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Review

Prospects of polysaccharide aerogels as modern advanced food materials

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Aerogels are porous and lightweight materials capable of active sorption and releasing desired compounds and/or bearing mechanical load. Using polysaccharides as aerogel matrices instead of silicate or synthetic polymers has additional benefits. Polysaccharides can be developed as bio-based, biodegradable, and/or edible materials in food applications. Polysaccharides that could be used to prepare aerogels include cellulose, hemicelluloses, marine polysaccharides, and starch, all of which have in common the ability to form gels either by themselves in the presence of water or with dications, other cross-linking agents, and/or other, blended, or mixed polysaccharides. After the liquid phase is removed, the dry aerogels form solid particles of various shapes and sizes that have high porosity and surface area. These characteristics indicate vast possibilities for the use of polysaccharide aerogels as advanced food materials.

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Premises of novel food materials research

Producing an adequate supply of food involves great challenges due to population growth, climate change, and increase in the price of energy. In addition, decreasing petroleum sources have led to the development of advanced bio-based materials to replace conventional synthetic plastics and to create novel environmentally compatible applications. Polysaccharides are envisioned as highly valuable resources in modern industrial applications, as the importance of renewable, non-toxic, and biodegradable materials increases. Polysaccharides are also of interest due to the increasing price of oil.

At the same time, food scientists are seeking improved methods for producing, packaging, and distributing safe, healthy, and tasty food products for a diverse group of consumers. Novel processing techniques, including aroma or antioxidant encapsulation, controlled release, as well as active and intelligent packaging, could provide the means for preserving and utilizing the properties of health-beneficial compounds, and for retaining the food quality to increase products' shelf life.

Aerogels are advanced materials that have low weight and density, a large surface area, and high mechanical strength (Cheng, Lu, Zhang, Shi, & Cao, 2012; García-González, Alnaief, & Smirnova, 2011). They can be formed in various shapes and sizes (Quignard, Di Renzo, & Guibal, 2010). Conventionally, aerogels are prepared from inorganic compounds (Kistler, 1931; Pierre & Pajonk, 2002). For example, silica aerogels show high thermal insulation capacity and are optically transparent in the visible region of the spectra; thus, silica aerogels have potential, e.g., as double-pane windows (Dorcheh & Abbasi, 2008). In addition, organic materials, such as resorcinol–formaldehyde polymers (phenolic resins) are used. Resorcinol–formaldehyde aerogels are stiffer and stronger than silica aerogels, and even more effective thermal insulators (Mulik & Sotiriou-Leventis, 2011).

The concept of polysaccharides as aerogel-forming materials is relatively novel and has many advantageous aspects in food and non-food areas. Polysaccharide-based aerogels are new, sustainable materials, with the potential to transform various industrial processes from petroleum-dependent into bio-economic (Fig. 1). Food applications of polysaccharide-based aerogels do not currently exist on the market, but the outlook for such products is considered major. El Kadib and Bousmina (2012) and Quignard,

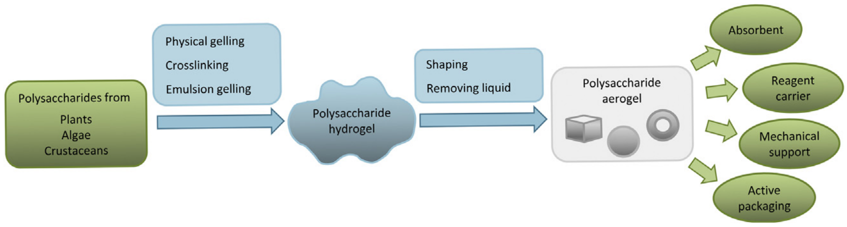

Fig. 1. Polysaccharides from different sources can be processed into aerogels and used in modern food applications.

Valentin, and Di Renzo (2008) reviewed the formation and properties of marine polysaccharide-based aerogels and García-González *et al.* (2011) discussed the applicability of polysaccharide aerogels in the pharmaceutical field. The present review addresses the properties of both marine- and plant-derived polysaccharide aerogels from the perspective of food applications, aiming to raise interest among food scientists in such materials and advance research on the area. Potential polysaccharides studied as aerogel-forming materials are introduced. Aerogel preparation, focusing on hydrogel formation from polysaccharides, is described. The morphology and physical characteristics of polysaccharide aerogels are discussed, emphasizing properties that are significant in the food area. The application potential and targets for future research and development are evaluated.

Potential polysaccharides for aerogel matrices

As the most abundant polysaccharide on Earth, cellulose is an interesting choice for aerogel raw material. Cellulose occurs in all plants; in addition, some animals and certain bacteria can produce cellulose. Other polysaccharide sources include crustacean shells, algae, and numerous plant parts, some of which can be obtained as residual products of industrial processes.

Cellulose

Cellulose has a linear structure comprised of β-(1 → 4) linked D-glucopyranosyl units (Fig. 2(A)). With different processing methods, various cellulose materials with altered fiber structures can be produced. For example, nanofibrillated cellulose (NFC), which has been studied in the aerogel field, is produced by mechanical high-shear disintegration and homogenization. When used to reinforce other materials, these biofibrils show excellent mechanical properties. NFC is biocompatible and transparent. Nano-sized cellulose can be applied in the biomedicine, adhesives, electronics and automotive industries. As a constituent of all plant cell walls, cellulose forms a natural part of human diet (fiber) and is widely used to produce safe packaging materials well compatible with food. Microcrystalline cellulose as well as many cellulose derivatives, such as carboxymethylcellulose and hydroxypropyl cellulose, are also used as approved food additives. In addition to patent applications (Rein & Cohen, 2011; Thielemans & Davies, 2013), many research articles describe the preparation and properties of cellulose aerogels (Aaltonen & Jauhiainen, 2009; Aulin, Netrval, Wågberg, & Lindström, 2010; Granström *et al.*, 2011; Heath & Thielemans, 2010; Hoepfner, Ratke, & Milow, 2008; Innerlohinger, Weber, & Kraft, 2006; Jin *et al.*, 2011; Kettunen *et al.*, 2011; Korhonen, Kettunen, Ras, & Ikkala, 2011; Lee & Deng, 2011; Liebner *et al.*, 2010; Nogi, Kurosaki, Yano, & Takano, 2010; Pääkkö *et al.*, 2008; Sehaqui, Zhou, & Berglund, 2011; Tan, Fung, Newman, & Vu, 2001; Zhang, Zhang, Lu, & Deng, 2012).

Hemicelluloses

Hemicelluloses include structurally different polysaccharides, which exist in plant cell walls, and are closely associated with cellulose. Due to their origin, hemicelluloses are consumed in the human diet within cereals, fruit, and vegetables. They are not digested, but function as dietary fiber. Some hemicelluloses show health promoting properties, including reducing plasma cholesterol and postprandial serum glucose levels (Comin, Temelli, & Saldaña, 2012a). Of the hemicelluloses, xylans, β-glucan, and xyloglucan have been studied in the aerogel field so far (Comin *et al.*, 2012a; Comin, Temelli, & Saldaña, 2012b; Köhnke, Lin, Elder, Theliander, & Ragauskas, 2012; Salam, Venditti, Pawlak, & El-Tahlawy, 2011; Sehaqui, Salajkova, Zhou, & Berglund, 2010).

Xylans occur in various plants and agricultural products, and the type and substitution patterns vary depending on plant species and the location in the plant parts. The backbone of xylan consists of β-(1 → 4) linked D-xylopyranosyl units. Acetyl, feruloyl, α-D-glucopyranosyl uronic acid (or its 4-*O*-methyl ether), or α-L-arabinofuranosyl groups are possible substituents of xylans (Ebringerová & Heinze, 2000). For example, water-soluble birch *O*-acetyl-(4-*O*-methylglucurono)xylan contains one 4-*O*-methylglucuronic acid substituent at every 15 xylose units, acetyl groups at C-2 and/or C-3 with a degree of acetylation of 0.4 (Teleman, Tenkanen, Jacobs, & Dahlman, 2002), and has a molecular weight (M_w) of ca. 20 kg/mol (Fig. 2(B), Table 1).

β-Glucans are highly viscous, gel-forming bioactive polysaccharides associated with various health claims. A significant source of β-glucan is oat, of which β-glucan comprises 3.5–5.0% of the dry matter, depending on growth conditions (Asp, Mattsson, & Önning, 1992). Oat β-glucan has a linear structure consisting of β-D-