rich product from the biodiesel industry, lignocellulosic materials, cheese whey, molasses) have also been proposed as substrates for microbial cultivation as a strategy to lower polysaccharides production costs.[40,80–83] The selling prices for the commonly used substrates for production of most microbial polysaccharides, sugar and starch, are currently around 350 to 518 US$/ton (www.sugaronline.com) and 279 to 310 US$/ton (www.indexmundi.com), respectively. In contrast, the market prices for most wastes/byproducts is considerably lower. For example, cheese whey powder, a nutrient rich material derived from the cheese industry, is sold for 1.02 to 1.11 US$/ton (www.clal.it), while the price of glycerol byproduct from the biodiesel industry is around 0.88 to 1.07 US$/ton (www.icispricing.com). Since the substrate cost accounts for up to 40% of the total production costs of microbial polymers,[29] the use of such inexpensive raw materials considerably contributes to reduce the overall costs of the bioprocesses. However, the use of some agricultural and industrial wastes/byproducts is hindered by the difficulty in guarantying their supply in terms of both quantity and quality. For example, lignocellulosic materials encompass many different types of materials (e.g. agricultural straws and husks, paper, wood), which often need to be processed differently and usually require costly pretreatments prior to their use.

The use of such substrates may also have some drawbacks, due to their different nutrient composition and the presence of contaminants that may induce different cellular metabolic pathways, resulting in reduced biopolymer production or the synthesis of different polymers and/or (unwanted) byproducts. Moreover, nonreacted components may accumulate in the broth and eventually be carried over to the final product. Hence, for applications, wherein high purity and high quality products are needed, the use of wastes or byproducts may not be an option or, otherwise, higher investment must be put in downstream procedures.

The synthesis of microbial polysaccharides is generally favored by the presence of carbon source in excess, concomitant with limitation by another nutrient (e.g. nitrogen, oxygen),[29] but the amount of biopolymer produced is highly influenced by media composition and cultivation conditions. The functional properties of microbial polysaccharides are determined not only by their chemical composition, but also by their molecular structure, average molecular weight and polydispersity.[29,84,85] These characteristics can be manipulated by altering the growth conditions of the producing strains. For example, the material properties of bacterial alginates depend mainly on the molar ratio and sequence of mannuronic acid and guluronic acid residues, degree of acetylation and molecular mass of the molecules[85] and these characteristics are influenced by the cultivation conditions.[81]

The extracellular nature of the microbial polysaccharides reported to be used in membrane applications (Table I) makes their recovery from the culture broth a rather simple process. The downstream processing of microbial exopolysaccharides commonly involves: (1) cell removal, usually achieved by centrifugation or filtration; (2) polymer precipitation from the cell-free supernatant by the addition of a precipitating agent consisting of a water-miscible solvent in which the polymer is insoluble (e.g. methanol, ethanol, isopropanol, acetone); (3) drying of the precipitated polymer, namely by freeze drying (laboratory scale) or drum drying (industrial scale).[81,84] To obtain a higher purity grade polysaccharide, which is a requirement for some applications, the polymer is subjected to one or several additional methods: re-precipitation of the polymer from diluted aqueous solution, deproteinization by chemical or enzymatic methods, and membrane processes, such as dialysis, ultrafiltration and diafiltration.[86–88] The most appropriate downstream procedure must be carefully selected to guaranty

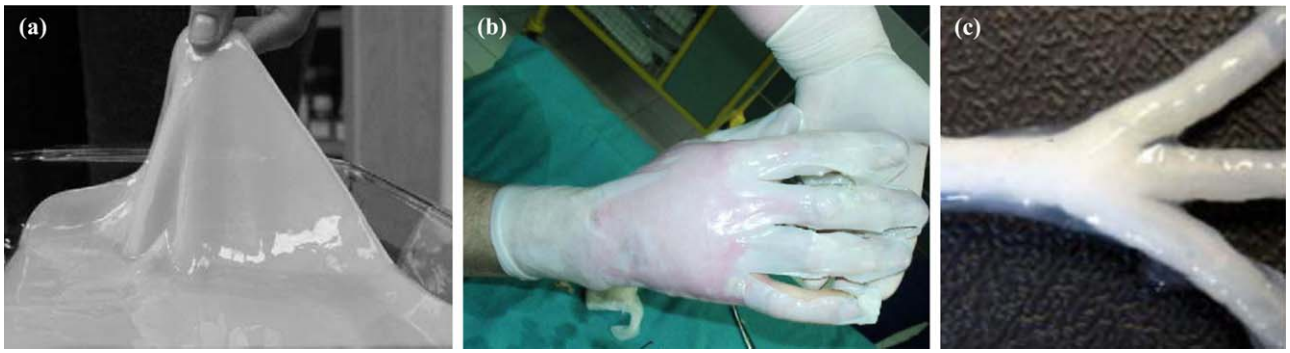

Figure 3. Bacterial cellulose pellicle produced by *Acetobacter xilynum* (a) and its use for the treatment of burns (b) (Reproduced from Ref. 92, with permission from Elsevier). Tubular cellulose grown on branched silicone tubing (c) (Reproduced from Ref. 93, with permission from Wiley). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the required product purity, without disregarding product recovery, which may be decreased by the methods used. Additionally, the impact of purification on the polymer's properties must also be taken in consideration.

APPLICATIONS

Microbial polysaccharides are characterized by high molecular structure variability (Figure 1), which is translated into a wide range of different properties (Table I), offering interesting opportunities for application in many different areas, including membrane-based products and processes.

Medical and Pharmaceutical Biomaterials

The biocompatibility and biodegradability of natural polysaccharides have made them suitable for use in numerous medical applications. Biomedical materials based on animal and algal polysaccharides, such as chitosan and alginate, respectively, are already commercially available and used in clinical practice,[89,90] while several microbial polysaccharides (e.g. gellan, pullulan, hyaluronan, bacterial alginate, and bacterial alginate) are being investigated for their use in such applications.[6,41,91]

Depending on their intended clinical use, different properties are sought for the medical biomaterials. Bioabsorbable membrane materials for use in tissue regeneration must provide a physical barrier that is maintained for a period of time long enough for the tissue to reach sufficient healing stage. Dense structures are necessary at the initial time of healing, while porous structures are essential in later stages for cellular adaptation and nutrient permeation. Hence, the biomaterials must have an appropriate degradation rate (4–6 weeks) to assure the successful restoration of tissues.[91] On the other hand, wound dressings should maintain proper wound moisture during the healing process to promote the penetration of the active substances, protect wounds against bacterial invasion, and provide a painless removal from wound surface after recovery.[38,41,42,92] Other medical applications of microbial polysaccharides include drug delivery agents, coatings of medical devices, adhesives, and surgical sealants.[5,7,27]

Bacterial cellulose [Figure 3(a)] has been proposed for wound dressings for burn or wound repair[38,41,42] [Figure 3(b)], the manufacture of artificial blood vessels for microsurgery[43,44] [Figure 3(c)], and scaffolds for tissue engineering.[40,45] Hyaluronan-based membranes have also been proposed for several biomedical applications, including scaffolds for tissue engineering,[64] tympanic membrane wound healing,[46] transdermal patches for localized drug delivery[47] and ophthalmic contact lenses.[48]

Membranes for Food Applications

In the area of food industry, microbial polysaccharides are widely used as thickening, stabilizing, texturizing or gelling agents, conferring the products good sensory properties, extended shelf life and easier processing.[94] Beyond that, there has been also a great interest on using this class of molecules for the development of edible and/or biodegradable membranes, consisting either on stand-alone films or coatings, to serve as barriers in food packaging. This interest relies on the need of searching materials that may consist on alternatives to conventional non-biodegradable polymers, either because they are obtained from renewable resources or due to their unique properties enabling the achievement of designed barriers for specific applications.

Microbial polysaccharides, such as gellan,[16,20–22] pullulan,[8–13] xanthan,[76,95–97] bacterial cellulose,[2] curdlan,[30,31] and Galacto-Pol[71] have been applied in the development of stand-alone films. In addition, some of those polysaccharides, mostly gellan, pullulan, and xanthan, have been also applied in edible coatings, which consist on a relatively thin layer of material with a specific composition applied and formed directly on food product's surface, which may be eaten along with the product.[98]

Polysaccharide films are considered effective barriers against gas (e.g. oxygen and carbon dioxide) due to their hydrogen-bonded dense polymer matrix. However, their hydrophilic nature limits the film's moisture barrier properties, narrowing the range of applications. Water soluble films are sometimes required when they are used as edible packaging, such as an edible pouch for premeasured portions, which will be gradually dissolved in water or in hot food.[99] Though, resistance towards water is needed for applications where the films are exposed to high water activity or come in direct contact with liquid water. Crosslinking reactions between polymer chains are one of the strategies applied to increase the resistance to water of

polysaccharide films. Yang et al.[16] reported the ionic cross-linking of gellan films using a $CaCl_2$ soaking solution, which improved the films water vapor barrier properties and decreased significantly the swelling degree when in contact with water. Alves et al.[71] presented the evidence of auto-crosslinking esterification reactions between carboxyl and hydroxyl groups of GalactoPol chains, taking place in the filmogenic solution at low pH, upon drying after casting, turning the resulting films insoluble in water (Figure 2).

The increase of the films barrier to water vapor has also been promoted with the addition of lipids to the polymeric matrix, by using oil in water emulsions as filmogenic formulations. As illustration, Tapia et al.[22] have greatly increased the water vapor resistance of gellan-based coatings applied on fresh-cut papaya with the addition of olive oil; and Shih et al.[11] reported a substantial decrease of the water vapor permeability of edible films based on pullulan with the inclusion of rice wax in the polymeric matrix. Furthermore, layers based on lipids have also been applied on previously prepared polysaccharide films to form multilayered barriers, resulting in a drastic decrease in water vapor permeability, which was the case of beeswax on pullulan films.[9]

Edible and/or biodegradable films and coatings are excellent vehicles of bioactive components and nutrients, such as antimicrobials, antioxidants, flavor compounds, probiotics, and prebiotics. Interesting barriers based on microbial polysaccharides have been referred, such as antimicrobial coatings against food spoilage bacteria based on pullulan and tymol,[10] nanocomposite thin films of pullulan and silver with antifungal activity;[12] as well as probiotic-residing pullulan/starch edible films.[13] In addition, edible films based on gellan have been evaluated as carriers for stabilizing ascorbic acid, for nutritional purposes, and antioxidant effect;[20] as well as other antioxidants (e.g. L-acetylcysteine and glutathione) to be applied on fresh-cut fruits.[21]

The development of biodegradable films based on polymer blends involving microbial polysaccharides has been quite explored, in order to obtain polymeric matrices with enhanced characteristics (e.g. mechanical, barrier, water affinity, and bioactives stabilization/release properties). Xanthan gum is mainly used as thickening agent in the food industry. When applied in the development of biodegradable films, it has been used mostly in polymer blends, namely with starch[76,96,97] and zein protein.[95] Studies regarding the improvement of the mechanical and oxygen barrier properties of single pullulan films, by blending it with other polymers, namely chitosan[14] and gelatin,[1] were reported. In addition, curdlan was blended with konjac glucomanan and chitosan, enabling the production of films with good moisture barrier properties and antibacterial activity, respectively.[30,31]

As it happened with petrochemical-based polymers, and more recently with a large variety of biodegradable polymers, nanocomposites based on microbial polysaccharides have also been developed. Nanocomposites consist of polymers filled with particles that have at least one dimension in the nanometer range. Because of their very high surface area to volume ratio, nanoparticle incorporation into polymer matrices leads to materials with unique properties in comparison to the polymer matrix itself and to their conventional microcomposite counterparts.[100] Pullulan films reinforced with starch nanocrystals,[8] and with nano/microfibrils of bacterial cellulose,[2] are examples of such nanocomposites. In addition, Introzzi et al.[15] reported the development of a high oxygen barrier coating consisting on a pullulan/montmorillonite nanocomposite. When applied on polyethylene terephthalate (PET), the oxygen permeability of the double layer was significantly lower in comparison to the original PET layer. This fact was observed even at high relative humidity conditions, at which the polysaccharide matrices tend to lose their barrier properties to gases due to the plasticizing effect of the adsorbed water molecules.

Other Industrial Applications

Due to their hydrophilic character and charge, microbial polysaccharide based membranes are being developed for solvent dehydration by pervaporation, and for wastewater treatment, where they demonstrated a high adsorption capacity for aromatic compounds, dyes and heavy metal ions. They also have been applied for the development of components for electronic devices.

Solvent Dehydration. Solvent dehydration processes have a high economic and environmental relevance in the pharmaceutical, fine-chemistry, and chemical industry. Among the available dehydration techniques, pervaporation is attractive due to its relative simplicity of operation and high selectivity, making possible to circumvent the formation of azeotropes. Additionally, pervaporation may operate under mild conditions, which translates into a process economy.[101]

Hydrophilic polymers, such as, polyvinyl alcohol, polysulfone, polyamides, among others have been selected as membrane material for the dehydration of various solvents. Membranes of polyvynilalcohol (PVA) have been commercialized by Sulzer Chemtech due to their excellent water perm-selective properties.

With growing environmental concern, it is very important to obtain polymers from renewable sources and many efforts have been devoted to the development of new membranes with high separation performance and reliability. However, these new membranes should present a good compromise between flux and selectivity and also chemical and mechanical stability, when compared with commercial membranes.

Among the biopolymeric materials used in hydrophilic pervaporation, polysaccharides have received much attention, due to their good selectivity and high flux.[102] Chitosan and sodium alginate are examples of polysaccharides that have already been tested in pervaporation for dehydration of solvents, such as ethanol, isopropanol, tetrahydrofuran, and acetone, with high separation performance in terms of selectivity and water flux.[103–106]

Although they show an excellent affinity for water, as membrane materials they lack mechanical strength and stability in aqueous solutions.[107] Membranes with enhanced water resistance and water selectivity have been developed using selected strategies, such as polymer cross-linking, incorporation of inorganic

Table III. Selectivity and Flux for Ethanol Dehydration by Pervaporation with Feed Water Content of 10 wt %

Membrane	T (°C)	Selectivity[a]	Flux (g/m^2 h)	References
Sodium alginate and cellulose blend	30	1175	170	103
Ca^{2+} crosslinked sodium alginate	50	300	230	107
GA[b] crosslinked sodium alginate	60	1000	300	108
Al^{3+} Cr^{3+} crosslinked sodium alginate	70	2750	942	109
GA[b] crosslinked chitosan	50	6000	1100	110
GA[b] crosslinked chitosan/sodium alginate	60	1000	210	111
Chitosan/HEC[c]	60	10,490	112	112
Phosphorylated chitosan	30	180	240	113

[a] Permeability ratio water/ethanol.
[b] Glutaraldeyde.
[c] hidroxyethylcellulose.

particles in the polymer matrix and blends or self-assembly of layer-by-layer polyelectrolyte polymers.

The degree of crosslinking affects the flux, selectivity and stability behavior of the membranes. A decrease of water permeability is expected with increasing crosslinking, but an improved selectivity and long-term stability is obtained. Composite membranes are often used, since they can offer a higher flux due to a much thinner thickness of the active membrane supported on a porous substrate, which should present negligible resistance to mass transfer.

Stable sodium alginate membranes using glutaraldehyde or ionic cross-linking with multivalent metal ions (e.g. Ca^{2+}, Al^{3+}) were obtained, by suppressing excessive swelling. Chitosan membranes are also extremely hydrophilic and can lose integrity in aqueous solutions, thus cross-linking and blend strategies were also employed.

Multilayer polyion membranes can be obtained using a layer-by-layer deposition method, in alternate mode, with chitosan as polycation and polyanion polymers, such as hydroxyethylcellulose, cellulose acetate and cellulose sulfate. These membranes demonstrated an excellent dehydration performance as shown in Table III. The values of the selectivity and flux obtained for the ethanol dehydration by pervaporation with 10 wt % of water in the feed, range from 1000 to 10,000 and the fluxes are always higher than 100 g/m^2 h.[104,107,108]

It is necessary to take into account that, the flux increases with higher feed concentration, higher temperature, and with lower membrane thickness. So, the performance of the process should be quantified in terms of permeability and selectivity which allow for describing the intrinsic properties of the separation membranes and compare results obtained at different experimental conditions.

Regarding microbial biopolymers there is, so far, not much work on their application as membranes for pervaporation. Bacterial cellulose membranes have been used for ethanol dehydration.[49] For feed compositions containing less than 30% water, the selectivity toward water was in the range of 125 to 287 and the flux was higher than 100 g/m^2 h. Recently, it has been reported a new extracellular polysaccharide (GalactoPol) produced with a low cost, abundant carbon source, the glycerol byproduct of the biodiesel industry, using *Pseudomonas oleovorans*. Two types of membranes, homogeneous (EPS) and composite of EPS with polyethersulfone (PES) as support (EPS-PES), were developed and used for ethanol dehydration by pervaporation. The homogeneous membrane, at a water feed concentration of 5.0% (w/w), showed a water/ethanol selectivity of 110. For the composite membrane a denser EPS polymer was used leading, under the same operating conditions, to much higher water/ethanol selectivity (3000). Moreover, the mechanical resistance was also improved in comparison with the homogeneous membrane, due to the physical characteristics of the commercial support used.[72]

The fluxes obtained were lower than the reported previously, 11 to 22 g/m^2 h, however the temperature used was 30°C and the water concentration in the feed was only 5 wt %. Increasing the water concentration in the feed to 10 wt % the fluxes increased to 40 to 60 g/m^2 h and the selectivity decreased to 69 and 134. A higher water concentration leads to membrane swelling and higher mobility of the polymer chains. As a consequence, permeability increases and selectivity decreases.

These new membranes may become an interesting alternative to commercial hydrophilic pervaporation membranes for the dehydration of ethanol. Strategies, for further improvement should include optimization of polymer cross-linking conditions, in order to improve selectivity for higher concentration of water in the feed stream. Additionally, it will be important to evaluate the performance of these new membranes in other industrially relevant processes, such as the separation of polar and non-polar compounds in organic mixtures, and also for solvent-resistant nanofiltration processes.

Water and Wastewater Treatment. Polysaccharide-based materials have demonstrated good removal capabilities for certain pollutants, such as aromatic compounds, dyes, and heavy metal ions as compared with other commercial sorbents currently used in wastewater treatment processes. Sorbents containing polysaccharides possess a high capacity and high rate of

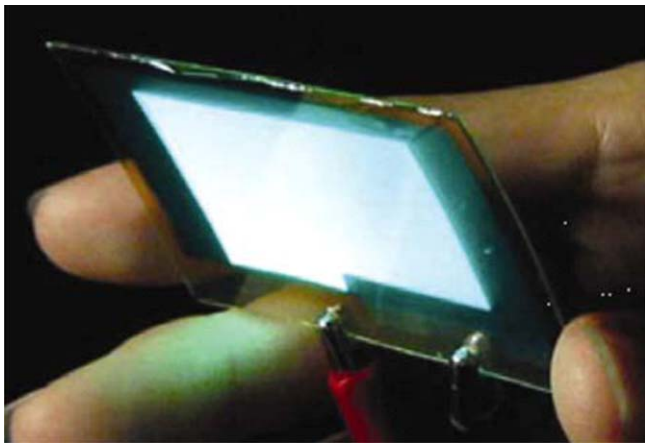

Figure 4. Electroluminescent bacterial cellulose–acrylic resin composite (Reproduced from Ref. 51, with permission from Wiley). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

adsorption, high detoxifying efficiency, and selectivity.[114] They can be used in the form of insoluble beads, gels, sponges, capsules, films, membranes, or fibers. There has been a recent interest on the development of sorbents based on natural polysaccharides, mostly focused on the use of chitin, starch and their derivatives. Additionally, many microbial polysaccharides have been reported to have metal binding capacity[115–118] and have been proposed as possible alternatives to the traditional sorbents used.

Other Emerging Uses. There is still limited use of membranes based on microbial polysaccharides for other industrial applications. Nevertheless, there are promising reports of the investigation of curdlan[118] and bacterial cellulose[50–56] for the development of components for electronic devices.

Bacterial cellulose (BC) exhibits a nanofibrous porous network structure with high strength and low density. The relatively stable and inert nature of BC allows the incorporation of metallic, ceramic and polymeric materials into its porous structure, which imparts BC biomaterials increased functionality. Promising research reports about the use of BC for the development of electronic components include: the synthesis of electrically conducting BC by the incorporation of multiwalled carbon nanotubes;[50] an organic LED (light-emitting diode) fabricated with an electroluminescent BC–acrylic resin composite[51] (Figure 4); an electro-active LiCl-impregnated BC composite;[53] electronic paper made of BC embedded in an electrochromic dye;[52] and magnetic composites synthesized by incorporation of ferrite, copper, and/or niquel nanoparticles.[54–56]

Phosphate-containing bacterial cellulose (PCBC) has also been proposed as a fire retardant compound.[58] Compared with cellulose, PCBC produced by cultivation of *Gluconacetobacter* subsp. *xylinus* using corn steep liquor as a nitrogen source had lower decomposition temperature and higher char formation, which are fire-retardant characteristics.

Bacterial cellulose has already been used by Sony for several years for the fabrication of diaphragms for electroacoustic transducers in several products, such as earphones or loudspeakers.[59,60] BC membranes have acoustic response in a wider frequency range, higher crystallinity and higher Young's modulus than the traditionally used plant cellulose membranes.[61]

CONCLUSIONS AND FINAL REMARKS

Microbial polysaccharides are renewable, biodegradable and biocompatible, which turns them attractive to be used in membrane-based products and/or processes, in a wide range of applications ranging from chemical industry to food, medicine and cosmetics. They can advantageously be used as alternatives to other natural biopolymers, such as plant or algae derived products, due to their novel or improved properties.

These polymers offer the advantage of being produced from renewable resources, under controlled environmental conditions that assure both the quantity and the quality of the final products. However, their wide spreading has been hindered mainly by their production costs that are higher than for most of the traditional petrochemical-based polymers.

Several agricultural and industrial wastes and byproducts have been proposed as substrates for microbial cultivation, as a strategy to lower polysaccharides production costs, however for high-purity applications, the use of wastes or by-products, implies higher investment in downstream processes.

The choice of the most appropriate process must be carefully made because some of these purification procedures may have a negative impact on the polymer's product recovery and properties. As such, research effort is still needed, either for the improvement of the existing extraction and purification processes, or for the development of new approaches, focused on the specifications required for the final product.

The current applications of microbial polysaccharide membranes in medical, food, and industrial processes have been addressed and future applications can be envisaged due to their unique and promising properties.

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REFERENCES

1. Zhang, C.; Gao, D.; Ma, Y.; Zhao, X. *J. Food Sci.* **2013**, *78*, 805.
2. Trovatti, E.; Fernandes, S. C. M.; Rubatat, L.; Perez, D. S.; Freire, C. S. R.; Silvestre A. J. D.; Neto, C. P. *Compos. Sci. Technol.* **2012**, *72*, 1556.
3. Teramoto, N.; Saitoh, M.; Kuroiwa, J.; Shibata, M.; Yosomiya, R. *J. Appl. Polym. Sci.* **2001**, *82*, 2273.
4. Kou, X.-H.; Guo, W.-L.; Guo, R.-Z.; Li, X.-Y.; Xue, Z.-H. *Food Bioprocess Tech., to appear.*
5. Cheng, K.-C.; Demirci, A.; Catchmark, J. M. *Appl. Microbiol. Biotechnol.* **2011**, *92*, 29.

6. Prajapati, V. D.; Jani, G. K.; Khanda, S. M. *Carbohydr. Polym.* **2013**, *95*, 540.
7. Mishra, B.; Vuppu, S.; Rath, K. *J. Appl. Pharm. Sci.* **2011**, *1*, 45.
8. Kristo E.; Biliaderis, C. G. *Carbohyd. Polym.* **2007**, *68*, 146.
9. Kristo, E.; Biliaderis, C.G.; Zampraka, A. *Food Chem.* **2007**, *101*, 753.
10. Gniewosz, M.; Synowiec, A. *Flavour Fragr. J.* **2011**, *26*, 389.
11. Shih, F. F.; Daigle, K. W.; Champagne, E. T. *Food Chem.* **2011**, *127*, 118.
12. Pinto, R. J. B.; Almeida, A.; Fernandes, S. C. M.; Freire, C. S. R.; Silvestre, A. J. D.; Neto, C. P.; Trindade, T. *Colloid Surface B.* **2013**, *103*, 143.
13. Kanmani, P.; Lim, S. T. *Food Chem.* **2013**, *141*, 1041.
14. Wu, J.; Zhong, F.; Li, Y.; Shoemaker, C. F.; Xia, W. *Food Hydrocoll.* **2013**, *30*, 82–91.
15. Introzzi, L.; Blomfeldt, T. O. J.; Trabattoni, S.; Tavazzi, S.; Santo, N.; Schiraldi, A.; Piergiovanni, L.; Farris, S. *Langmuir.* **2012**, *28*, 11206.
16. Yang, L. A.; Paulson, T.; Nickerson M. T. *Food Res. Int.* **2010**, *43*, 1439.
17. Lee, K. Y.; Shim, J.; Lee, H. G. *Carbohydr. Polym.* **2004**, *56*, 251.
18. Sudhamania, S. R.; Prasada, M. S.; Sankar, K. U. *Food Hydrocoll.* **2003**, *17*, 245.
19. Bajaj, I. B.; Survase, S. A.; Saudagar, P. S.; Singhal, R. S. *Food Technol. Biotechnol.* **2007**, *45*, 341–354.
20. León, P. G.; Lamanna, M. E.; Gerschenson, L. N.; Rojas A. M. *Food Res. Int.* **2008**, *41*, 667.
21. Oms-Oliu, G.; Soliva-Fortuny, R.; Martín-Belloso, O. *Postharvest Biol. Tech.* **2008**, *50*, 87.
22. Tapia, M. S.; Rojas-Grau, M. A.; Carmona, A.; Rodríguez, F. J.; Soliva-Fortuny, R.; Martin-Belloso, O. *Food Hydrocolloid*, **2008**, *22*, 1493.
23. Abramovic, H.; Klofutar, C. *J. Food Eng.* **2006**, *77*, 514.
24. Azarakhsh, N.; Osman, A.; Ghazali, H. M.; Tan, C. P.; Adzahan, M. N. *Int. Food Res. J.* **2012**, *19*, 279.
25. Ullrich, M., Eds. Bacterial Polysaccharides: Current Innovations and Future Trends; Caister Academic Press, Norfolk, UK, **2009**.
26. Nedovic, V.; Kalusevic, A.; Manojlovic, V.; Levic, S.; Bugarski, B. *Proc. Food Sci.* **2011**, *1*, 1806.
27. Costa, R. R.; Neto, A. I.; Calgeris, I.; Correia, C. R.; Pinho, A. C. M.; Fonseca, J.; Oner, E. T.; Mano J. F. *J. Mater. Chem. B* **2013**, *1*, 2367.
28. Kang, S. A.; Jang, K.-H.; Seo, J.-W.; Kim, K. H.; Kim, Y. H.; Rairakhwada, D.; Seo, M. Y.; Lee, J. O.; Ha, S. D.; Kim, C. H.; Rhee, S.-K. In Microbial Production of Biopolymers and Polymer Precursors: Applications and Perspectives; Rehm, B. H. M., Eds.; Caister Academic Press: UK, **2009**; Chapter *6*, p 145.
29. Kumar, A.S.; Mody K. In Microbial Production of Biopolymers and Polymer Precursors: Applications and Perspectives; Rehm, B. H. M., Eds.; Caister Academic Press: UK, **2009**; Chapter *10*, p 229.
30. Sun, Y.; Liu, Y.; Li, Y.; Lv, M.; Li, P.; Xu, H.; Wang, L. *Carbohydr. Polym.* **2011**, *84*, 952.
31. Wu, C.; Peng, S.; Wen, C.; Wang, X.; Fan, L.; Deng, R.; Pang, *J. Carbohydr. Polym.* **2012**, *89*, 497.
32. Dobashi, T.; Nobe, M.; Yoshihara, H.; Yamamoto, T.; Konno, A. *Langmuir* **2004**, *20*, 6530.
33. Lehtovaara, B. C.; Gu, X. *J. Agric. Food Chem.* **2011**, *59*, 6813.
34. McIntosh, M.; Stone, B. A.; Stanisich, V. A. *Appl. Microbiol. Biotechnol.* **2005**, *68*, 163.
35. Zhan, X.-B.; Lin, C.-C.; Zhang, H.-T. *Appl. Microbiol. Biotechnol.* **2012**, *93*, 525.
36. Remminghorst, U.; Rehm, B. H. A. In Microbial Production of Biopolymers and Polymer Precursors: Applications and Perspectives; Rehm, B. H. M., Eds.; Caister Academic Press: UK, **2009**; Chapter *2*, p 13.
37. Sabra, W.; Zeng, A.-P.; Deckwer, W.-D. *Appl. Microbiol. Biotechnol.* **2001**, *56*, 315.
38. Lin, W.-C.; Lien, C.-C.; Yeh, H.-J.; Yu, C.-M.; Hsu, S.-H. *Carbohydr. Polym.* **2013**, *94*, 603.
39. Valla, S.; Ertesvarg, H.; Tonouchi, N.; Fjaervik, E. In Microbial Production of Biopolymers and Polymer Precursors: Applications and Perspectives; Rehm, B. H. M., Eds.; Caister Academic Press: UK, **2009**; Chapter *3*, p 43.
40. Oliveira, C. R.; Carvalho, J. L.; Novikoff, S.; Berti, F. V.; Porto, L. M.; Gomes, D. A.; Goes, A. M. *J. Tissue Sci. Eng.* **2012**, *11*, S11:001.
41. Czaja, W. K.; Young, D. J.; Kawecki, M.; Brown, R. M. *Biomacromolecules* **2007**, *8*, 1.
42. Fu, L.; Zhang, J.; Yang, G. *Carbohydr. Polym.* **2013**, *92*, 1432.
43. Andrade, F. K.; Costa, R.; Domingues, L.; Soares, R.; Gama, M. *Acta Biomater.* **2010**, *6*, 4034.
44. Klemm, D.; Schumann, D.; Udhardt, U.; Marsch, S. *Prog. Polym. Sci.* **2001**, *26*, 1561.
45. Svensson, A.; Nicklasson, E.; Harrah, T.; Panilaitis, B.; Kaplan, D. L.; Brittberg, M.; Gatenholm, P. *Biomaterials* **2005**, *26*, 4.
46. The, B. M.; Shen, Y.; Friedland, P. L.; Atlas, M. D.; Marano, R. *J. Expert Opin. Biol. Ther.* **2012**, *12*, 23.
47. Brown, M. B.; Jones, S. A. *J. Eur. Acad. Dermatol. Venereol.* **2005**, *19*, 308.
48. Rah, M. *J. Optometry* **2011**, *82*, 38.
49. Dubey, V.; Saxena, C.; Singh, L.; Ramana; K. V.; Chauhan, R. S. *Sep. Purif. Tech.* **2002**, *27*, 171.
50. Yoon, S. H.; Jin, H. J.; Kook, M. C.; Pyun, Y. R. *Biomacromolecules* **2006**, *7*, 1280.
51. Nogi, M.; Yano, H. *Adv. Mater.* **2008**, *20*, 1849.
52. Shah, J.; Brown, R. M. *Appl. Microbiol. Biotechnol.* **2005**, *66*, 352.
53. Jeon, J.-H.; Oh, I.-K.; Kee, C.-D.; Kim, S. *J. Sens. Actuators B* **2010**, *146*, 307.
54. Olsson, R. T.; Azizi Samir, M. A. S.; Salazar-Alvarez, G.; Belova, L.; Ström, V.; Berglund, L. A.; Ikkala, O.; Nogués, J.; Gedde, U. W. *Nat. Nanotechnol.* **2010**, *5*, 584.

55. Pirkkalainen, K.; Vainio, U.; Kisko, K.; Elbra, T.; Kohout, T.; Kotelnikova, N. E.; Serimaa, R. *J. Appl. Crystallogr.* **2007**, *40*, S489.
56. Pirkkalainen, K.; Leppänen, K.; Vainio, U.; Webb, M. A.; Elbra, T.; Kohout, T.; Nykänen, A.; Ruokolainen, J.; Kotelnikova, N.; Serimaa, R. *Eur. Phys. J. D* **2008**, *49*, 333.
57. Vitta, S.; Thiruvengadam, V. *Curr. Sci.* **2012**, *102*, 1398.
58. Basta, A. H.; El-Saied, H. *J. Appl. Microbiol.* **2009**, *107*, 2098.
59. Nishi, Y.; Uryu, M.; Yamanaka, S.; Watanabe, K.; Kitamura, N.; Iguchi, M.; Mitsuhashi, S. *J. Mater. Sci.* **1990**, *25*, 2997.
60. Uryu, M.; Kurihama, N. *Patent* EP0457474 (B1), **1995**.
61. Markienwicz, E.; Hilczer, B.; Pawlaczyk, C. *Ferroelectrics* **2004**, *304*, 39.
62. Petersen, N.; Gatenholm, P. *Appl. Microbiol. Biotechnol.* **2011**, *91*, 1277.
63. Xu, H.; Ma, L.; Shi, H.; Gao, C.; Han, C. *Polym. Adv. Technol.* **2007**, *18*, 869.
64. Weidenbecher, M.; Henderson, J. H.; Tucker, H. M.; Baskin, J. Z.; Awadallah, A.; Dennis, J. E. *Laryngoscope* **2007**, *117*, 1745.
65. Boeriu, C. G.; Springer, J.; Kooy, F. K.; van den Broek, L. A. M.; Eggink, G. *Int. J. Carbohydr. Chem.*, to appear.
66. Marcellin, E.; Chen, W.; Nielsen, L. K. In Microbial Production of Biopolymers and Polymer Precursors: Applications and Perspectives; Rehm, B. H. M., Eds.; Caister Academic Press: UK, **2009**; Chapter *7*, p 163.
67. Reis, M. A., Oliveira R., Freitas, F., Alves, V. D., Pais, J., Oliveira, C. Int. Pat. Appl. WO2008127134, **2008**.
68. Freitas, F.; Alves, V. D.; Pais, J.; Costa, N.; Oliveira, C.; Mafra, L.; Hilliou, L.; Oliveira, R.; Reis, M. A. M. *Bioresour. Technol.* **2009**, *100*, 859.
69. Freitas, F.; Alves, V. D.; Carvalheira, M.; Costa, N.; Oliveira, R.; Reis, M. A. M. *Carbohydr. Polym.* **2009**, *78*, 549.
70. Alves, V. D.; Freitas, F.; Costa, N.; Carvalheira, M.; Oliveira, R.; Gonçalves, M. P.; Reis, M. A. M. *Carbohydr. Polym.* **2010**, *79*, 981.
71. Alves; V. D.; Ferreira, A. R.; Costa, N.; Freitas, F.; Reis, M. A. M.; Coelhoso, I. M. *Carbohydr. Polym.* **2011**, *83*, 1582.
72. Meireles, I.; Brazinha, C.; Crespo, J. G.; Coelhoso, I. M. *J. Membr. Sci.* **2013**, *425*, 227.
73. Xiao, Q.; Limb, L.-T.; Tonga, Q. *Carbohydr. Polym.* **2012**, *87*, 227.
74. Fernandes, S. C. M.; Oliveira, L.; Freire, C. S. R.; Silvestre, A. J. D.; Neto, C. P.; Gandini; A.; Desbrieres, *J. Green Chem.* **2009**, *11*, 2023.
75. Tapia, M. S.; Rojas-Grau, M. A.; Rodriguez, F.J.; Ramirez, J.; Carmona, A.; Martin-Belloso, O. *J. Food Sci.* **2007**, *72*, 190.
76. Soares, R. M. D.; Lima, A. M. F.; Oliveira, R. V. B.; Pires, A. T. N.; Soldi, V. *Polym. Degrad. Stab.* **2005**, *90*, 449.
77. Bellini, M. Z.; Pires, A. L. R.; Vasconcelos, M. O.; Moraes, A. M. *J. Appl. Polym. Sci.* **2012**, *125*, E421.
78. Lv, R.; Sun, Y.; Yu, F.; Zhang, H. *J. Appl. Polym. Sci.* **2012**, *124*, 855.
79. Singh, R. S.; Saini, G. K.; Kennedy, J. F. *Carbohydr. Polym.* **2008**, *73*, 515.
80. Banik, R. M.; Santhiagu, A.; Upadhyay, S. N. *Bioresour. Technol.* **2007**, *98*, 792.
81. Freitas, F.; Alves, V. D.; Reis, M. A. M. *Trends Biotechnol.* **2011a**, *29*, 388.
82. Mikkelsen, D.; Flanagan, B. M.; Dykes, G. A.; Gidley, M. J. *J. Appl. Microbiol.* **2009**, *107*, 576.
83. Premjet, S.; Sameshima, K.; Ohtani, Y. *Sen'I Gakkaishi* **2007**, *63*, 193.
84. Freitas, F.; Alves, V. D.; Coelhoso, I.; Reis. M. A.M. In Engineering Aspects of Food Biotechnology. Part I: Use of Biotechnology in the Development of Food Processes and Products; Teixeira, J. A., Vicente A. A., Eds.; Editora: Local, **2013**; Chapter *3*, p 61.
85. Rehm, B. H. A. *Nat. Rev. Microbiol.* **2010**, *8*, 578–92.
86. Ayala-Hernández, I.; Hassan, A.; Goff, H. D.; de Orduña, R. M.; Corredig, M. *Int. Dairy J.* **2008**, *18*, 1109.
87. Bahl, M. A.; Schultheis, E.; Hempel, D. C.; Nörtemann, B.; Franco-Lara, E. *Carbohydr. Polym.* **2010**, *80*, 1037.
88. Wang, X.; Yuan, Y.; Wang, K.; Zhang, D.; Yang, Z.; Xu, P. *J. Biotechnol.* **2007**, *128*, 403.
89. Sun, J.; Tan, H. *Materials* **2013**, *6*, 1285.
90. Anaya1, P.; Cárdenas, G.; Lavayen, V.; García, A.; O'Dwyer, C. *J. Appl. Polym. Sci.* **2013**, *128*, 3939.
91. Chang, S.-J.; Ku, S.-M.; Liu, W.-T.; Niu, C.-C. G.; Lee, M.-W.; Wu, C.-S. *J. Med. Biol. Eng.* **2010**, *30*, 99.
92. Czaja, W. K.; Krystynowicz, A.; Bielecki, S.; Brown R. M., Jr. *Biomaterials* **2006**, *27*, 145.
93. Bodin, A.; Bäckdahl, H.; Fink, H.; Gustaffson, L.; Risberg, B.; Gatenholm, P. *Biotechnol. Bioeng.* **2007**, *97*, 425.
94. Sworm, G. In Handbook of Industrial Water Soluble Polymers; Williams, P. A., Ed.; Blackwell Publishing; Oxford, **2007**; Chapter *2*, p 10.
95. de Almeida, C. B.; Filho, J. F. L. *Macromol. Symp.* **2011**, *299*, 20.
96. Flores, S. K.; Costa, D.; Yamashita, F.; Gerschenson, L. N.; Grossmann, M. V. *Mater. Sci. Eng. C.* **2010**, *30*, 196.
97. Arismendi C.; Chillo, S.; Conte, A.; Del Nobile, M. A.; Flores, S.; Gerschenson, L. N. *Food Sci. Tech.* **2013**, *53*, 290.
98. Pavlath, A. E.; Orts, W. In Edible Films and Coatings For Food Applications; Embuscado, M. E.; Huber, K. C., Eds.; Springer: New York, **2009**; Chapter *1*, p 1–24.
99. Labell, F. *Food Process* **1991**, *52*, 24.
100. Smith, J. S.; Bedrov, D.; Smith, G. D. *Compos. Sci. Technol.* **2003**, *63*, 1599.
101. Neel, J. In Introduction to Pervaporation, Pervaporation Membrane Separation Processes; Huang, R. Y. M., Ed.; Elsevier: Amsterdam, **1991**.
102. Dei, Z. W.; Wan, L. S.; Xu, Z. K. *J. Membr. Sci.* **2010**, *348*, 245.
103. Bhat, S. D.; Aminabhavi, T. M. *Separation Purif. Rev.* **2007**, *36*, 203.

104. Chapman, P. D.; Oliveira, T.; Livingston, A. G., Li, K. *J. Membr. Sci.* **2008**, *318*, 5.

105. Shao, P.; Huang, R. Y. M. *J. Membr. Sci.* **2007**, *287*, 162.

106. Bolto, B.; Hoang, M.; Xie, Z. *Chem. Eng. Process.* **2011**, *50*, 227.

107. Huang, R. Y. M.; Pal, R.; Moon, G. Y. *J. Membr. Sci.* **1999**, *160*, 101.

108. Yeom, C. K.; Jegal, J. G.; Lee, K. H. *J. Appl. Polym. Sci.* **1996**, *62* 1561.

109. Shi, Y.; Wang, X.; Chen, G.; Golemme, G.; Zhang, S.; Drioli, E. *J. Appl. Polym. Sci.* **1998**, *68* 959.

110. Yeom, C. K.; Lee, K.-H. *J. Appl. Polym. Sci.* **1998**, *67*, 209.

111. Moon, G. Y.; Pal, R., Huang, R. Y. M. *J. Membr. Sci.* **1999**, *156*, 17.

112. Chanachai, R.; Jiraratananon, R.; Uttapap, D.; Moon, G. Y.; Anderson, W. A.; Huang, R. Y. M. *J. Membr. Sci.* **2000**, *166*, 271.

113. Sunithaa, K.; Satyanarayanab, S. V.; Sridhar, S. *Carbohydr. Polym.* **2012**, *87* 1569.

114. Crini, G. *Prog. Polym. Sci.* **2005**, *30*, 38.

115. Moppert. X.; Le Costaouec, T.; Raguenes, G.; Courtois, Anthony; Colin, C. S.; Crassous, P.; Costa, B.; Guezennec, J. *J. Ind. Microbiol. Biotechnol.* **2009**, *36*, 599.

116. Morillo, J. A.; Aguilera, M.; Ramos-Cormenzana, A.; Monteoliva-Sanchez, M. *Curr. Microbiol.* **2006**, *53*, 189.

117. Poli, A.; Anzelmo, G.; Nicolaus, B. *Mar Drugs* **2010**, *8*, 1779.

118. Qiang, L.; Yumei, L.; Sheng, H.; Yingzi, L.; Dongxue, S.; Dake, H.; Jiajia, W.; Yanhong, Q.; Yuxia, Z. *PLoS One* **2013**, *8*, e53542.

119. Laroche, C.; Michaud, P. *Recent Pat. Biotechnol.* **2007**, *1*, 59.