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Review

Unexplored possibilities of all-polysaccharide composites

Ivan Šimkovic*

Institute of Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 38 Bratislava, Slovak Republic

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ABSTRACT

Composites made solely from polysaccharides are mostly ecological because they can degrade without leaving behind ecologically harmful residues, in contrast to composites which contain synthetic polymers. Herein, the following groups of all-polysaccharide composites (APCs) are discussed: an all-cellulose group that includes cotton composites, cellulose combined with other polysaccharides, as well as those based on chitin/chitosan, heparin, hyaluronan, xylan, glucomannan, pectin, xyloglucan, arabinan, starch, carrageenan, alginate, galactan as one of the components in combination with other polysaccharides. They can be used in medical, paper, food, packing, textile, electronic, mechanical engineering and other applications. The composites were tested for absorptivity, biodegradability, crystallinity, rheology, and mechanical, optical, separation, gelling, pasting, film-forming, adhesive, antimicrobial properties, as well as water vapor permeability, water repellency, dye uptake, and fire-retardancy. Except for food applications, composites based on more than two types of polysaccharides have rarely been used and many possible combinations remain unexplored.

Contents

1. Introduction

Composites are hybrid materials with properties different from their individual components of which they are made. In the environment of polysaccharide interactions the definition is somewhat simplified in comparison to the past. Even systems like hydrogels are referred as composites (BeMiller, 2011). Bringing components together to make composites often links industries that were never linked in the past. The goal of the preparation is to improve some property to be better than that of one of the components. Although the wood industry has produced composites for more than one hundred years, many new composite materials are produced annually (Stark, Cai, & Caril, 2010, chap. 11). One

* Tel.: +421 2 59410289; fax: +421 2 59410222.
E-mail address: chemsimk@savba.sk

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important factor is the size of solid or particulate composite components. The size ranges from meters down to nanometers (John & Thomas, 2012a, 2012b). Perhaps with the exceptions of nanoclay, nanotubes or graphene, decreasing dimensions can make the preparation more challenging. In the present review, the main focus is on nanoparticles that are based on polysaccharides.

Historically, composite components were considered as either the matrix or the reinforcing parts. That is a point for consideration when a composite has a major and a minor component or a synthetic polymer as a component (Dufresne, 2012). In that case the typical feature of matrix is the continuity and it needs not represent major component in respect to its content. For composites made solely from polysaccharides, however, it is not that significant and can even be hard to determine due to their identical surface properties in contrast to fiber/polymer compatibility (Šimkovic, 2008). For example, when both components are different forms of cellulose in equal amounts, then it is not important which is which as far as the name. Under some circumstances, a mixture of cotton fibers and cellulose dissolved in ionic liquid could result in a heterogeneous product. But other production methods could result in a product which is that homogeneous that all or several components are at the nanoscale level and then the matrix and the reinforcing components could not be distinguished.

Composites and especially polysaccharide-based composites must be considered in the context of ecology. Synthetic polymers have dominated the composite industry in the past, but they are on decline due to their bioincomatability (Šimkovic, 2008; Vilaplana, Stromberg, & Karlsson, 2010; Waisman, 2007). Even "green" synthetic polymers like polylactic acid (PLA) or polyhydroxybutyrate (PHB) are economically and ecologically more problematic than the use of polysaccharides such as cellulose that are provided by nature in excess. If starches used for fermentation to prepare PLA monomers were instead consumed by people suffering from hunger, then that would be a more sustainable use (admittedly a controversial point) (Vilaplana et al., 2010). Any functional advantages of synthetic fibers, such as in the case of nanotubes over abundant natural fibers, should be balanced against the financial and ecological costs. There are many sources of cellulose fibers available that can function as natural nanotubes which remain unexplored (Khalil, Bhat, & Yusra, 2012). This review does also not discuss those composites when synthetic polymers are involved in the preparation process.

ACPs could be divided into several groups. The first and the most logical choice would be according to the matrix or predominant polysaccharide type to demonstrate the structure–property relationship. According to that approach the first group would be all-cellulose composites (ACCs). Cotton composites are also included in ACCs. Cotton fibers are not part of cell wall architecture as it is in a case of plant cell wall cellulose fibers which are surrounded by hemicellulose polysaccharide and lignin. In this way cotton fiber crystalline surface could be chemically modified by direct solvent impregnation. The next group includes the combination of all available polysaccharides that were used for composite preparation. All types of polysaccharides are suitable as components of the composites except starch when the application is not in the food industry (BeMiller, 2011; Khalil et al., 2012). That exception is because the use of starch in applications other than food might raise food prices. This factor has not been proven yet, and starch-based composites are included in this review.

Another competing topic to polysaccharide utilization for composite preparation is the production of fuel from phytomass in the form of hydrogen (Ishida, Takenaka, Yamanaka, & Otsuka, 2006), hydrocarbons (Mousdale, 2010), alcohols or glycerol esters (Kargbo, 2010) which might affect the sustainability of phytomass consumption (Bartle & Abadi, 2010; Blažej & Košík, 1993; Kumar, Barrett, Delwiche, & Stroeve, 2009). Authors consider the term: phytomass, the organic mass resulting from photosynthesis of green plants as more exact than the term biomass, which has more general meaning ascribing all the mass produced by biological and biochemical transformations. It is especially important for distinguishing between mammal and plant cell architecture. APCs represent also an alternative to "fuel" processes as they could be part of technologies producing batteries, construction materials and other energy and carbon producing technologies due to economical and ecological factors (Ma & Sahai, 2013; Mousdale, 2010).

Another way of distinguishing APCs groups would be based on the polysaccharide solvent used for composite preparation, although there are methods for composite preparation which do not require solvents (extruder use, plasma or pressing at elevated temperatures). The exciting development in this category is the use of ionic liquid (IL) solvents. This topic will be discussed mainly in cellulose chapter but might be applied to all polysaccharides. But the best and probably the cheapest way to obtain a composite is to mix two or more polysaccharide derivatives that are soluble in the same solvent. The best and the most ecological solvent for this category would be water. On the basis of the above text we would like to add to the recent papers on the related topics (Habibi, Lucia, & Rojas, 2010; Huber et al., 2012; Khalil et al., 2012; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Siró & Plackett, 2010). Most cellulose derivatives require a complicated solvent system for their preparation. Probably they could be substituted with already used noncellulosic polysaccharides that were modified with acetyl-, hydroxypropyl-, carboxymethyl-, trimethylammoniumhydroxypropyl-, sulfate-, or other groups for polysaccharide composite applications in analogy to those discussed for cellulose (Fox, Li, Xu, & Edgar, 2011; Klemm, Heublein, Fink, & Bohm, 2005; Klemm et al., 2011; Liebert, 2010). Whenever possible, it is an advantage to be able to choose among several preparations according to economic and ecological considerations. Microfibrillated cellulose (MFC) technology has been determined to be healthy and environmentally safe (Vartiane et al., 2011). It is likely that all composites made solely from polysaccharides listed in Tab 1 are also safe. Here they are divided according to the application and chemistry basics they were prepared. In most of the cases they were divided according to the used matrix component.

2. All-cellulose and cotton related composites

Technically speaking, native celluloses from many sources are already composites, consisting of a mixture of two similar allomorphs (I_α and I_β) packed in parallel chain arrangement along with some less-crystalline material. Spruce wood cellulose consists of elementary fibrils composed of about 24 cellulose chains, possibly twisted, and with disorder on the surfaces (Fernandes et al., 2011). Other sources list 36 individual cellulose macromolecules assembled into each elementary microfibril. Celluloses from different sources will have different sizes and shapes of crystals (Dufresne, 2012; Elazzouzi-Hafraoui et al., 2008; Habibi et al., 2010; Leppänen et al., 2009). In contrast the chains of regenerated or mercerized cellulose II are arranged antiparallel in a two chain unit cell (Zugenmaier, 2001). The transition of cellulose I to cellulose II caused by pretreatment with IL is also affected by used source cell wall architecture (Chen et al., 2011). The reported values for stiffness of cellulose nanocrystals indicate that they are comparable to those reported for synthetic polymers with top value of polyethylene (235 GPa), when cross-sectional area of each individual molecule is considered (Dufresne, 2012). According to the reference the geometrical characteristics of cellulose nanocrystals from various sources indicate that the ratio of length (varies from

Table 1
All-polysaccharide composites[a].

Application	Components	Preparation method	Reference
Fiber	AC Cellulose I	Dissolution of pulp in DMAc/LiCl and subsequent fiber impregnation	Nishino, Matsuda, & Hirao (2004)
Films	Cellulose I Cellulose II	Dissolution of MCC in DMAc/LiCl	Gindl and Keckes (2005)
Fiber	Cellulose I AC	Fiber surface dissolution in DMAc/LiCl	Nishino and Arimoto (2007)
Sheets	Cellulose I AC	Partial dissolution of MCC in DMAc/LiCl at 5–20% conc.	Duchemin et al. (2007)
Fiber	Cellulose I Cellulose II PC	Mercerization of ramie fiber surface after impregnation	Qin et al. (2008)
Films	MCC NCC PC	DMAc/LiCl dissolution regeneration in water	Abbot and Bismarck (2010)
Fiber	Cellulose I AC	Surface dissolution of BC in LiCl/DMAC	Soykeabkaew, Sian, Gea, Nishino, & Peijs (2009)
Films	Cellulose I AC	CNW/MCC = 15/85 (v/v); in LiCl/DMAc 1.2 T magnetic field	Pullawan et al. (2012)
Films	Cellulose I Cellulose II	Dissolution in NaOH/urea/H_2O and mixed with CNW	Qi et al. (2009)
Films	NOC AC	Dissolution of cotton linters in DMAc/LiCl	Kondo et al. (2001)
Films	Cellulose iβ AC	Water-acetone solvent exchange; partial dissolution of NFC in BMIC	Yousefi et al. (2011)
Films	Cellulose I PM	Partial dissolution of MFC and filter paper in BMIC	Duchemin et al. (2009)
Films	Cellulose I Cellulose II	Dissolution in HEMIC	Ma et al. (2011)
Fiber	Cellulose I Cellulose II AC	Dissolution of NPNM in BMIC	Gindl-Altmutter et al. (2012)
Films	CAB CNW	Dispersing 5–10% CNW in the CAB matrix with or without TEC	Ayuk et al. (2009)
Films	TMSC CTA	Spin coating from chloroform	Taajamaa et al. (2011)
Films	CMC Cellulose I	Dispersion CNXLs in CMC water solution and drying	Choi and Simonsen (2006)
Hydrogels	QC CMC	Crosslinking at different QC/CMC ratios	Chang et al. (2011)
Fiber	TMAHP-C Cotton	Cross-linking of TMAHP-C and cotton with citric acid	Harifi and Montazer (2012)
Fiber	O-QCTSS Cotton fabric	Cross-linking of O-QCTSS and cotton fabric with citric acid	Fu et al. (2011)
Wound healing	Gauze Chitosan	Citric acid grafting of chitosan onto cellulose	Edwards et al. (2009)
Wound healing	Gauze Alginate	Citric acid grafting of alginate onto cellulose	Edwards et al. (2003)
Fiber	Cotton fiber Chitosan PA	LbL coating of cotton fiber with chitosan and phytic acid	Laufer et al. (2012)
Films	Chitosan MFC	Homogeneous fibril distribution due to chitosan charge (95%)	Nordqvist et al. (2007)
EPA	Cellulose II Chitosan	Dissolution in TFA, casting and drying at 60 °C	Cai and Kim (2009)
Films	BC Chitosan	Biosynthesis by *Acetobacto* xylinum and mixing with chitosan	Phisalaphong and Jatupaiboon (2008)
Wound healing	Methylcellulose Chitosan $TPPS_4$	Films formed from chitosan–methylcellulose mixture interacted with TPPS4 by binding to chitosan	Synytsya et al. (2012)
Films	Methylcellulose Chitosan	Suspension casting	Garcia et al. (2004)
Bacterial digestion	BC Xylan	Fermentation of BC/xylan composite	Weimer et al. (2000)
Fiber	CF Xylan	Sorption of xylan on CF surface	Henriksson and Gatenholm (2001)
Films	CNF BaX	Suspension casting from 5/95 to 20/80 (w/w) ratio	Peng, Ren, et al. (2011) and Peng, Chen, et al. (2011)
Films	NOC Xylan/XG	Dissolution of cotton linters and xylan or XG in DMAc/LiCl	Roubroeks and Kondo (2012)

Table 1 (*Continued*)

Application	Components	Preparation method	Reference
Plates	CI AC Hemi	Disintegrated, beated, molded and cold/hot-pressed	Nilsson et al. (2012)
Films	MC GM	Casting from 50/50 (w/w) water solution	Chambi and Grosso (2011)
Films	MC Pectin	Casting from 50/50 (w/w) water solution	Chambi and Grosso (2011)
Films	MC GM Pectin	Casting from 1:4:1 (w/w/w) water solution	Chambi and Grosso (2011)
Films	CL Chitosan	Dissolution in water/NaOH/thiourea	Morgado et al. (2011)
Films	Cellulose Chitosan	Dissolution in NMMO	Shin et al. (2009)
Films	CNC Chitosan	Cross-linking with adipoyl chloride	de Mesquita et al. (2012)
Films	Cellulose Chitosan	NaOH/thiourea dissolved suspension at 50/50 (w/w)	Almeida et al. (2010)
Drug delivery	CNCs Chitosan	Polyelectrolyte complex with charge dependent upon ratio	Wang and Roman (2011)
Battery	Cellulose Alginate	Dissolution in NaOH/urea Na^+ ions movement to anode	Kim et al. (2007)
Hydrogels	Chitin Cellulose	Dissolution in LiCl/NMP; crosslinking with BTCA	Kono and Zakimi (2013)
Fibers	Chitin Chitosan	Partial acetylation	Qin (2008)
Films	NFC Chitosan	Water-based suspension at 0–60% NFC content	Fernandes et al. (2010)
Sponges	Chitosan HA nCS	EDC cross-linking followed by lyophylization 10% nCS presence	Anisha et al. (2013)
Membrane	Chitosan Xanthan	Complexation at 1–1.15:1 weight ratio	Veiga and Moraes (2012)
Hydrogels	Chitosan Xanthan	Solution mixing (0.1 M HCl) at equal amounts and volumes	Martínez-Rubalcaba et al. (2007)
Foam	Chitosan Xylan	Citrate cross-linking at 1:1 (w/w)	Salam et al. (2011)
Membrane	Chitosan Pectin	Polyelectrolyte complex Ionic cross-linking	Chen et al. (2011)
Coacervate	Chitosan Gum Arabic	Electrostatic complexes	Espinosa-Andrews et al. (2007)
Films	Chitosan Guargun	Casting method	Rao et al. (2010)
Drug delivery	Chitosan Polyuronan	Amino-carboxyl interaction	Muzzarelli et al. (2004)
Films	Chitosan Starch	Pseudoplastic behavior	Garcia et al. (2006)
Films	Chitosan Starch	Mixed water solutions containing 25% of glycerol	Xu et al. (2005)
Fuel cell	Chitosan Alginate	Chitosan/Alginate 3/1 acidic water solution casting for film	Smitha et al. (2005)
Fuel cell	Chitosan HEC	Membrane with methanol permeability & conductivity	Mohanapriya et al. (2009)
Films	Chitosan Cellulose I	Reinforced chitosan with cellulose nanoparticles	Khan et al. (2012)
Films	Chitosan Heparin	Poyelectrolyte complex nanoparticles	Boddohi et al. (2009)
Medical	Chitosan Heparin	Cross-linking of mixed solutions with glutaraldehyde	Yu, Wu, Mi, & Shyu (2008)
Films/fiber/spheres	Heparin Cellulose	Dissolution in RTIL	Murugesan et al. (2006)
Fiber	Heparin Cellulose	Dissolution in EMIB Dissolution in BMIC	Viswanathan et al. (2006)
Artificial tissue	Heparin Cellulose	Epoxy-crosslinking of heparin with cellulose	Tseng et al. (2011)
Artificial tissue	Hyaluronan Chitosan	Oxidized coupling	Nair et al. (2011)
Films	Hyaluronan PC-CH	Electrolyte multilayer	Kujawa et al. (2007)
Microgels	Hyaluronan Heparin	Inverse emulsion polymerization of hyaluronan and heparin	Zhao et al. (2011)

Table 1 (*Continued*)

Application	Components	Preparation method	Reference
Antioxidant	Xylan Chitosan	Maillard reaction products	Li et al. (2013)
Films	Xylan Chitosan	Ionic interaction	Gabrielii et al. (2000)
Films	CNW Xylan	Suspension casting	Saxena et al. (2009)
Films	BX CNF	Suspension casting from 50/50 to 80/20 (w/w) ratio	Hansen et al. (2012)
Films	AX MFC	Casted of enzymatically modified rice AX with 15% MFC	Mikkonen et al. (2012)
Films	AX MFC	Casted suspension of AX containing 5–15% MFC	Stevanic et al. (2011)
Hydrogels	Xylan kC	Swelling increase	Meena et al. (2011)
Films	GGM MFC	Drying of casted suspension containing 5–15% MFC	Mikkonen et al. (2011)
Films	KGM Curdlan	Different blending ratios	Wu et al. (2012)
Films	GM Pectin	Casting from 50/50 (w/w) water solution	Chambi and Grosso (2011)
Films	GM Chitosan	Solution casting of GM/Chitosan blends	Du et al. (2013)
Films	GGM KGM	Casting of GGM/KGM mixtures	Mikkonen et al. (2010)
Hydrogels	GM Xanthan	Coil–helix transition	Fitzpatric et al. (2013)
Antiadhesion membrane	PGA-ADH sHA-CDI	Cross-linking	Peng, Ren, et al. (2011) and Peng, Chen, et al. (2011)
Sorbent	Pectin Cellulose	Sorption of pectin on cellulose	Zykwinska et al. (2007)
Films	XG Chitosan Starch	Casting/solvent evaporation	Simi and Abraham (2010)
AMA	Cellulose XG	Conjugation	Albersheim et al. (2004)
Cell adhesion	Cellulose XG	Prolification of endothelial cells	Bodin et al. (2007)
Drug delivery	XG HA	Drug/mucin/XG/HA interaction in solution using NMR	Uccello-Barretta et al. (2013)
Films	HPPS kC	Casting method	Lafargue et al. (2007)
Hydrogel	Agarose CNW	Humidity changes; particle reorientation in magnetic field	Osorio-Madrazo et al. (2012)
Drug delivery	Starch Pectin	Blends loaded with diclofenac	Soares et al. (2013)
Films	Starch Alginate SDA/RE	Food shelf life prolongation due to antibacterial properties	Yan et al. (2013)
Films	CNP GPS	Casting	Chang, Jian, Zheng, et al. (2010) and Chang, Jian, Yu, et al. (2010)
Films	CMC Starch	CA cross-linking	Ghanbarzadeh et al. (2011)
Plates	CF PIS	Mixing at 170 °C and hot pressed at 160 °C	Curvelo et al. (2001)
Films	Starch Agar	Casting method	Wu et al. (2009)
Films	PIS SNC	SNC-PIS mixed solutions degassing and drying	Garcia et al. (2011)
Films	TPS NFC	Dispersion of NFC in TPS and film casted	Kaushik et al. (2010)
Films	MFC AP	Nanostructured network with 50/50 AP/glycerol matrix	Svagan et al. (2007)
Foams	AP MFC	Mixing NFC (up to 70 wt%) with AP and freeze drying	Svagan et al. (2008)
Films	PIS CN	CN filler in GPS matrix by casting process	Chang, Jian, Zheng, et al. (2010) and Chang, Jian, Yu, et al. (2010)
Films	SNC Pullulan	SNC reinforced pullulan films	Kristo and Biliaderis (2007)
Films	Cellulose I Starch	Mixing BCC (0–20%) with plasticized starch and casting	Liu et al. (2010)
Films	PIS Cellulose I	Film casted-ReNC-reinforced PIS suspension	Lu et al. (2006)

Table 1 (*Continued*)

Application	Components	Preparation method	Reference
Plates	PlS Cellulose I	Mixing starch, plasticizers, NFC with water and hot-pressing	Teixeira et al. (2009)
Hydrogels	Alginate Pullulan	Blend solutions shear-thinning behavior	Xiao et al. (2012)
Sponges	Alginate OCN	Ca^{2+}-crosslinked alginate with OCN and lyophylization	Lin et al. (2012)
Membrane	Alginate HEC	Phosphoric acid crosslinking	Kalyani et al. (2006)

[a] *Abbreviations*: AC, amorphous cellulose; AMA, antimicrobial agent; AP, amylopectin; BaX, bamboo xylan; BC, bacterial cellulose; BMIC, 1-butyl-3-methylimidazoliu chloride; BTCA, 1,2,3,4-butaneteracarboxylic dianhydride; BX, birch xylan; CAB, cellulose acetate butyrate; CF, cellulose fiber; CL, cellulose linters; CMC, carboxymethyl cellulose; CN, cellulose nanoparticles; CNF, cellulose nano-fibers; CNP, chitosan nanoparticles; CNW, cellulose nanowhiskers; CNXLs, cellulose nanocrystals; CS, condroitin sulfate; CTA, cellulose triacetate; DA, debranched arabinan; EC, ethylcellulose; EMIB, 1-ethyl-3-methyl-imidazolium benzoate; EPA, electoactive paper actuator; GC, glycol chitosan; GM, glucomannan; GGM, galactoglucomannan; GPS, glycerol plasticized starch; GX, glucurono-xylan; HA, hyaluronic acid; HEC, hydroxyethyl cellulose; Hemi-hemicelulose; HEMIC, 1-(2-hydroxyetyl)-3-metylimidazolium chloride; HPPS, hydroxy-propylated pea starch; kC, kappa-carrageenan; KGM, konjac glucomannan; LbL, layer by layer; MC, methylcellulose; MBC, microbial cellulose; MCC, microcrystalline cellulose; MFC, microfibrillated cellulose; NC, nanocrystallinintes; NCC, nano-crystalline cellulose; NFC, nanofibrilated cellulose; NMP, N-methyl-2-pyrrolidinone; NOC, nematic ordered cellulose; NPNM, needle-punched nonwoven mats; NPs, nanoparticles; nCS, nano-condroin sulfate; ONC, oxidized nanocellulose; O-QCTSS, O-quaternized-N-chitosan Schiff bases; PA, phytic acid; PC, paracrystalline cellulose; PC-CH, phosphoryl-choline-modified chitosan; PCWC, primary cell wall cellulose; PGA-ADH, adipic acid dihydrazide grafted polygalacturonic acids; PM, paracrystalline matrix; PMCC, pretreated microcrystalline cellulose; PlS, plasticized starch; QC, quaternized cellulose; RC, regenerated cellulose; RE, rosemary extract; ReNC, ramie nanocrystallites; RTIL, room-temperature ionic liquid; SDA, sodium dehydroacetate; sHA-CDI, carbonyldiimidazole grafted short-chain hyaluronic acid; SNC, starch nanocrystals; TC, thiolated chitosan; TEC, triethyl citrate; TFA, trifluoroacetic acid; TMAHP-C, trimethylam-monium-2-hydroxyprophyl-cotton; TMC, trimethylchitosan; TMSC, trimethylsilyl cellulose; $TPPS_4$, *meso*-tetrakis-(4-sulfonato-phenyl)-porphyrin; TPS, thermoplastic starch; XG, xyloglucan.

over 1000 to 80 nm)/cross section (2–120 nm) is proportional to the modulus value.

The diameter of cotton fiber is about 10–20 μm, while its length is about 20 mm at 1.5–1.6 g/cm^2 density, 287–800 MPa tensile strength, 5.5–12 GPa Young's modula and 7–8% elongation at break. Its production (21.2 Mt in 2003) is the highest of all types of fiber on the market (Charlet, 2012; Zeronian, 1991). Cotton fiber is not bound to lignin, hemicelluloses, or pectin but it is necessary to "scour" the cotton before processing the fiber since the harvested bolls do contain all of the above materials. Wood cellulose, of course, differs greatly from cotton fiber in the size from crystalline molecular sizes. ACCs could be prepared also by using cotton as a component.

Unmodified cotton contains mostly monoclinic cellulose I as confirmed by combination of FTIR, XRD and compared with an in situ protein-binding methodology using cellulose-directed cellulose-binding models (Kljun et al., 2011). It is not known if it is in alpha or beta alloform or how many cellulose macromolecules are building a fibril like structure as it was observed on wood cellulose fibril. During mercerization intermolecular hydrogen bonds are broken and Na-cellulose I is formed. At higher alkali concentrations Na-cellulose II forms, wherein intermolecular and intramolecular hydrogen bonds are broken and the cellulose takes a 3-fold helical shape (Zugenmaier, 2001). When studied on a single cotton fiber using synchrotron radiation microdiffraction and microdrop technique it was possible to transform cellulose I to Na-cellulose I by exposure of the fiber to 1 N NaOH locally in a 50 μm in diameter microdrop (Schoeck, Davies, Martel, & Riekel, 2007). Subsequent exposure of the NaOH containing macrodrop to a stream of H_2O or HCl microdrop converted part of the Na-cellulose I back into cellulose I.

There are two distinct strategies for preparation of ACCs. The first involves dissolving a portion of cellulose which is then in the second step regenerated in the presence of undissolved cellulose. A second route involves partial dissolution of the surface of cellulosic fibers and then regenerated in situ to form matrix around the undissolved portion. It is evident that mechanical properties of ACCs are less attractive than those of poor cellulose alloforms (Huber et al., 2012). The total amount of crystalline form of the final material and the dimensions of the homogeneous regions might be influentional, although the used solvent might also affect the future technology. The viscoelastic properties of ACCs could not be exactly interpreted due to lack of data and their interpretation problems, while the optical properties depend upon the degree of dissolution which is related to the dimensions of cellulose crystalinites.

From all ACC examples nine times N,N-dimethylacetamide/LiCl (DMAc/LiCl) solvent system was used (Table 1). In one case the tensile strength of formed ACC was further improved by mercerization in the second step (Qin, Soykeabkaew, Xiuyuan, & Peijs, 2008; Table 2). In eight cases beyond cellulose II also amorphous cellulose was formed as confirmed by crystallinity decrease. By dissolution of cotton linters in DMAc/LiCl solution and subsequent precipitation in water a swollen films were prepared with a new cellulose supramolecular structure called *nematic order cellulose* (NOC; Kondo, Togawa, & Brown, 2001; Table 1). In this way a non-crystalline, but ordered ACC was prepared consisting of regions with architecture ranging from non-crystalline nematic to amorphous.

During the last decade microfibrillated cellulose (MFC) was essentially used in nanocomposites due to its reinforcement property (Lavoine, Desloges, Dufresne, & Bras, 2012; Siró & Plackett, 2010). Its nano-scale dimensions and its ability to form a strong entangled nanoporous network, however, have encouraged the emergence of new high-value applications. New sources, new mechanical processes, and new pre- and post-treatments are currently under development to reduce the high energy consumption and produce new types of MFC materials on an industrial scale. For all of the examples of ACCs preparation when MFC was chosen there was cellulose I a reinforcing component (Table 1). In two example that were created by partial dissolution of two different forms of cellulose, filter paper and MFC in DMAc/LiCl or 1-butyl-3-methylimidazolium chloride (BMIC) yielded a composites with matrix consisting from amorphous and paracrystalline cellulose (Duchemin, Mathew, & Oksman, 2009; Duchemin, Newman, & Staiger, 2007; Table 1). From other three examples when IL solvents were used for ACCs preparation follows that amorphous cellulose could be formed beside cellulose I and cellulose II in dependance uppon conditions used (Gindl-Altmutter et al., 2012; Ma, Zhao, Li, Li, & Ou, 2011; Yousefi, Nishino, Faezipour, Ebrahani, & Shakeri, 2011; Tables 1 and 2).

ACC films were prepared, for the first time, from native cellulose nanowhiskers and cellulose matrix regenerated from aqueous NaOH–urea solvent system on the basis of their temperature-dependent solubility (Qi, Cai, Zhang, & Kuga, 2009). The cellulose whiskers retained their needlelike morphology with mean length and diameter of 300 and 21 nm, respectively, as well as native

Table 2
Properties of two-component APC fibers/films[a].

MC/unit content	RC	E [GPa]	σ_b [MPa]	Other parameter	Reference
AC	C I	20 (at 200 °C)	480 (at 25 °C)	10^{-7} K^{-1} (LTEK)	Nishino et al. (2004)
C II/0.41	C I	14.9	215.1	ε = 3.6%	Gindl and Keckes (2005)
AC	C I	8.2 (at 25 °C)	211 (at 25 °C)	E'20 GPa/−150 °C	Nishino and Arimoto (2007)
C I/0.85	C II	25	440–540	–	Qin et al. (2008)
AC	C I	18	411	WTF = 9.0 MJ/m^3	Soykeabkaew et al. (2009)
AC/0.15	C I	9.9–12.5	149–176	ε = 3.8–4.1%	Pullawan et al. (2012)
CAB/0.9	C I	E' = 1.4 ± 0.1*	E' = 2.1 ± 0.9°	Tan δ peak 147°	Ayuk et al. (2009)
AC	C I	20	208	ε = 9.8%	Yousefi et al. (2011)
AC	C I	5.75–10.8	91.8–124.1	–	Duchemin et al. (2009)
Cellulose II	C I	3.634	49	ε = 2.11%	Ma et al. (2011)
C II/AC	C I	7.2 ± 1.0	78 ± 4	ε = 5.2 ± 2.6%	Gindl-Altmutter et al. (2012)
C II/0.8–1	C I	5	124–157	ε = 5–8%	Qi et al. (2009)
Mc/0.5	GM	–	41.2	ε = 3.7%	Chambi and Grosso (2011)
Mc/0.5	P	–	42.7	ε = 3.5%	Chambi and Grosso (2011)
GM/0.5	P	–	64.7	ε = 3.3%	Chambi and Grosso (2011)
Ch/0.4	C I	3.7	108	–	de Mesquita et al. (2012)
Ch/0.95	C I	4.31 ± 0.61	89 ± 14	ε = 4 ± 1%	Nordqvist et al. (2007)
Ch/0.95	C I	3.0	98	ε = 4%	Khan et al. (2012)
Xylan/0.8	C I	3.404	39.5 ± 2.2	ε = 1.4 ± 0.1%	Peng, Ren, et al. (2011) and Peng, Chen, et al. (2011)
H/0.05–0.2	C I	6.3–12.0	109–74	ε = 6.3–2.4%	Nilsson et al. (2012)
Xylan/0.5	C I	5.2–7.6	23–57	W = 1.9–2.8 × 10^{-11}	Hansen et al. (2012)
GGM	C I	0.800–0.900	–	–	Mikkonen et al. (2011)
AX/0.85	C I	2.5	95 ± 19	ε = 11%	Mikkonen et al. (2012)
AC	Ch	–	23.8 ± 1.3	ε = 2.14 ± 0.1%	Morgado et al. (2011)
AC	Ch	–	65	–	Shin et al. (2009)
Ch/0.4	C I	6.7	115	OT = 227 °C	Fernandes et al. (2010)
Corn starch	C I	0.020–0.210	2.5–12.8	–	Lin et al. (2012)
Starch	Ch	–	–	W = 3.8–4.5 × 10^{-11}	Garcia et al. (2006)
Starch	Ch	–	34–40	ε = 59–61%	Xu et al. (2005)
SA	Ch	–	–	C = 0.042 S/cm	Smitha et al. (2005)
KGM	Curd	–	42.93 ± 1.92	–	Wu et al. (2012)
Starch/0.92	C I	0.2103	12.8	ε = 22%	Liu et al. (2010)
Starch	CM	–	16.11	W = 2.34 × 10^{-7}	Ghanbarzadeh et al. (2011)
PIS/0.84	C I	0.32 ± 0.07	11 ± 2	ε = 11 ± 0.2%	Curvelo et al. (2001)
Starch	Agar	–	11.76	ε = 58.3%	Wu et al. (2009)
PulI/0.6	SN	1.200	30	ε = 18%	Kristo and Biliaderis (2007)
TPS/0.6	C I	0.480	6.9	ε = 15%	Lu et al. (2006)
TPS/0.95–1	C I	–	11	ε = 110%	Chang, Jian, Zheng, et al. (2010) and Chang, Jian, Yu, et al. (2010)
TPS/50	C I	0.843	4.8	ε = 71%	Teixeira et al. (2009)
TPS/0.85–1	C I	0.224 + 15.4	6.78 + 0.55	SM = 486	Kaushik et al. (2010)
AP/0.3	C I	6.2	160	9.4 MJ/m^3 (WOF)	Svagan et al. (2007)
AP/0.6	C I	0.007	510	FWC = 8.4%	Svagan et al. (2008)

[a] *Abbreviations:* AC, amorphous cellulose; AP, amylopectin; AX, arabinoxylan; C, conductivity; CF, cellulose fiber; Ch, chitosan; C I, cellulose I; C II, cellulose II; CM, carboxymethylcellulose; Curd, curdlan; E, tensile modulus; E', storage modulus at 30 °C (*) or at 155 °C (°); σ_b, tensile strength at the break; ε, elongation at the break; FWC, foam water content; GGM, galactoglucomannan; GM, glucomannan; KGM, konjac glucomannan; LTEK, linear thermal expansion coefficient; MC, matrix component; Mc, methyl-cellulose; NC, nanocrystals; OT, onset temperature; Pull, pullulan; P, pectin; RC, reinforcing component; SA, sodium alginate; SM, storage modulus [MPa] at 30 °C; SN, starch nanocrystals; T, transparency; Tan δ peak 147°Tan δ peak the E' vs. temperature relation was at 147 ± 1 °C; T_d, DTG peak; TPS, thermoplastic starch; W, water vapor permeability [g Pa^{-1} m^{-1} s^{-1}]; WTF, work-to-fracture.

crystallinity when added to the latter solution at ambient temperature. The composite films were isotropic and transparent to visible light and showed good mechanical properties as a result of the reinforcement by the whiskers. By varying the ratio of the cellulose whiskers (0–20%) to regenerated cellulose matrix (cellulose II), the tensile strength and elastic modulus of the nanocomposite films could be tuned to reach 124 MPa and 5 GPa, respectively (Table 2). By preventing the shrinkage of the film during drying the tensile strength could be improved up to 157 MPa with calculated Hermans' orientation parameter of 0.30.

Cellulose acetate butyrate (CAB) nanocomposite films were prepared by dispersing cellulose nanowhiskers (5 and 10 wt%) in the CAB matrix with and without plasticizer in aceton as the dispersing and casting medium (Ayuk, Mathew, & Oksman, 2009). The plasticized nanocomposites using triethylcitrate at 5 wt% were more transparent than the unplasticized composites, indicating a better dispersion of cellulose nanowhiskers in CAB in the presence of a plasticizer. Dynamic mechanical properties and thermal stability increased, whereas transparency decreased, with increased cellulose nanowhiskers content.

The preparation of ultrathin (<100 nm) films from mixture of trimethylsilylcellulose (TMSC) and cellulose triacetate (CTA) with phase-specific pore growth was demonstrated (Taajamaa, Rojas, Laine, & Kontturi, 2011). The films were constructed, in a single-step process, by spin coating mixtures from chloroform. Atomic force microscopy (AFM) revealed a nano- and micron-scale phase separated structure, typical for interfacial polymer blends. Vertical phase separation had resulted in a continuous layer of TMSC next to the substrate with laterally phase separated CTA and TMSC on top. Furthermore, X-ray photoelectron spectroscopy (XPS) and contact angle measurements indicated the presence of thin overlayer of TMSC. In addition, increased relative humidity conditions during spin coating resulted in the formation of pores when the CTA weight percent in the blend was in the range from 17 to 83% (TMSC/CTA blend ratios 5:1, 2:1, 1:2, and 1:5). Closer analysis of the morphology indicated that the pores resided exclusively in the CTA phase. It is concluded that the obtained ultrathin polysaccharide films with tailored surface pores, morphology and wettability are expected to be useful in emerging nanotechnologies while having the advantage of an effortless manufacturing process.

The effect of cellulose nanocrystals (CNXLs) as fillers on the properties of CMC-based composites is of interest in the development of novel or improved applications for hydrogel polymers (Choi & Simonsen, 2006). The composite material was composed of CMC, MCC or CNXL, with glycerin as a plasticizer. CNXL and MCC concentrations ranged from 5 to 30%. Glycerin concentrations were kept constant at 10%. CNXLs improved the strength and stiffness of the resulting composite compared to MCC. In addition, a simple heat treatment was found to render the nanocomposite water-resistant.

A different category of composite processing is represented by cross-linking quaternized cellulose (QC) and carboxymethyl cellulose (CMC) with epichlorohydrin in NaOH aqueous solution (Chang, He, Zhou, & Zhang, 2011). The swelling behavior of the QC/CMC hydrogels was studied as a function of polymer composition, pH, and salt concentration. The equilibrium swelling ratio of the hydrogel in ultrapure water depended strongly on the composition, and increased dramatically from 8.6 to 498 g/g with change of the weight ratio of QC to CMC from 3:1 to 1:3 (w/w). The results revealed that CMC mainly contributed to increasing the swelling as a result of strong water adsorption, whereas QC played a role in controlling of the charges in the QC/CMC system, leading to the pH sensitivity. It is a pity that the authors also did not test the swelling behavior of CMC/QC mixtures that were not cross-linked. That might have shown the behavior to be dependent more on the ratio of the oppositely charged groups functioning like ionic crosslinkers.

New insight into nano-composite preparation represents cotton cross-linking (Harifi & Montazer, 2012). This has been introduced as a necessary process for various purposes especially creating cotton fabric with anti-wrinkling properties. Generally, in a cross-linked cotton fabric, cellulose chains are bridged through chemical reaction with certain bifunctional reagents. Various approaches have been developed to cross-link cellulose along with imparting other properties, like flame retardancy, mechanical properties, antimicrobial properties, improved coloration and dyeing, water repellency, etc. From the possible cross-linkers functioning as anti-wrinkling agents, we could mention tetramethylolacetylenediurea, dimethylethylurea, triazones, dimethyldihydroxyethylurea, dimethyloldihydroxyethyleneurea and carbamate. All of them have advantages and disadvantages, the worst of which is formaldehyde release. Among the new agents being developed, polycarboxylic acids are the most promising non-formaldehyde durable press finishes. Cellulose esterification by polycarboxylic acid proceeds in two steps: formation of cyclic anhydride intermediate by the dehydration of two carboxyl groups, and the reaction between cellulose and the anhydride intermediate to form ester. Another possibility is ionic cross-inking, which can be accomplished by subjecting cotton fabric successively to partial carboxymethylation using monochloroacetic acid and sodium hydroxide and then cationization using 3-chloro-2-hydroxypropyl trimethylammonium chloride. While partial carboxymethylation introduces negatively charged groups into the cotton, the cationization reaction provides positively charged groups thereby causing ionic cross-linking. Ionic cross-linking of cotton fabric significantly improved its wet crease recovery angle, tensile strength and elongation at break with a little improvement in dry recovery angle compared with that of untreated cotton fabric.

The best mechanical properties on ACCs were obtained for ramie fiber in combination with dissolved craft pulp using DMAc/LiCl (Qin et al., 2008). The values has dropped when IL were used as solvents. Also use of nanowhiskers in combination with regenerated cellulose II matrix obtained by dissolution in NaOH/urea/water solvent resulted in lower modulus and tensile strength than DMAc/LiCl treatment. The tensile strength obtained under magnetic field using cellulose nanowhiskwrs (CNWs) was smaller than those of previous examples (Pullawan, Wilkinson, & Eichorn, 2012; Table 2).

3. Composites made by combining cellulose with other polysaccharides

Chitosan has attracted considerable interest in relation to cotton cross-linking due to its biological activities such as antimicrobial effects (Fu, Shen, Jiang, Huang, & Yan, 2011). Cellulose fibers are negatively charged due to carboxyl groups introduced by air oxygen oxidation. Composites based on a combination of cotton and chitosan fiber might be beneficial and find application in the textile industry and many medical applications. Quaternized chitosan/cotton fiber composites have been prepared to remove Au^{3+}, Pb^{2+}, Ni^{2+}, Cd^{2+} and Hg^{2+} ions. Most of the chitosan composites find application in removing heavy metals, but all-polysaccharide composites of this type seem to be environmentally safer because they would be more easily degraded by microorganisms after recycling the heavy metals, than the synthetic polymer composites (Ngah, Teong, & Hanafiah, 2011).

A derivatized cotton wound dressing bearing a net positive charge was designed to accelerate thrombosis and aggregation of blood platelets and promote hemostasis (Edwards et al., 2009). Cellulose and chitosan dressing bearing aminoglucan functionality, were created by grafting chitosan onto cotton and preparing aminized cotton. The preparation of chitosan-grafted cotton dressings was completed with a citric acid grafting onto cellulose. Aminated cotton was functionalized as an ethylamino-ether cellulose derivative. The chitosan-grafted and aminized cotton demonstrated a dose–response gelling of citrated sheep blood.

Occlusion and elasticity were combined in a novel cotton-based alginate dressing containing a nontoxic elastase inhibitor (Edwards, Bopp, Batiste, & Goynes, 2003). Cotton gauzes were modified with a textile finishing process for incorporating alginate to yield a dressing material that retains elasticity while enhancing absorption. The algino-cellulose conjugates were formed through citric acid crosslinking of cellulose and alginate. The alginate-citrate finishes were combined with the neutrophilic elastase inhibitor, oleic acid, to demonstrate the ability of the algino-cellulose fibers to release the inhibitor and neutralize destructively high levels of neutrophil elastase found in nonhealing and burn wounds. Wetting of the gauze surface resulted in formation of hydrated gel on the yarns with apparent swelling of the film and the fiber-coated alginate.

An effort to reduce flammability was examined by preparation of films of cationic chitosan and anionic phytic acid (PA) on cotton fabric via LbL assembly (Laufer, Kirkland, Morgan, & Grunlan, 2012). Altering the pH of aqueous deposition solutions modifies the composition of the final nanocoating. Films created at pH 6 were thicker and had 48 wt% PA in the coating, while the thinnest films (PA content of 66 wt%) were created at pH 4. In a vertical flame test, fabric coated with PA content in 30 layers completely extinguished the flame, while uncoated cotton was completely consumed. This superior performance is believed to be due to high phosphorus content that enhances the intumescent behavior of these nanocoatings.

The combination of MFC with chitosan for film preparation resulted in slight improvement in mechanical properties at 5% MFC content (Nordqvist et al., 2007). Transparent films could be shaped in the wet state. The uniform film transparency indicated that MFC did not scatter light to any significant degree because the thin fibril/fibril bundles were well dispersed. The mechanical data obtained under dry and wet conditions indicated that the MFC played a more important role in a “weak” wet chitosan matrix than in “strong” dry matrix. The values listed in Table 2 were obtained on dry state, while the values obtained under wet condition were measured by wetting the dryed film.

The combinations of methylcellulose and chitosan (3:1; 1:1, and 1:3) were used for preparation of composites modified with *meso*-tetrakis-(4-sulfonatophenyl)-porphyrin suitable for drug delivery or wound healing application (Synytsya, Grafová, Slepička, Gedeon, & Synytsya, 2012). It was confirmed that the porphyrin macrocycles had a strong affinity toward chitosan and did not interact with the methylcellulose. SEM and AFM images confirmed that the porphyrin macrocycles caused structural changes on the film surface and within the film layer. The addition of methylcellulose improved film mechanical and physical properties due to water-solubility. Methylcellulose films and composite chitosan–methylcellulose films have intermediate tensile properties (Garcia, Pinotti, Martino, & Zaritzky, 2004). Apparent viscosity and consistency index of the mixtures are higher than those of methylcellulose or chitosan suspensions.

Agarose hydrogels filled with cellulose nanowhiskers were strained in uniaxial stretching under different humidity conditions (Osorio-Madrazo et al., 2012). The orientation of the cellulose whiskers was examined before and after testing with an X-ray laboratory source and monitored in situ during loading by synchrotron X-ray diffraction. The aim of this approach was to determine the process parameters for reorienting the cellulose nanowhiskers toward a preferred direction. Results show that a controlled drying of the hydrogel is essential to establish interaction between the matrix and the cellulose nanowhiskers, which allows for a stress transfer during stretching and thereby promotes their alignment. Rewetting of the sample after reorientation of the cellulose nanowhiskers circumvents a critical increase of stress. This improves the extensibility of the hydrogel and is accompanied by further moderate alignment of the cellulose nanowhiskers. Following this protocol, cellulose nanowhiskers with an initial random distribution can be reoriented toward a preferred direction, creating anisotropic nanocomposites.

The first cellulose–xylan composites were prepared from bacterial cellulose and tobacco xylan at 88/12 weight ratio (Weimer, Hackney, Jung, & Hatfield, 2000). The XRD profiles of bacterial cellulose and cellulose/xylan composite prepared by fermentation in media supplemented with 5% glucose and 0.2% xylan were virtually identical. This confirms that cellulose component of the produced composite is in crystalline form while xylan is amorphous. The data suggest that intimate association of xylan and cellulose, as is typically found in secondary plant cell walls, does not inhibit the rate of digestion of the component polysaccharides.

When cotton linters were exposed to a 5% water solution of xylan from birchwood at 110 °C for 2 h at pH 8, the substrates showed an increase of weight of approximately 6.5%, and visualization by AFM revealed regular particles on fiber surfaces (Henriksson & Gatenholm, 2001). The amount of xylan deposited on the fibers could be varied form 2% up to 20% depending on treatment conditions. At low yields the fibers were coated with a homogeneous layer, while at higher yields (20%) regular particles of micron size were identified.

Cast films were also prepared from cellulose nanofibers (CNFs) and bamboo xylan mixtures in water. They had better mechanical properties when the cellulose was in the majority in comparison to mixtures with 80% xylan content (Peng, Ren, Zhang, & Sun, 2011). Similar method was used for preparation of films from CNFs and birch xylan at 50/50 to 20/80 (w/w) ratio (Hansen, Blomfeld, Hedenqvist, & Plackett, 2012). Without the use of plasticizer the modulus values were from 7.6 to 5.2 GPa and stress values between 57 and 23 MPa (Table 2).

An attempt was made to characterize an order of state of a matrix consisting of cotton linters cellulose and hemicellulose induced by stretching never-dried binary blended films (Roubroeks & Kondo, 2012). In non-stretched films, the beech xylan component easily adapted into the semicrystalline state, while the Tamarind seed xyloglucan component remained amorphous. Once both blended films were stretched, each component tended to be close enough to the adherent macromolecule, and the interaction resulted in typical morphological orders at the nano- and microscale levels. Xylan semicrystalline state was confirmed to be a liquid crystalline form. Analogical situation was observed on seaweed xylan in mixture with cellulose when presence of both components contributed to XRD profile (Lahaye, Rondeau-Mouro, Deniaud, & Buleon, 2003).

Three different softwood pulps are compared; an acid sulfite dissolving grade with high cellulose purity, an acid sulfite paper grade pulp and a paper grade kraft pulp, the later two both containing higher amounts of hemicelluloses (Nilsson, Galland, Larsson, Gamstedt, & Iverson, 2012). Composites based on the acid sulfite pulps exhibited twice as high Young's modulus as the composite based on paper grade kraft pulp, 11–12 and 6 GPa, respectively. The explanation is most likely the difference in beating response of the pulps. Also the water retention value (WRV) is similarly low for the two molded sulfite pulps (0.5 g/g) as compared to the molded kraft pulp (0.9 g/g). During compression molding, cellulose fibril aggregation occurs to higher extent in the acid sulfite pulps as compared to the kraft pulp. The difference in hemicellulose content and structure seems to affect the aggregation behavior and WRV of the investigated biocomposites.

Films casted from water solution mixtures of methylcellulose and glucomannan or methylcellulose and pectin at 50/50 (w/w) ratio have similar mechanical properties (Chambi & Grosso, 2011; Table 2). Their WVP values are 0.317 or 0.272 g mm/h m^2 kPa at 6.7 or 4.3% humidity content.

In the next example cotton-linter cellulose (3 g) and chitosan (1.5 g) in water/NaOH/thiourea mixture at ratio 89/5/6 (w/w/w) was dissolved by adding to 97 g or 98.5 g of solution within 5 min. Subsequent separation of undissolved parts the films were prepared by casting on polypropylene plate (Morgado, Frollini, Castellan, Rosa, & Coma, 2011). The ratios of individual components were 50/50, 60/50, 70/30, 80/20, and 90/10. The highest asperity thickness (1.2 μm) was observed for 90/10 film (chitosan/cellulose), while for cellulose film it was 0.21 μm. The tensile strength ($\sigma_b = 23.8 \pm 1.3$ MPa) and elongation at the break ($\varepsilon_b = 2.14 \pm 0.1\%$) were measured for 90/10 chitosan/cellulose film, while at 50/50 ratio it was 4.0 ± 1.0 MPa and $0.76 \pm 0.02\%$. In this way high quality films were prepared.

Cellulose/chitosan blend films were prepared also by dissolution in N-methylmorpholine-N-oxide (NMMO) at 100 °C and subsequent processing under a pressure of 70 kg/cm^2 for 8 min (Shin, Shieh, & Twu, 2009). The optimal content of chitosan was proved to be at 3%, when the surface was smooth and the tensile strength at a peak (65 MPa). The films were non-diffusible with antibacterial properties. The better mechanical properties of this work in comparison with the previous might be in processing, when under pressure the intermolecular dehydration and crosslinking took place.

New nanocomposites were obtained through covalent linkage between cellulose regions containing nanocrystals (CNCs) and chitosan (CH; de Mesquita, Donnici, Teixeira, & Pereira, 2012). The CNCs were first functionalized with methyl adipoyl chloride and the reactive end groups on the surface of the CNCs were reacted with the amino groups of the CH in an aqueous medium. The nanocomposites demonstrated a significant improvement in the mechanical performance and considerable decrease in the hydrophilicity relative to the neat chitosan.

Environmentally friendly composites were successfully prepared by dissolving cellulose and chitosan (50/50, w/w, ratio) in an NaOH/thiourea solvent with subsequent film casting (Almeida, Frollini, Castellan, & Coma, 2010). Under the considered conditions, NaOH/thiourea led to chain depolymerization of both biopolymers

without a dramatic loss of film forming capacities. DSC analyses led to exothermic peaks close to 285 and 315 °C for composite, compared to the exothermic peaks of chitosan (275 °C) and cellulose (265 and 305 °C), suggesting interactions between chitosan and cellulose.

Novel polyelectrolyte–macroion complex between chitosan and CNCs for potential application in drug delivery was prepared (Wang & Roman, 2011). CNCs were prepared by sulfuric acid hydrolysis of wood pulp. In titration of chitosan solution with CNC suspension, the turbidity reached a plateau, but it had a maximum and then decreased when the direction of titration was reversed. The particles were composed primarily of CNCs and ranged in size from few hundred nanometers to several micrometers, depending on the cellulose/chitosan ratio. Particles formed at amino/sulfate group molar ratio > 1 were nearly spherical in shape and positively charged, whereas particles formed at ratios < 1 had well-defined nonspherical shapes and were negatively charged.

Electro-active paper was made from cellulose and sodium alginate (up to 5%) by dissolution in NaOH/urea system (Kim, Wang, Chen, Lee, & Yun, 2007). The blended films were tested under conditions of varying frequency, voltage, humidity and time. The DC voltage activation showed that sodium ions in the actuator moved to the negative electrode, which dictates ion migration effect in the actuator. The actuation principle is a combination of two mechanisms: ion migration and piezoelectric affect associated with dipolar orientation. This combination has the potential for enhancing the properties of electro-active paper as a new smart material that has a low actuation voltage and fast response along with the many advantages of cellulose material.

Most of the applications obtained on composites consisting of cellulose and other polysaccharide were fiber and film materials. More applications are listed than for ACCs, but the mechanical properties are less exciting (Table 2). The best Young's modulus values observed in this group were on sulfite pulps sheets with hemicellulose content up to 20 wt%. Cellulose I/xylan as well as the combination of chitosan with cellulose nanoparticles gave comparable mechanical properties.

4. Chitin/chitosan-based composites

Chitin is a non-toxic, biodegradable and biocompatible polysaccharide. It is used in biomedical applications. Chitin is insoluble in most of the organic solvents due to its rigid crystalline structure. However, it can be dissolved in calcium chloride dehydrated methanol solvent system. The α- and β-chitin hydrogel can easily be developed using this solvent system. Using these hydrogels it is possible to develop scaffolds and membranes for the variety of biomedical applications such as tissue engineering and wound dressing (Tamura, Furuike, Nair, & Jayakumar, 2011). This is the first step for chitin/chitosan composites preparation. Additionally all the chitosans and their derivatives could be considered as chitin/chitosan composites as they always have certain degree of acetyl content. Also chitin nanofibers could be prepared from prawn shell by a simple grinding treatment after the removal of protein and minerals. Since the exoskeleton of prawn is made up of finer structure than crab shell, nano-fibrillation of prawn shell is easier than that of crab shell, which allows chitin nanofibers to be prepared under neutral pH conditions. The prepared chitin nanofibers were highly uniform and the width was 10–20 nm, which was similar to nanofibers from crab shell treated under acidic conditions (Ifuku et al., 2011).

Novel biodegradable superabsorbent hydrogels were prepared from chitin dissolved in LiCl/N-methyl-2-pyrrolidinone via esterification crosslinking with 1,2,3,4-butanetetracarboxylic dianhydride (Kono & Zakimi, 2013). Cellulose/chitin hybrid hydrogels were obtained from the homogeneous mixture of cellulose and chitin by a method similar to that for the preparation of the chitin hydrogels. The water absorbance of cellulose/chitin mixtures, and 1:1 cellulose/chitin hybrid hydrogels could be obtained by esterification crosslinking of a mixture with a 1:1 molar ratio of cellulose and chitin. The optimal molar BTCA/anhydro-monomer unit of 5 resulted in the cellulose/chitin hydrogel with the highest water adsorbency (329 g/g-polymer). The hybrid hydrogels were degraded by cellulase as well as chitinase.

Production of chitin/chitosan fibers is important for textile industry due to its antibacterial and anti-allergy effect. By partial acetylation of chitosan nonwoven dressings by its adsorption capacity is improved accompanied with a lower wet strength and reduced antimicrobial activity in comparison to original and fully acetylated samples (Qin, 2008). Test results showed that the partially acetylated chitosan wound dressings can absorb a large amount of water into the fiber structure, hence reducing the capacity space of the nonwoven dressing and making it difficult for liquid to migrate laterally along the fabric structure.

Transparent chitosan films reinforced with high content of nanofibrilated cellulose (NFC) were also prepared (Fernandes et al., 2010). A simple procedure of casting a water-based suspension of chitosan and NFC was used and characterized by tensile and dynamic-mechanical analysis. The Young's modulus values up to 6700 MPa were obtained and the initial temperatures of the films degradation were from 227 °C.

Nontoxic composite sponge consisting of chitosan/HA and chondroitin sulfate nanoparticles (nCS; 10% content) was prepared (Anisha et al., 2013). The nanocomposite showed porosity in the range 60–70% which is adequate for wound dressing. It also showed controlled swelling and biodegradation, enhanced blood clotting and platelet activation. An improved proliferation of the human dermal fibroblast (HDF) cells was observed on SEM images. As a future perspective nCS can be used as a delivery vehicle for growth factor to promote wound healing and it can be incorporated into chitosan-HA sponge to further aid in wound healing.

The production of stable membranes formed by chitosan-xanthan complexation (at 1–1.15:1 weight ratio) employed different polysaccharide concentrations and chitosan flow rates were described (Veiga & Moraes, 2012). The membranes were characterized in terms of their morphology, thickness, and maximal uptake capacity, mass loss in physiological solutions, water drainage ability, and mechanical resistance. The results obtained show that it is possible to produce membranes with high swelling capacity (up to 61 g of water per gram of dry membrane and permeability of 5900 g/m^2 per day, respectively) without significant mass loss when exposed to aqueous solutions (maximum 13%). The membranes obtained at the chitosan solution flow rate of 300 mL/h had the most suitable mechanical properties. Increases in polysaccharide concentration produced higher water absorption and reduction in tensile strength at break. Therefore, the material obtained showed properties that suggest its promising application as wound dressings or as scaffolds for animal cell cultures.

Another example of chitosan/xanthan composite hydrogels was accomplished by mixing equal volumes of water solution of xanthan with the same amount of chitosan dissolved in 0.1 M HCl diluted to the same volume with water at pH 5.6 (Martínez-Rubalcaba, Chrnet, & Rodrigue, 2007). After washing with water the hydrogel was lyophylized. The oscillatory shear measurements show that chitosan/xanthan hydrogels behave like weak gels. The shear modulus increased almost linearly with frequency in the range studied (0.1–65 s^{-1}). The effects of hydrogel concentration and dispersion medium have been related to electrostatic equilibrium and by the presence of counter-ions modifying the structure of the hydrogel.

When chitosan was cross-linked with xylan citrate at 1:1 (w/w) ratio at 110 °C for 2.5 h, the obtained foam was elastic, very soft, highly porous and durable (Salam, Venditti, Pawlak, & El-Tahlawy, 2011). The composite can absorb up to 100 g of a saline solution per gram of material and up to 80 g of water per gram of material.

The formation of electrostatic complexes of chitosan and gum arabic, two oppositely charged polysaccharides, as a function of component ratio, total concentration, pH and ionic strength, was investigated (Espinosa-Andrews, Báez-González, Cruz-Sosa, Vernon, & Carter, 2007). Results indicate that optimum coacervate yield was achieved at ratio of gum arabic/chitosan, $R_{GA/Ch} = 5$, independently of total biopolymer concentration at the resulting pH of solution under mixing conditions. High coacervate yields occurred in a pH range from 3.5 to 5.0 for $R_{GA/Ch} = 5$. Coacervate yield was dramatically diminished at pH values bellow 3.5 due to a low degree of ionization of GA molecules, and at pH values above 5 due to a low solubility of chitosan. Increasing ionic strength decreased coacervate yield due to shielding of ionic groups.

Composite films were prepared by casting method using chitosan (CH) and guar gum (GG) in different ratios (Rao, Kanatt, Chawla, & Sharma, 2010). The concentration of GG ranged from 0 to 50% (v/v). The optical properties such as transparency, opacity and color were measured. Addition of GG in varied proportions to CH solutions led to changes in transparency and opacity of films. The water vapor transmission rate did not change significantly upon addition of GG. Films containing 15% (v/v) GG showed very low oxygen permeability, good tensile and puncture strength. The antimicrobial activity of films containing 15% (v/v) GG was comparable to CH films against *Escherichia coli* and *Staphylococcus aureus*. Composite films obtained by combining CH and GG may reduce environmental problems associated with synthetic polymer packaging.

When chitosan carbamate was mixed with alginic acid, polygalacturonic acid, carboxymethyl cellulose, carboxymethyl guaran, acacia gum, 6-oxychitin, xanthan, hyaluronic acid, pectin, κ-carrageenan, and guaran, clear solutions were obtained from which chitosan-polyuronan microspheres were easily manufactured by spray-drying (Muzzarelli, Stanic, Gobbi, Tosi, & Muzzarelli, 2004). The structural alterations detected were mainly due to interactions between the amino groups and the carboxyl groups. These results suggest the importance of chitosan composites for drug delivery applications (Agnihotri, Mallikarjuna, & Aminabhavi, 2004).

Chitosan and starch blend filmogenic suspensions showed a pseudoplastic behavior, similar to that of chitosan solutions (Garcia, Pinotti, & Zaritzky, 2006). Smooth surfaces, homogeneous and compact film structures were observed. The addition of glycerol reduced film opacity and increased film solubility. Water vapor permeability values of composite films plasticized with glycerol ranged between 3.76 and 4.54×10^{-11} g/s m Pa, lower than those of the single component films. Tensile strength values of composite films were comparable to those of low-density and high-density polyethylenes but lower than that obtained for cellophane. However, composite biodegradable films showed lower elongation at break values than the synthetic commercial ones.

By combining chitosan with regular or waxy cornstarch, films were prepared with 25% glycerin content (Xu, Kim, Hanna, & Nag, 2005). The composite films had increased tensile strengths (34–40 MPa at 1:1 ratio) and elongation-at-breaks (59–61% at 1.5:1 starch to chitosan ratio), and decreasing water vapor transmission rates (55–58 g/m^2 h at 0.5:1 starch to chitosan ratio) with increasing starch to chitosan ratios.

The viability of using polyionic complex (PIC) membrane made by blending 84% deacetylated chitosan and sodium alginate for direct methanol fuel cell (DMFC) was investigated (Smitha, Sridhar, & Khan, 2005). The blend was found to be suitable for DMFC applications because of the low methanol permeability (4.6×10^{-8} cm^2/s at 50 vol.% methanol concentration), excellent physicomechanical properties (72 MPa tensile strength; 6.3% elongation; 140 μm thickness) and relatively high proton conductivity (0.042 S/cm). The cost effectiveness and simple fabrication technique involved in synthesis of such PICs make their applicability in DMFC quite attractive. For chitosan/hydroxyethyl cellulose hydrated membrane stabilized with phosphotungstic acid the conductivity was 5.9×10^{-3} S/cm at 70 °C (Mohanapriya et al., 2009).

Nanocrystalline cellulose (NCC) reinforced chitosan-based films were prepared by solution casting (Khan et al., 2012). The NCC content in the films was varied from 1 to 10% (dry wt. basis). The tensile strength of film with 5% NCC content was optimum (Table 2). WVP of the composite was decreased by 27% for the optimum 5% (w/w) NCC content. Swelling studies revealed a decrease in water uptake of the NCC reinforced chitosan films. The thermal properties were not significantly affected by NCC although it was homogeneously dispersed into chitosan matrix.

The formation of polyelectrolyte complex nanoparticles (PCN) was investigated at different charge mixing ratios for the chitosan–heparin and chitosan–hyaluronan polycation–polyanion pairs (Boddohi, Moore, Johnson, & Kipper, 2009). The range of 0.08–19.2 for charge mixing ratio was examined. The one-shot addition of polycation and polyanion solutions used for the formation of the PCN permitted formation of both cationic and anionic particles from both polysaccharide pairs. For most conditions studied, colloidically stable, nonstoichiometric PCN were formed in solution. However, PCN formation was inhibited by flocculation at charge mixing ratio near 1. Hydrodynamic radii of the produced particles (170–329 nm) and starting chitosan (34 nm), heparin (3.68 nm) and hyaluronan (61 nm) were determined by GPC equipped with low-angle and right-angle laser light scattering detector.

In this chapter the best composite film was produced by combination of chitosan with cellulose I. Its mechanical properties are comparable to ACCs and all other previously mentioned films (Nordqvist et al., 2007; Table 2). The fuel-cell application as the predominant seams to be very promising.

5. Heparin-based composites

A novel heparin- and cellulose-based biocomposite at 7/100 (w/w) ratio is fabricated by exploiting the enhanced dissolution of polysaccharides in room temperature ionic liquids (RTILs). This represents the first reported example of using a new class of solvents, RTILs, to fabricate blood-compatible biomaterials. Using this approach, it is possible to fabricate the biomaterials in any form, such as film or membranes, fibers and spheres (nanometer- or micron-sized), or any shape using templates (Murugesan, Mousa, Vijayaraghavan, Ajayan, & Linhardt, 2006). Surface morphological studies on the biocomposite film showed the uniformly distributed presence of heparin through the cellulose matrix. Activated partial thromboplastin time and thromboelastography demonstrate that this composite is superior to other exiting heparinized biomaterials in preventing clot formation in human blood plasma and in human whole blood. Membranes made of these composites allow the passage of urea while retaining albumin, representing a promising blood-compatible biomaterial for renal dialysis, with a possibility of eliminating the systematic administration of heparin to the patients undergoing renal dialysis.

An electrospinning processing was demonstrating by using 10% cellulose solution in 1-butyl-3-methylimidazolium chloride or 2% (w/w) heparin in 1-ethyl-3-methylimidazolium benzoate (Viswanathan et al., 2006). The solutions were combined and mixed by using vortex for 2 min to afford a clear cellulose-heparin solution. Both cellulose and heparin-cellulose solution were subjected

to electrospinning. A 1 mL sample of polysaccharide RTIL solution was transferred to a syringe attached to a syringe pump, and a voltage of 15–20 kV was applied to a needle of the syringe, with a ground charge, in the form of an aluminum sheet placed beneath the ethanol collector. The nozzle-to-grounded-target distance was fixed at 15 cm. The flow rate of the syringe pump (0.03–0.05 mL/min) was adjusted in tandem with the applied voltage affording fiber formation. Both of the RTILs selected for the study, are completely miscible in ethanol, while neither of the polysaccharides are ethanol soluble. Hence, as the fibers formed, the ethanol extractively removed the RTIL solvents, affording pure polysaccharide fibers. The fibers in the form of a tangled web were washed with additional ethanol and then dried in vacuum to remove the residual ethanol.

Heparinized cellulose matrices (H-CM) were used as affininty substrates for binding of basic fibroblast growth factor, a heparin-binding peptid, to facilitate cellular prolification and substrate-mediated transgene delivery. It was shown that H-CM was a friendly substarte for cellular adhesion using HT-1080 fibroblasts and Saos-2 osteoblasts (Tseng, Chen, & Tang, 2011).

It is probable that cheaper polysaccharides will be used for APCs preparation with properties close to heparin and heparin-containing APCs.

6. Hyaluronan-based composites

Oxidized hyaluronic acid was coupled with chitosan to form porous scaffolds after freeze drying (Nair, Remya, Remya, & Nair, 2011). The percentage porosity of the freeze-dried chitosan–hyaluronic acid dialdehyde composite (CHDA) gels increased with increasing oxidation. Fibroblast cells seeded onto CHDA porous scaffold adhered, prolifered and produced extracellular matrix components on the scaffold. Chondrocytes encapsulated in CHDA gels retained their viability and specific phenotypic characteristics. The gel material is hence proposed as a scaffold and encapsulated material for tissue engineering applications.

Films of hyaluronan (HA) and a phosphorylcholine-modified chitosan (PC-CH) were constructed by the electrolyte multilayer (PEM) deposition technique (Kujawa, Schmauch, Vitala, Badia, & Winnik, 2007). The HA/PC-CH films were stable over a wide pH range (3.0–12.0), exhibiting a stronger resistance against alkaline conditions as compared to HA/CH films. The fluid gel-like characteristics of HA/PC-CH multilayers were attributed to their high water content (50 wt%), which was estimated by comparing the surface coverage values derived from SPR and QCM measurements. Given the versatility of the PEM methodology, HA/PC-CH films are attractive tools for developing biocompatible surface coatings of controlled mechanical properties.

Heparin-conjugated hyaluronan (HA-Hp) microgels with different heparin content, i.e. 1%, 5%, and 10% (w/w), were synthesized for the controlled release of bone morphogenetic protein-2 (BMP-2; Zhao et al., 2011). Hyaluran microgels showed a smooth surface and dense network, whereas HA-Hp microgels exhibited a rougher surface with holes and concaves, and a looser internal structure with increasing the heparin content instead. However, the major microgel size of about 3 μm was independent of the heparin amount. Among the samples, HA-Hp-10% microgels existed the highest equilibrium swelling ratio of 11.8 due to its least crosslinking network. A higher BMP-2 loading efficiency and a microgels was in favor of BMP-2 binding and the sustained delivery may be attributed to the electrostatic interaction between heparin and BMP-2.

By crosslinking of HA with different polysaccharides new possibilities are open in medical applications and also preparation of HA analogs from different polysaccharides gives new perspectives for APCs.

7. Xylan-based composites

Maillard reaction products (MRPs) were prepared by co heating xylan and chitosan at different time periods and used for lipid food storage in lecithin model system and refrigerated pork meat (Li, Shi, Jin, Ding, & Du, 2013). The results of antioxidant protective effect on lecithin liposome peroxidation induced by 2,2′-azobis (2-methylpropionamide) dihydrochloride revealed that the MRPs heated for 120 min and 180 min showed much higher inhibitory activity than chitosan or MRP heated for 60 min. In the experiment of fresh pork protection, the MRPs heated for 60 and 120 min retarded the growth of spoilage organisms more effectively. Lipid oxidation potential of the meat determined by thiobarbituric acid reactive substances also showed that the samples treated by the MRPs heated for 60 and 120 min had higher acceptance than others. These results demonstrate that composites made from xylan and chitosan are promising controllable antioxidative preservatives for lipid food formulations, and the antioxidant behavior depends not only on the antioxidant substances, but also on the interaction of the food systems. On the other hand chitosan or xylan alone did not possess any antioxidant activity.

Aspen xylan mixed with chitosan formed films due to interaction of 4-O-methyl-D-glucuronic acid units with amine groups the chitosan (Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000). The crystallinity of the films decreased with increasing chitosan content while the films from chitosan alone showed no crystallinity, as studied by wild-angle X-ray spectroscopy of the powdered films. The origin of the crystalline structure might be in cellulose structures extracted with xylan from aspen wood. The water uptake of the mixed film composites increased with increasing chitosan content.

Composite films were formed also by adding an aqueous suspension (35 mL) of sulfonated whisker to oat spelt xylan (0.25 g). The solid whisker content in the whisker suspension used was 0, 2.5, 5, 7 and 10 wt% of the total mixture of xylan, whisker and sorbitol. The plasticizer (20, 40 and 50 wt% of sorbitol) was added to the mixture with stirring and then heated to 95 °C for 15 min. The solution was poured to Petri dishes and was allowed to dry at RT for three days. The film had a thickness of 0.080 ± 0.007 mm. The maximal tensile strength of the composite film with 10% of sulfate whisker content was 6 MPa, while for pure xylan it was 2 MPa and the strain was the highest for 7% sulfate whisker content at 30%, while for pure xylan film it was 22% (Saxena, Elder, Pan, & Ragauskas, 2009).

When birch wood xylan was combined with nanofibrilated cellulose (NFC; up to 50 wt%) and films were cast with or without plasticizers, the agglomerations were observed in the composite (Hansen et al., 2012). Tensile testing revealed increases in tensile strength with increased NFC content in the xylan/NFC composition range from 50:50 to 80:50 and plasticizer addition generally provided less brittle films. The oxygen permeability of unplasticized xylan-NFC films fell into a range which was similar to that for previously measured pure NFC films and was statistically independent of the xylan/NFC ratio. Water vapor permeability (WVP) values of $1.9–2.8 \times 10^{-11}$ g Pa^{-1} m^{-1} s^{-1} were found for unplasticized composite films, but these values were significantly reduced in the case of films plasticized with 10–40 wt% sorbitol.

When MFC (15 wt%) was mixed with enzymatically-modified arabinoxylan for film preparation, $E = 2000–2500$ MPa was obtained (Mikkonen et al., 2012). The arabinose/xylose ratio did affect the results as could be expected due to sorption of unbranched xylan onto cellulose surface. The results are better than on GGM probably due to more linear xylan structure. There

were crystalline structures present which were attributed to be related to arabinoxylan hexagonal orientation, while the MFC component impact was not discussed. This is contrary to related paper (Stevanic et al., 2011) where it was shown that the overall pattern of the XRD profile is determined by MFC. The arabinoxylan pattern was considered to be identical with xylan hydrate (Nieduszynski & Marchessault, 1972). The existence of xylan crystalline structure is controversial and could be interpreted as a residue of cellulose Iβ and II mixture extracted from the source under alkaline conditions or attributed to some semiordered cellulose or xylan conformation. This is review writer's hypothesis on the basis of the similarity of XRD profiles of nanocrystalline cellulose (Ma et al., 2011), or mixtures of cellulose I and cellulose II obtained by IL treatment of different wood sources (Chen et al., 2011). Also holocelluloses from hardwoods and softwoods exhibited similar XRD profiles as isolated hemicelluloses (Yamamoto, Kuramae, Yanagisawa, Ishii, & Isogai, 2011). Xylan structure was also considered to be of semicrystalline type close to liquid crystal structures (Roubroeks & Kondo, 2012).

Hydrogels were prepared by mixing xylan from oat spelt (OSX) and beech (BX) with kappa-carrageenan (kC). At total polysaccharide concentration of 1% (w/w), a kC concentration in the interval between 10% and 50% (w/w), and xylan concentrations 50–90% were used. Syneresis in kC gels was decreased significantly, while swelling ability was increased radically, after mixing with xylans (Meena, Lehnen, Schmitt, & Saake, 2011). Gelling and melting temperatures of the composites were increased in kC/BX_{50-90} hydrogels, while decreased in kC/OSX_{50-90}.

Xylan-based APCs will find many applications in paper industry and film-forming applications due to its low price and special ability to interact with cellulose because of similarities in structure and conformation.

8. Glucomannan-based composites

A series of novel edible blend films of konjac glucomannan (KGM) and curdlan were prepared by a solvent-casting technique with different blending ratios of two polymers (Wu et al., 2012). The results show that the strong intermolecular hydrogen bonds took place between KGM and curdlan. The interaction was the most intense when the KGM content in the blend films was around 70 wt% (KC7), resulting in excellent miscibility. The KC7 blend film showed the maximal tensile strength (42.93 ± 1.92 MPa). The blend films displayed lower moisture barrier properties than the film made from pure KGM component.

Film casted from the mixture of glucomannan (GM) and pectin (P) at 50/50 (w/w) ration have better machanical properties as analogical filme prepared from methyl cellulose (MC) and GM or MC and P (Chambi & Grosso, 2011; Tables 1 and 2). The WVP of the film is similar like for films from MC/Gm or MC/P mixtures. The film with the best mechanical properties (tensile strength = 72.63 MPa; elongation = 9.85%) was obtained from MC/GM/P at 1:4:1, respectively. Results showed significant improvement in WVP when films were made at pH 5 and at polysaccharides/gelatin ratio of 90/10 and 10/90, reaching 0.094 and 0.118 g mm/h m^2 kPa values, respectively. This is an example of properties improvement with increasing number of polysaccharide components in composite.

Antibacterial activity of glucomannan/chitosan blend films and their irradiation-modified counterparts were tested (Du, Yang, Ye, & Li, 2013). Antibacterial activity of the blend films increased with the increase of chitosan. After different dose irradiation, there was no obvious change in the antibacterial effects against *St. aureus* of the blend films, but the antibacterial effects against *E. coli* and *Pseudomonas aeruginosa* increased significantly.

Composite films were also prepared from spruce galactoglucomannan (GGM) and microfibrillated spruce wood cellulose by mixing their water solutions/suspensions (Mikkonen et al., 2011). At 5 and 15% of MFC content of the composite film the Young's modulus increased to 800 and 900 MPa in comparison to GGM film value (E = 750 MPa) at the presence of 40% of glycerol as plasticizer.

Films were prepared also from sorbitol-plasticized spruce galactoglucomannans (GGM), mixture of GGM/KGM, GGM/poly (vinyl alcohol) (PVOH), GGM/cellulose nanowhiskers (CNW; Mikkonen, Heikkilä, Helén, Hyvönen, & Tankanen, 2010). GGM-based films had lower water vapor permeability than the films formed from any of the other mannan. The oxygen permeability of GGM films was of the same magnitude as that of commercial polyethylene/ethylene vinyl alcohol/polyethylene laminate film. The aroma permeability of GGM films was low. All films were transparent in the visible region, but GGM films blocked the light transmission in the ultraviolet region of the spectra.

The interaction of konjac glucomannan with xanthan gum, deacetylated xanthan gum and depyruvated xanthan gum has been studied by DSC and controlled stress rheometry (Fitzpatric, Meadows, Ratcliffe, & Williams, 2013). In the absence of electrolyte the DSC cooling curve for native xanthan and deacetylated xanthan showed a single peak and there was a corresponding sharp increase in the storage modulus indicating gel formation. It is apparent that on cooling, association of the konjac glucomannan with native xanthan molecules is triggered by the xanthan coil–helix transition. In the presence of electrolyte, there were two DSC peaks observed. The higher temperature peak was attributed to the xanthan coil–helix transition while the lower temperature DSC peak was attributed to glucomannan-xanthan association as noted by an increase in the storage modulus. The gels formed were much weaker than those in the absence of electrolyte.

Glucomannans as available wood hemicelluloses are important source for APCs and their properties need to be compared with other polysaccharide-based APCs to meet the optimal application.

9. Pectin-based composites

A polygalacturonic acid (PGA)-based hydrogel was prepared using a short-chain hyaluronate (sHA) for medical applications (Peng, Chen, et al., 2011). PGA was grafted with adipic acid dihydrazide (ADH) to yield PGA-ADH, an amine-containing PGA derivative. This PGA-ADH formed a water-insoluble hydrogel by reacting with 1,1′-carbonyldiimidazole (CDI)-grafted sHA (sHA-CDI) in aqueous solution. The sHA-cross-linked PGA hydrogel has a water content of about 94–97% and compressive modulus of 10.7–26.9 kPa. The in vitro data indicated that the sHA-cross-linked PGA hydrogel is degradable and noncytotoxic, thus suitable for biomedical applications. Animal implant studies showed that the sHA-cross-linked PGA hydrogel membrane exhibited antiadhesion potency, significantly higher than that in untreated rats and has great potential for clinical applications.

Applications mentioned in other chapters of this review related to pectin use will also develop new possibilities for use of pectin-based APCs.

10. Arabinan-based composites

Arabinan is branched pectin related polysaccharide present in large amount in agricultural plants like sugar beet (Šimkovic, Uhliariková, Yadav, & Mendichi, 2010). Its debranched fraction consists of $[\rightarrow 5)$-α-L-Ara$f$-$(1\rightarrow]_n$ chain, which was proved to be in crystalline state (Janaswamy & Chandrasekaran, 2005). X-ray intensity data using a powder diffractometer were interpreted as monoclinic cell with a = 5.444(7), b = 6.395(10), c = 8.680(5) Å, and

$\gamma = 99.6(3)^\circ$, $V = 298$ Å^3. According to the authors one 2-fold helix along the *c*-axis can be accommodated in the unit cell. Such a structure could be a good base for composite material with expected good film-forming properties. There are no data on this topic probably because the arabinan extracts from sugar beet are branched polysaccharides. The substrate used for the above data was probably prepared by some enzymatic treatment not disclosed by the manufacturer or author of the paper. Also neutral sugar arabinan sides of pectin are able to interact with cellulose microfibrils through hydrogen bonding and are potential resources for cellulose/pectin composites (Zykwinska et al., 2007). There are no examples of all-arabinan or arabinogalactan mixed composites at the present. They need to be considered due to arabinan presence in many agricultural plants.

11. Xyloglucan-based composites

Composite film consisting of xyloglucan, chitosan and rice starch was obtained by the casting/solvent evaporation method (Simi & Abraham, 2010). Xyloglucan/chitosan blend film shows better mechanical properties. Hydrophobicity and crystallinity of xyloglucan film was increased by blending with chitosan. Scanning electron microscopy observations indicated that the xyloglucan chitosan blend films were smooth and homogeneous. Thermogravimetric and differential scattering calorimetry analysis showed a higher thermal stability and melting temperature of xyloglucan chitosan film compared with others. The swelling properties of the xyloglucan chitosan blend film, studied as a function of pH showed that the sorption ability of the blend film was high at a pH 7.4. This indicates its controlled release property at that pH. Controlled drug release property of the film was studied by using streptomycin as a model drug.

Xyloglucan conjugates are also useful as molecular anchors for attaching various functional chemical groups to cellulose or cellulosic materials (Albersheim et al., 2004). The functional groups in xyloglucan conjugates can serve as dyes, fabric softeners, antimicrobial agents, and flame retardants and the like.

Cellulose–xyloglucan composite was used to enhance adhesion and proliferation of endothelial cells (Bodin et al., 2007). The adsorption maximum of the XGs reached at 180 mg/g on bacterial cellulose (BC), which was three times as much than on cotton linters. The specific surface area of BC measured with XG and XG-peptide was 200 m^2/g, while for cotton linters it was 60 m^2/g.

Mixtures of tamarind-seed polysaccharide (TSP) and hyaluronic acid (HA), which are employed as artificial tears for ophthalmic applications in the eye dry syndrome, were investigated by NMR spectroscopy by analyzing the effect of TSP/HA ratio and total concentration on their capacity to form stable aggregates with enhanced mucoadhesive properties over those of the separate polysaccharides (Uccello-Barretta, Balzano, Vanni, & Sanso, 2013). The effect of TSP, HA or TSP/HA mixtures on the affinity of diclofenac sodium salt (DS) to mucin (BSM) was ascertained by means of proton selective relaxation rate measurements and assumed as the basis to compare polysaccahrides mucoadhesive properties. The NMR relaxation parameters of pure DS (2 mM), binary DS/BSM (5 mg/mL or 10 mg/mL) and ternary DS/BSM/polysaccharide systems (TSP, HA or variable ratios) were compared in aqueous medium. The experimental data demonstrate that the minimum concentration of 1.5 mg/mL of each polysaccharide is needed to have formation of a stable TSP/HA aggregate endowed with NMR detectable muco-adhesive properties and inside which reciprocal synergistic interaction occurs.

Xyloglucan behavior in water solution makes its use very attractive for many applications.

12. Galactan-based composites

Galactans commonly exist in red seaweed and consist of alternating 3-linked β-D-galactopyranose (Gal, unit G) and 4-linked α-D or L-galactopyranose often occurring as its 3,6-anhydro form (anGal, unit A), which are classified either as carrageenan, if the 4-linked residue is D-conformation or as agaran, if that is L-configuration (Falshaw, Furneaux, & Stevenson, 1998).

The mechanical and calorimetric properties of κ-carrageenan (κC)/acid hydrolyzed hydroxypropylated pea starch (HPPS) cast films were investigated in relation to the rheological behavior of the gelled film-forming dispersions (Lafargue, Lourdin, & Doublier, 2007). The mixture was prepared by mixing HPPS (25%, w/w), an easily slurried non-gelling polysaccharide, and a K^+ κ-carrageenan (<1%, w/w) used its gelling properties. Whatever was the κ-carrageenan content, the total ionic concentration (K^+) was maintained constant to control the transition temperatures. Compared to individual components, the rheological properties of the hot mixture at 60 °C showed a dramatic increase in the viscosity. Upon cooling, stronger gels were formed compared to the pure κ-carrageenan in similar ionic conditions. Meanwhile, these gels set and melted at temperatures around 10 and 20 °C higher than those of κ-carrageenan alone in the same conditions. These phenomena were attributed to the excluded volume effects between κ-carrageenan and starch resulting in the increased concentration of the carrageenan forming the network. Overall the final film properties of the blends were similar to those of the films with starch alone. This means that the influence of the κ-carrageenan on the solid state behavior of the blends was hidden, in spite of the strong influence of κ-carrageenan on the rheological behavior in the solution and in gel state.

Agarose hydrogels filled with cellulose nanowhiskers (5/1; w/v) were strained in uniaxial stretching under different humidity conditions (Osorio-Madrazo et al., 2012). The orientation of the cellulose whiskers was examined before and after testing with an X-ray laboratory source and monitored in situ during loading by synchrotron X-ray diffraction. The aim of this approach was to determine the process parameters for reorienting the cellulose nanowhiskers toward a preferred direction. Results show that a controlled drying of the hydrogel is essential to establish interaction between the matrix and the cellulose nanowhiskers, which allows for a stress transfer during stretching and thereby promotes their alignment. Rewetting of the sample after reorientation of the cellulose nanowhiskers circumvents a critical increase of stress. This improves the extensibility of the hydrogel and is accompanied by further moderate alignment of the cellulose nanowhiskers. Following this protocol, cellulose nanowhiskers with an initial random distribution can be reoriented toward a preferred direction, creating anisotropic nanocomposites.

Seaweed galactans are important sources of sulfated polysaccharides which are useful as heparin analogs and testing their properties in preparation of new APCs is a big challenge.

13. Starch-based composites

Starch is a polysaccharide dominating the food industry (BeMiller, 2011). Here all-polysaccharide composites were explored the most. The combinations of galactomannans, xanthan, sulfated galactans, agar, pectin, glucomannan, CMC, HPC, alginate, glucan, xyloglucan, arabinoxylan, dextran, starch and proteins affect the rheological properties of gels and pastas.

A drug delivery system was developed with aim to evaluate the influence of drug loading and polysaccharide ratio on the physicochemical properties of microcapsules of cross-linked high amylase starch-pectin blends loaded with diclofenac (Soares, de Castro,

Cury, & Evangelista, 2013). The rheological properties demonstrated that drug loading resulted in formation of weaker gels while the increase of pectin ratio contributes to origin stronger structures.

Antimicrobial films were prepared with oxidized and acetylated corn starch–sodium alginate by incorporating sodium dehydroacetate (>0.1%) or rosemary extract (>0.3%; Yan, Zhang, Dong, Hou, & Guo, 2013). The non-polysaccharide components reduced the tensile strength and elongation at break, and increased the water vapor permeability of films. These findings had potential applications in prolonging food shelf life based on different needs.

Chitin nanoparticles (CNP) of about 50–100 nm were added in up to 5% quantity to glycerol plasticized starch (GPS) to prepare composite by casting and evaporation (Chang, Jian, Yu, & Ma, 2010). CNP were uniformly dispersed and the GPS matrix and had good interaction between the filler and the matrix, which led to improvements in tensile strength, storage modulus, decease in glass transition temperature, and water vapor barrier properties. However at higher loadings aggregation of CNP had a negative effect on these properties.

Cellulose cassava bagasse nanofibrils (CBN; 2–11 nm thick and 360–1700 nm long) were used as reinforcing nanoparticle in thermoplastic cassava starch (CS) matrix (Teixeira et al., 2009). The reinforcing effect of the filler was found to be depend on the nature of plasticizer employed. The best mechanical properties of the hot-pressed plates (at 140 °C into 1 and 2 mm thick) consisting of 50% CS, 15% of glycerol, 15% of sorbitol, 15% of water and 5% of CBN (Table 2).

Films were prepared by dispersing cellulose nanofibers (30–70 nm in diameter) from wheat straw in thermoplastic starch (TPS) and casting (Kaushik, Singh, & Verma, 2010). Mechanical properties increased with nanofiber concentration (up to 15%; Table 2). Barrier properties also improved with addition of nanofibers up to 10% but further addition deteriorated properties due to possible fiber agglomeration.

Homogeneous films with a microfibrillated cellulose (MFC) and amylopectin-glycerol (50/50) matrix blend were successfully casted (Svagan, Azizi Samir, & Berglund, 2007). High tensile strength is combined with high modulus and very high work of fracture in nanocomposite with 70 wt% MFC (Table 2). The reason for this interesting combination of properties includes nanofiber and matrix properties, favorable nanofiber–matrix interaction, good dispersion, and the ability of the MFC network to maintain its integrity to a strein of at least 8%.

Novel amylopectin–cellulose nanocomposite foam with 0 and 40 wt% MFC content were prepared by freeze drying of the water–starch–cellulose mixture (Svagan, Azizi Samir, & Berglund, 2008). The amylopectin foams with 0, 10, and 40 wt% MFC are anisotropic with irregular cell shape. The cells of these foams are elongated in the plane normal to the cylinder axis of the foam. However, these elongated cells are randomly oriented in the plane. The macroscopic properties of the foams believed to be axisymmetric. The mean cell area and the mean principal cell diameter both increase with increasing MFC content, whereas the anisotropy ratios decrease. The MFC is homogeneously distributed within the amylopectin matrix. The mechanical properties of the foams depend both on the cell wall properties and the cell-structure. The 0 and 10 wt% MFC foams have closed cells, whereas the 40 wt% MFC foam contains a mixture of open and closed cells. The difference in cell-structure of the foams influences mechanical behaviors in both the linear-elastic and the cell collapse region. In the case of open cell structures, cell-edge bending occurs during linear-elastic deformation. If the foam contains closed cells, the Young's modulus is the sum of cell-edge bending, compression of the entrapped gas in the cell, and cell-face stretching. Modulus of the closed-cell foam is higher than for an open-cell foam of the same relative density and cell-wall modulus. The modulus and strength reaches maximum at 40 wt% MFC content (Table 2). The nanocomposite foams showed microcellular structure with cell dimensions in the range 20–70 μm. Compared to the neat amylopectin foam, a significant improvement in modulus and yield strength was observed. From the relation of the normalized storage modulus at constant temperature as a function of relative humidity for an amylopectin foam with 0 and 40 wt% MFC content it is clear that water is a plasticizer to the amylopectin matrix. For all foams, softening takes place as the relative humidity increases. At 40 wt% MFC content, the storage modulus does not decrease as fast and is higher than for the amylopectin foam at all relative humidities.

The glycerol plasticized-wheat starch (GPS)/cellulose nanoparticles (CN) nanocomposites were prepared using CN as filler in GPS matrix by a casting process (Chang, Jian, Zheng, Yu, & Ma, 2010). CN (50–100 nm size) were coagulated from a NaOH/urea/H_2O solution of microcrystalline cellulose using ethanol/HCl aqueous solution as the precipitant. The tensile strength increased from 3.15 to 10.98 MPa when CN content went from 0 to 5 wt%. CN may increase the thermal stability of GPS/CN composites. Moreover, water vapor permeability decreased from 5.75×10^{-10} to 3.43×10^{-10} g/m s Pa. The improvement in these properties may be attributed to the good interaction between CN filler and GPS matrix because the similar polysaccharide structure of cellulose and starch.

Nanocomposite films were prepared using sorbitol-plasticized pullulan as the amorphous matrix and an aqueous suspension of starch nanocrystals (prepared by submitting native granules from waxy maize starch to acid hydrolysis at 35 °C) as the reinforcing phase (Kristo & Biliaderis, 2007). The water absorption as well as water barrier properties of nanocomposite films filled with 0–40% (w/w) starch nanocrystals (starch nanocrystals/pullulan + sorbitol) were investigated. The water uptake decreased with increasing filler content whereas WVP remained constant up to 20% (w/w) and than decreased significantly with further addition of nanocrystals. The glass transition temperature (T_g) shifted toward higher temperatures with increasing amount of nanocrystals, which can be attributed to a restriction of the mobility of pullulan chains due to the establishment of strong interactions not only between starch nanocrystals but also between the filler and the matrix. Moreover, the addition of nanocrystals caused strong enhancement of Young's modulus and the tensile strength, but led to a drastic decrease of the strain at break in samples conditioned at different environment (from 43 to 75% RH).

Bamboo fiber/pea starch films were prepared by mixing plasticized starch with bamboo cellulose crystals (BCC; 50–100 nm at diameter) at up to 20% content (Liu, Zhang, Chang, Li, & Wu, 2010). Tensile strength and Young's modulus of the starch/BCC composite films were enhanced by the incorporation of the crystals due to reinforcement of BCCs and reduction of water uptake. BCCs at the optimal 8% loading level exhibited a higher reinforcing efficiency for plasticized starch than any other level.

Glycerol plasticized starch (PS) composites were prepared, using ramie cellulose nanocrystals (RN; lengths of 538 and diameters of 85 nm) of 0–40 wt% as filler (Lu, Weng, & Cao, 2006). Young's modulus and tensile strength increased from 56 to 480 MPa and 2.8 to 6.9 MPa with increasing filler content. The performance improvement may be ascribed to three-dimensional networks of intermolecular hydrogen bonding interactions between filler and filler and between filler and PS matrix.

The films produced from pure starch are brittle and difficult to handle. Chemical modification (e.g. cross-linking with citric acid; CA) and the use of carboxymethyl cellulose (CMC) in the starch based composite have been studied to produce low water sensitive and relatively high strength materials (Ghanbarzadeh, Almasi, & Entezami, 2011). At the level of 15% (w/w) CMC,

the starch films showed the lowest water vapor permeability values (2.34×10^{-7} g Pa^{-1} h^{-1} m^{-1}) and ultimate tensile strength increased from 6.57 MPa for the film without CMC to 16.11 MPa for containing 20% CMC.

The composites were with regular cornstarch plasticized with glycerol and reinforced with short cellulosic fibers (16%, w/w) from bleached pulp (Curvelo, de Cargalho, & Agnelli, 2001). The fibers were added to the thermoplasticized starch directly in an intensive batch mixer at 170 °C. The mixture was hot pressed in 2–3 mm-thick palates and then cut to prepare the specimen for mechanical tests. The composite shows an increase of 100% in tensile strength and more than 50% in modulus with respect to non-reinforced thermoplastic starch.

Films made of potato starch and agar were elaborated and tested for a potential use for food packaging. FTIR spectroscopy confirmed that starch and agar were compatible and inter-molecular hydrogen bonds existed between them. SEM of composite films with 15% content of agar showed a compact and homogeneous structure. XRD indicate that the composite films were amorphous. At 50% relative humidity (RH), the addition of agar could enhance the tensile strength from 5.33 to 11.76 MPa. At 75% RH, the addition of agar could also enhance TS from 0.84 to 3.36 MPa. Fortunately the addition of 5% agar increased the elongation (E) from 32.5 to 58.3%, WVP decreased from 6.29 to 4.60×10^{-10} g Pa^{-1} s^{-1} m^{-1} (Wu, Geng, Chang, Yu, & Ma, 2009).

Fully bio-based nanocomposites were prepared from thermoplastic starch and starch nanocrystals obtained by acidic hydrolysis of waxy maize starch granules (Garcia, Ribba, Dufresne, Aranguren, & Goyanes, 2011). The same type of starch, which contains 99 wt% amylopectin, was used to prepare glycerol plasticized and unplasticized materials. The X-ray diffraction pattern of the plasticized reinforced materials displays both A and B-type peaks, showing that the crystalline structure of the nanocrystals was not affected by the processing. The storage modulus of the composite material increases, with respect to the unfilled film, by 470% at 50 °C, while the permeability increases by 70%. This is probably due to a good association of glycerol with the nanoparticles loading to a fibrillar structure, studied by SEM of plasticized and unplasticized composites.

Starch in combination with cellulose gives APCs with good properties which are attracting other industries beside food industry. Vise use of this source polysaccharide needs to be considered to prevent sustainability damages in many undeveloped countries.

14. Alginate-based composites

Rheological properties of sodium alginate, pullulan and blend solutions were studied at 20 °C, using steady shear and dynamic oscillatory measurements (Xiao, Tong, & Lim, 2012). The intrinsic viscosity of pure sodium alginate solution was 7.340 dl/g, which was much higher than that of pure pullulan (0.436 dl/g). Pure pullulan solution showed Newtonian behavior between 0.1 and 100 s^{-1} shear rate range. However, increasing sodium alginate concentration in pullulan-alginate blend solution led to a shear-thinning behavior. The effect of temperatures on viscosities of all solutions was well-described by Arrhenius equation. Results from dynamical frequency sweep showed that pure sodium alginate and blend solutions at 4% (w/w) polymer concentration were viscoelastic liquid, whereas the pure pullulan exhibited Newtonian behavior. The gelling properties are applicable for food industry.

Crosslinked polysaccharide sponges have been prepared by freeze-drying of amorphous alginate-oxidized nanocellulose in the presence of Ca^{2+} ionic crosslinking agent (Lin, Bruzzese, & Dufresne, 2012). The new carboxyl groups on the nanocellulose induced by chemical oxidation provided the possibility of participating in the construction of an alginate-based sponge's structure and played a fundamental role in the structural and mechanical stability of ensuing sponges. Furthermore, enhanced mechanical strength induced by oxidized cellulose nanocrystals and the formation of a semi-interpenetrating polymer network from oxidized microfibrillated cellulose were reported. Together with the facile and ionic crosslinking process, the ultrahigh porosity, promising water absorption and retention, as well as the improved compression strength of the crosslinked sponges should significantly extend the use of this soft material in diverse practical application.

Blend membranes of sodium alginate and hydroxyethylcellulose were prepared and ionically crosslinked with phosphoric acid and were used for the separation of t-butyl/water mixtures (Kalyani, Smitha, Sridhar, & Krishnaiah, 2006). The produced membranes were found to have good potential for breaking the azeotrope of 88 wt% t-butanol.

Alginate-based APCs have great potential for different application when combined with positively charged polysaccharides as was also demonstrated in other chapters of this review.

15. Conclusions

The discussed data and properties of APCs suggest that these types of materials might find application in many industrial fields. From over one hundred examples listed in Table 1, more than fifty are related to film applications. The best film properties were observed on ACCs due to nanocrystalline reinforcing component. Cotton-containing composites (5 applications) improved fabric properties or were involved in wound healing and flame retarding applications. Cellulose in combination with other polysaccharides represents the biggest group of APCs (23 examples with 14 film applications). Second largest group reviewed were chitosan-containing composites (17 examples with 4 examples of fuel cell applications; 6 for films and 3 for foam and drug delivery features). Other studied APCs were heparin (6 examples), hyaluronan (2 examples), xylan (4 examples), glucomannan (4 examples), pectin (2 example), arabinan (2 examples), xyloglucan (4 examples), galactan (2 film example), starch (11 examples; 9 film applications) and alginate (3 examples). The employment of hemicelluloses from agricultural by-products for preparation of suspension/solution blends in water seams to be the easiest way for preparation of new APCs and needs to be more studied. They might substitute many commercial products made from synthetic polymer composites due to biodegradability and the use of water as solvent during preparation. The properties of different types of APCs needs to be compared, to show the economically and ecologically more attractive candidates for certain applications.

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