Aerogels as porous structures for food applications: Smart ingredients and novel packaging materials

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ABSTRACT
Aerogels are nanostructured materials with low density, high surface area (>150 m²/g) and open porosity (typically 95–99.99 %). They are obtained by solvent removal from gels while preserving network structure. Hydrogels, organogels and even tissues can be optimal sources of aerogels with limitless customization of format and texture. Aerogels might be used for a range of advanced food applications: from smart ingredients controlling nutrient release to delivery systems for active compounds; from fat substitutes to novel biodegradable and intelligent food packaging materials. This review article summarizes recent developments of aerogels in food applications, analyzing research challenges and prospecting future markets.

1. Introduction

The advent of nanostructured materials for food applications is rather recent and mainly focused on nanoencapsulation of ingredients (protection, masking, flavoring, tuned bioavailability), packaging and nanosensors (Ghanbarzadeh, Oleyaei, & Almasi, 2015; Pathakoti, Manubolu, & Hwang, 2017). The most common approaches used for these purposes are micro- and nanoemulsions as well as liposomes but there is still a broad room for food research on other nanostructured materials.

Aerogels are defined as a special type of nanostructured material endowed with special physical features and obtained from a gel by removing the pore fluid (García-González et al., 2019). Solid, low bulk density and open porosity (mainly in the mesoporous range) stand out as specific physical properties that the material should fulfill to fit in the consensual definition of aerogel. Aerogel networks are formed by bonded particles or nanometric fibers that are loosely packed leading to specific physical properties that the material should fulfill to fit in the consensual definition of aerogel. Aerogel networks are formed by bonded particles or nanometric fibers that are loosely packed leading to high porosities (typically in the 95–99.99 % range) and very high specific surface areas (150 m²/g and above) (Fig. 1). These structures result in unique thermal and sound insulation properties and high loading capacities that are being exploited in many industrial fields (aerospace, buildings, petrochemical) and are under research in the recent years for environmental and biomedical applications (www.cost-aerogels.eu), including functional food and packaging (Lehtonen et al., 2020; Plazzotta, Calligaris, & Manzocco, 2018; Plazzotta, Calligaris, & Manzocco, 2018; Plazzotta, Calligaris, & Manzocco, 2020; Selmer et al., 2019).

Aerogels are obtained by the extraction of the solvent of wet gels (hydrogels or organogels) using a method that allows the preservation of the solid network structure, typically supercritical carbon dioxide (scCO2)-assisted drying being the gold-standard (Fig. 1a,b). Fig. 2 shows a schematization of the possible strategies to turn hydrogels into aerogels. Prior to supercritical drying, a solvent exchange may be needed depending on the gel solvent, as the solubility of water in supercritical CO2 is low but the solubility of ethanol or acetone is high (Sahin, Özbaşir, Inönü, Ulker, & Erkey, 2017). Other drying techniques, such as ambient/oven drying or freeze drying, can also lead to aerogel structures in very specific cases (Fig. 1c,d). For ambient/oven drying, surface functionalization (mainly with silanes) or flexible gels followed by the sequential use of solvents with low surface tension (hexane, pentane, ethanol, acetone) may be needed to avoid the shrinkage or cracking of the dry gel due to capillary forces (Budtova, 2019). For freeze drying of hydrogels, the higher volume of water in the solid than in the liquid form results in solvent expansion upon solidification with severe porous damages usually leading to the formation of foams with large macro pores, microchannels, cracks and loss of mesoporosity after sublimation (Fig. 3b) (Baudron, Gurikov, Smirnova, & Whitehouse, 2019;
Despite these limitations, certain biopolymer-based aerogels, typically nanofibrous cellulose aerogels but also chitin aerogels, may be also obtained by atmospheric drying or freeze-drying (Budtova, 2019; Gao, Lu, Xiao, & Li, 2017; Jimenez-Saelices, Seantier, Cathala, & Grohens, 2017; Li et al., 2019; Nemoto, Saito, & Isogai, 2015). A limitless customization of the format, shape, size and texture of the aerogels is possible and is mainly carried out during the gelation step using different molds and gelation conditions (gel source concentration, cross-linker concentration, etc.) (Figs. 1 and 3) (García-González, Alnaief, & Smirnova, 2011). For the specific case of aerogel particles, the use of molds is usually replaced by technological combinations of the sol-gel processing with powder technologies (e.g., emulsion-gelation, spraying, prilling, inkjet printing, jet-cutting) or by post-processing (grinding) (Auriemma et al., 2020; Ganesan et al., 2018). The size and texture of the aerogels can be also partially modulated during the solvent exchange step (solvent choice, direct or sequential procedure) or by post-processing (aerogel compression) (García-González et al., 2011; Plappert, Nedelec, Rennhofer, Lichtenegger, & Liebner, 2017). Finally, aerogels with dual formats like core-shell aerogel particles and coated aerogel particles are also possible by technological combinations (Antonyuk, Heinrich, Gurikov, Subrahmanyam, & Smirnova, 2015; Auriemma et al., 2020; Bugnone, Ronchetti, Manna, & Banchero, 2018; Veronovski, Knez, & Novak, 2013).

Most aerogels are inorganic or synthetic polymer-based, being often made of silica, metal oxides or polystyrenes (Du, Zhou, Zhang, & Shen, 2013; Gesser & Goswami, 1989). However, according to different authors (Kistler, 1931; Pierre & Pajonk, 2002, 1932; Zhao, Malfait, Guerrero-Alburquerque, Koebel, & Nystöm, 2018), not only inorganic polymerizing agents but all biopolymers are potential candidates to form aerogels. Namely, the second generation of aerogels eases the penetration of these materials in the food market since it comprises biopolymer-based aerogels, including food-grade polysaccharides and proteins (El-Naggar, Othman, Allam, & Morsy, 2020; García-González et al., 2011; Nita, Ghilan, Rusu, Neamtu, & Chiriac, 2020). These new aerogel sources provided new opportunities for food applications due to their compatibility with human diet, absence of adverse health effects and peculiar physical properties. Aerogels can be used as edible delivery systems for nutraceuticals, nutritional supplements, flavors and other additives or as intelligent components for food packaging. Aerogels can be designed to serve as hosts or carriers of food ingredients and can increase the stability of the loaded ingredient, mask its odor and allow for a controlled or pH-triggered release after intake (Betz, García-González, Subrahmanyam, Smirnova, & Koluzik, 2012; Del Gaudio et al., 2013; García-González, Jin, Gerth, Alvarez-Lorenzo, & Smirnova, 2015; Tkalec, Knez, & Novak, 2016). Food-grade aerogels can also contribute to an increased shelf life of the product by the encapsulation of labile or sensitive components (De Oliveira et al., 2020; García-González et al., 2021; Miranda-Tavares, Croguennec, Carvalho, & Bouhallab, 2014). The use of natural polymers can be also considered as an economical and environmentally-friendly approach to penetrate the food packaging sector.

Finally, aerogels as nanostructured materials should be assessed regarding food safety, mainly with respect to the overproduction of reactive oxygen species inducing cell oxidative stresses (Eleftheriadou, Pyrgiotakis, & Demokritou, 2017; Fu, Xia, Hwang, Ray, & Yu, 2014; Pathakoti et al., 2017). Accordingly, the changes in physicochemical and biological properties of aerogels with respect to the bulk unprocessed counterpart should be critically studied in food systems.

In this review article, the current state-of-the-art of aerogel processing for food applications is compiled for the first time. This work will firstly focus on different biopolymer-based aerogel sources obtained from hydrogels, organogels and tissues as the main sources of food-grade aerogels. Then, the evaluation of these aerogels for their potential direct uses as functional ingredients by themselves, as delivery systems and as fat replacers in food products, as well as their indirect food application

![Fig. 1. SEM images of the microstructures of (a) alginate and (b) pectin aerogels obtained by supercritical drying, (c) cellulose aerogels by freeze-drying, and (d) silica-cellulose composite aerogels by ambient drying.](https://doi.org/10.1016/j.carbpol.2018.05.026, https://doi.org/10.1021/acsami.5b05841, https://doi.org/10.1007/s10853-016-0514-3)
in packaging are discussed. Finally, current gaps and challenges in aerogel research for food are identified, and future niche markets for food-grade aerogels are prospected.

2. Bio-based materials for aerogel preparation

The preparation of aerogels intended for food applications is virtually possible from any bio-based material characterized by a tridimensional polymeric network. Table 1 compares the number of papers published on aerogels during the last two decades, in relation to specific materials that might be used for their preparation. The research was performed using not only Web of Science platform but also Food Science and Technology Abstracts ones to highlight current interest of food scientists towards aerogel materials. Data clearly unveiled that biomedical and environmental applications of aerogels are two important directions of current mainstream research. By contrast, research on aerogels intended for food applications is in its early steps and their full potential is still to be assessed. Following, the main bio-based materials that can be used for preparation of aerogels for food applications are discussed.

2.1. Hydrogels

2.1.1. Polysaccharide hydrogels

At present, the majority of bio-based aerogels are obtained from polysaccharide hydrogels (Table 1). To this regard, the prospects of polysaccharide hydrogels for the production of aerogels have been discussed by different authors (Baudron, Taboada, Gurikov, Smirnova, & Whitehouse, 2020; García-Gonzalez et al., 2011; Zheng, Tian, Ye, Zhou, & Zhao, 2020). Nevertheless, applications relevant to the food sector are limited and mainly relevant to the use of cellulose and starch (Table 1) (Ivanovic, Milovanovic, & Zizovic, 2016; Mikkonen, Parikka, Ghafar, & Tenkanen, 2013; Ubeyitogullari & Ciftci, 2016). Beside them, other polysaccharides traditionally used as food thickeners or dietetic fiber, have the potential of networking, begetting gels which could be turned into aerogels. This possibility has been demonstrated with reference to hemicelluloses (Comin, Temelli, & Saldana, 2012; Mikkonen et al., 2014; Parikka et al., 2017; Ubeyitogullari & Ciftci, 2020), pectin (White, Budarin, & Clark, 2010), alginites (Almaitoun, Garcia-Gonzalez, & Smirnova, 2011; Escudero, Robitzer, Di Renzo, & Quignard, 2009; Mallepally, Bernard, Marin, Ward, & McHugh, 2013), xanthan gum (Bilanovic, Starosvetsky, & Armon, 2016) and carrageenan (Manzocco et al., 2017).

2.1.2. Protein hydrogels

Gelatin and collagen are certainly the most studied proteins for aerogel preparation, being particularly suitable not only as drug carriers but also for the development of scaffolds for regenerative medicine and plastic surgery (Betz et al., 2012; Liu et al., 2019; Mehling, Smirnova, Guenther, & Neubert, 2009; Munoz-Ruiz et al., 2019; Zeynep & Erkey, 2014). By contrast, literature evidence about protein aerogels for food application is basically focus on dairy and egg white proteins (Chen,
Wang, & Schiraldi, 2013; Kleemann, Selmer, Smirnova, & Kulozik, 2018; Selmer, Kleemann, Kulozik, Heinrich, & Smirnova, 2015). Proteins are also used in combination with other biopolymers to drive the internal morphology of composite aerogels. For instance, soy proteins have been demonstrated to be suitable for controlling the transition from fibrillar- to network-like architecture in composite protein-cellulose aerogels (Arboleda et al., 2013), while zein has been suggested as sacrificial porogen to obtain macropores within continuous starch aerogels (Santos-Rosales et al., 2019).

2.1.3. Hydrogels from other biopolymers

Recently, it has also been demonstrated that not only biopolymers with building blocks of saccharides or aminoacids can beget gels, but also those made of polyphenolic compounds, such as lignin, which might gel upon cross-linking (Li, Ge, & Wan, 2015). In addition, polynucleotides seem to be excellent components for the construction of hydrogels with tunable mechanical properties (Gacanin, Synatschke, & Weil, 2019). This is due to the fact that the gel network is stabilized by covalent bonding and not by low energy and non-specific interactions, as occurs in polysaccharides.

2.2. Organogels

Despite the high number of literature results on aerogel preparation from hydrogels, information about the possibility of obtaining aerogels from organogels is almost absent. An organogel can be defined as tridimensional networks entrapping an organic liquid (Co & Marangoni, 2012; Patel & Dewettinck, 2016; Tétrech & Weiss, 1997). In the food sector, this organic fluid is often represented by oil, which accounts for the use of the organogel synonym “oleogel”. Most oleogelators are low molecular weight compounds that self-assemble to form thermo-reversible organogels. The latter are likely to be unsuitable for aerogel production. However, more recently, it has been demonstrated that even large biopolymers could be used for organogelation. Examples of biopolymers able to network in oil are cellulose derivative ethylcellulose, hydrophobic chitin “whiskers” and protein emulsions/foams (Davidovich-Pinhas, Barbut, & Marangoni, 2015; Huang et al., 2015; Laredo, Barbut, & Marangoni, 2011; Nikiforidis & Scholten, 2015; Patel, 2018; Romoscanu & Mezzenga, 2006). Removal of the solvent from these oleogels could be applied to turn them into highly lipophilic aerogels, with unique oil absorption features. The feasibility of producing hydrophobic aerogels from oleogels was recently investigated, allowing scaffolds entrapping 0.6 g oil/g (Manzocco, Basso, Plazzotta, & Calligaris, 2021).

2.3. Tissues

It has been inferred that even tissues could represent optimal candidates for the preparation of bioaerogel-like materials (Plazzotta et al., 2018b). For instance, vegetable matrices can be regarded as complex networks of cellulose, embedding water within intra- and inter-cellular spaces. Adequate drying of fresh-cut salad waste actually allowed obtaining aerogel-like materials with high internal surface (>100 m²/g) and low density (<0.5 g/cm³) (Plazzotta et al., 2018a, 2018b). The use of tissues for aerogel preparation could present the advantage of simplifying the production process, since the gelling phase is not required. In addition, development of aerogel from vegetable or animal wastes could allow valorization of industrial discards, which typically represent an environmental and economic burden.

3. Applications of aerogels in food

Aerogels are porous materials, mainly occupied by air, which could find applications as low-calorie ingredients, able to tune nutrient release and modulate satiety. In addition, because of the large surface area and open pore structure, aerogels can accommodate several components, begetting a full range of functionalized derivatives. Fig. 2 shows a schematization of the possible strategies for aerogels functionalization.

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**Fig. 3.** Aerogel engineering strategies: (a) Shape preservation; visual appearance of starch, and pectin hydrogels and their corresponding aerogels. (b) Effect of drying technique; optical appearance of a whey protein hydrogel prepared at pH 7 and the corresponding alcogels, aerogels and cryogels (above). The microstructure of the whey protein aerogels (bottom left) and cryogels (bottom right) obtained by supercritical drying and freeze-drying differed significantly in morphology and textural properties (S<sub>3</sub>, specific surface area determined from N<sub>2</sub> adsorption-desorption analysis). (c) Customized morphology; aerogels monoliths with personalized shape, aerogel particles from the millimetric to the micrometric sizes and coated aerogels. Adapted from https://doi.org/10.1016/j.supflu.2013.03.001, https://doi.org/10.1016/j.carbpol.2011.06.066, https://doi.org/10.1016/j.supflu.2012.08.019, https://doi.org/10.1038/s41586-020-2594-0, https://doi.org/10.1016/j.carbpol.2018.09.159, https://doi.org/10.1016/j.powtec.2015.
have demonstrated that wheat starch aerogels obtained from starch
tecting against diseases such as colon cancer, type 2 diabetes and
strategies to increase the amount of resistant starch in the diet. Resistant
polymer. Similarly, environmental conditions affecting digestion would
tion of polymer chains within an aerogel structure would occur ac
likely that diffusion, erosion, swelling and fragmentation during diges
undesired tastes and odors. On the other hand, based on their capacity to
- hydrogel
- alcogel
- ethylcellulose
- Xylan
- Xyloglucan
- Alginate
- Chitin
- Starch
- Pectin
- Carrageenan
- Gelose
- Gellan gum
- Xanthan gum
- Guar gum
- Locust bean gum
- Hyaluronan
- Gelatin
- Collagen
- Whey proteins
- Caseinate
- Egg white
- Lignin
- Polynucleotides
- Ethylcellulose
- Chitin “wiskers”
- Proteins

| Material | Building blocks | Biopolymer | Number of papers |
|----------|----------------|------------|-----------------|
| Hydrogel | Carbohydrates  | Cellulose  | 1129            |
|          |                | Hemicellulose | 28              |
|          |                | Glucan     | 10              |
|          |                | Xylan      | 4               |
|          |                | Xyloglucan | 4               |
|          |                | Alginate   | 231             |
|          |                | Chitin     | 65              |
|          |                | Starch     | 91              |
|          |                | Pectin     | 33              |
|          |                | Carrageenan| 23              |
|          |                | Gelose     | 24              |
|          |                | Gums       | 1               |
|          |                | Xylan      | 4               |
|          |                | Xyloglucan | 4               |
|          |                | Alginate   | 231             |
|          |                | Chitin     | 65              |
|          |                | Starch     | 91              |
|          |                | Pectin     | 33              |
|          |                | Carrageenan| 23              |
|          |                | Gelose     | 24              |
|          |                | Gums       | 1               |

| Aminoacids | Number of papers |
|------------|-----------------|
| Gelatin    | 52              |
| Collagen   | 24              |
| Whey proteins | 8           |
| Caseinate  | 2               |
| Egg white  | 4               |
| Lignin     | 1               |
| Polynucleotides | 1          |
| Ethylcellulose | 1        |
| Chitin “wiskers” | 1       |
| Proteins   | 1               |

| Tissues   | Number of papers |
|-----------|-----------------|
| 1         | 103             |

Search criteria: “aerogel” AND “name of biopolymer”; “aerogel” AND “tissue”. Search date: 28/11/2020.

From one side, aerogels can be used to protect and deliver target mole-
cules, potentially triggered by adverse environmental conditions or undesired tastes and odors. On the other hand, based on their capacity to
entrapp large amount of unsaturated lipids, aerogels could also be regarded as promising sources for the preparation of fat substitutes with
health protecting capacity.

3.1. Functional ingredients

Aerogel production steps (e.g. gel formation, solvent exchange, drying) are expected to modify the physical structure and the chemical interactions among the biopolymers used for their preparation. It is thus
likely that diffusion, erosion, swelling and fragmentation during diges-
tion of polymer chains within an aerogel structure would occur ac
rapping into account rates other than those typically associated to the unstructured polymer. Similarly, environmental conditions affecting digestion would be significantly altered. This opens up brand new possibilities for using aerogels as promising functional ingredients. In fact, in the simplest case, a functional food is requested to tune the release of nutritional compounds in the gastrointestinal tract, according to the specific con-
sumer needs. For instance, there is a growing interest in technological strategies to increase the amount of resistant starch in the diet. Resistant starch has actually the potential of improving human health by pro-
tecting against diseases such as colon cancer, type 2 diabetes and
obesity. In this context, Ubeyitogullari, Brahma, Rose, and Gifford (2018)
have demonstrated that wheat starch aerogels obtained from starch
gelatinised at 120 °C provided a 4.5-fold increase in resistant starch content, even after cooking. On the other hand, highly porous aerogel
particles could also be regarded as empty fillers, being inert or active depending on the occurrence of interactions with the other food

components. In addition, the proportion of air inclusion in a gel matrix is known to improve the food sensory properties by enhancing taste and
flavour perception. This is attributed to a higher diffusion rate of tustants when air is included, and contributes to an increased delivery and perception of saltiness, sweetness and flavor (Chiu, Hewson, Yang, Linforth, & Fisk, 2015; Goh, Leroux, Groeschild, & Busch, 2010). In
this sense, the introduction of aerogels in foods would represent an addi-
tional strategy to reduce energy and salt intake through the diet (Osterholt, Liane, Roe, & Rolls, 2007). Nevertheless, studies on the com-
patibility of aerogels with other food components during food pro-
cessing and storage are almost negligible, and no information is avail-
able on the effect of aerogels on food sensory properties and consumer
acceptability.

3.2. Delivery systems

The possibility of using aerogels as novel carriers has shown great promise and is certainly the most studied application in the food sector. Basically, the loading of the target compound in the aerogel can be performed at any step of its preparation (Fig. 2). Depending on this choice, two main strategies of aerogel functionalisation can be identi-
fied: wet and post drying impregnation. Table 2 compares the efficacy of these techniques when applied to impregnate differently prepared aerogels.

3.2.1. Wet impregnation

If target molecule incorporation is performed before drying, the process is generally referred to as wet impregnation (Fig. 2). In this case, the target compound is dissolved in one of the solvents that come into contact with the biopolymer during aerogel preparation (water or ethanol). Alternatively, the target molecule can be vehiculated by the SC-CO2 flow during supercritical drying of the alcogel following a drying impregnation approach (Comin et al., 2012). For instance, the target molecule could be simply inserted in the aqueous or ethanol solution used for hydrogel and alcogel preparation, respectively. This approach requires the molecule to exert a certain affinity to the selected solvent as well as to be resistant to environmental conditions of polymer gelation (e.g., high temperature, extreme pH and ionic force) and/or subsequent steps (solvent exchange and drying). Wet impregnation can be also performed into the alcogel. In this case, the alcogel is soaked in an ethanol solution containing the target molecule for a specific time. Following, drying is carried out using supercritical CO2, which extracts ethanol and causes precipitation of the target molecule within the aer-
ogel pores by an antisolvent mechanism (Miguel, Martin, Game, & Cocero, 2006). The efficacy of aerogel wet impregnation is strongly dependent on the target molecule-solvent affinity (Table 2). In fact, aerogel impregnation with phenol compounds, which are characterized by a high solubility in ethanol, seems quite effective. By contrast, oil impregnation by mixing with the aqueous phase of the hydrogel is efficacious only if water removal is performed by freeze drying, and thus avoiding possible oil transfer to supercritical CO2 (Comin et al., 2012; Lehtonen et al., 2020). A higher oil loading can be achieved by perform-
ing alcogel drying with a mixture of supercritical CO2 and oil (Comin et al., 2012). It has been postulated that the presence of oil in the supercritical CO2 may also assist in the removal of ethanol from the gel
pores, although the mechanisms is not clear (Comin et al., 2012).

3.2.2. Post-drying impregnation

In the post-drying impregnation, the active substance is loaded in the
dried aerogel. This can be performed by simply immersing the aerogel in the liquid target molecule (Table 2). Such procedure was used for
loading aerogels with an anti-fungal volatile (trans-2-hexanal) and can only be applied when the target molecule is a liquid that does not sol-
ubilize the aerogel polymer. In most cases, the target molecule to be
loaded in the aerogel is generally solubilised in an assisting solvent,
which is then allowed to diffuse into the aerogel pores. The subsequent

| Abstracts | Technology |
|-----------|------------|
| Food Science and | Food Science and |
| Technology Abstracts | Technology Abstracts |
| 1 | 1 |
| 103 | 103 |
| 10 | 10 |
| 28 | 28 |
| 1129 | 1129 |
| 13 | 13 |
| 2 | 2 |
| 2 | 2 |
| 1 | 1 |
| 1 | 1 |
| 1 | 1 |
removal of the solvent from the aerogel causes solute precipitation/absorption into the matrix pores. Depending on the characteristic of the target molecule, adequate solvents are selected. For instance, Ahmadi, Madadlou, and Saboury (2016) performed post drying oil impregnation by soaking a starch aerogel in a solution of hexane-oil. Following, hexane was evaporated under hood. Nevertheless, the most efficient and common methodology for post-drying impregnation is currently based on the use of supercritical CO$_2$ as assisting solvent (Table 2). In this case, a supercritical CO$_2$ solution saturated with the target molecule is allowed to diffuse into the aerogel pores. Molecule impregnation would result from chemical adsorption onto the aerogel pores as well as by capillary condensation and local precipitation upon depressurization (Gurikov & Smirnova, 2018). The depressurization of supercritical CO$_2$ is a critical step for impregnation: although fast depressurization is generally associated to higher loadings, slow depressurization allows avoiding the precipitation of the delivered compound on the surface of the material (Selmer et al., 2019). The latter is certainly undesired when particle agglomeration should be avoided to maintain the typical free-flowing property of dried materials.

Post drying loading assisted by supercritical CO$_2$ has been applied with reference to pharmaceutical compounds (Betz et al., 2012; García-González & Smirnova, 2013) as well as food ingredients (Table 2). The solubility of the target compounds in the solvent (i.e. supercritical CO$_2$) is a critical factor controlling the impregnation efficacy (Table 2) (Viganó et al., 2020).

Post drying impregnation of aerogels with non-polar compounds, such as oil, is generally reported to be quite effective, providing loading ratios in the range of 0.2–0.7 g oil/g aerogel (Kleemann et al., 2020; Selmer et al., 2019). By contrast, impregnation of molecules with lower polarity (vitamins or lactulose) seems more critical (Díez-Munio, Montilla, Herrero, Olano, & Ibañez, 2011; García-González et al., 2015; Ubayyogullari & Ciftci, 2019). Accordingly, when impregnation involves complex mixtures of molecules with different affinity for SC-CO$_2$, such as oils, the relative abundance of their components in the entrapped oil can be significantly different from that of the original oil. For instance, fish oil entrapped in protein aerogels presented much higher content in triglycerides and cholesterol, and lower content in free fatty acids than fish oil used for loading (Selmer et al., 2019). Comparing data reported in Table 2, it is interesting to note that high loading efficacy of lipids was observed for impregnation into both protein- and polysaccharide-based aerogels. This suggests that the contribution of physical entrapment into the aerogel pores is probably the most critical factor controlling lipid impregnation. In other words, oil absorption into the pores would be driven by number, dimension, interconnectivity and size distribution of pores rather than by the chemical interaction of oil components with the functional groups available on the aerogel surface.

3.2.3. Stability and functionality of aerogel delivery systems

Despite the abundance of papers dealing with impregnated aerogels, limited information is available about their capacity of modifying stability and functionality of the entrapped components. Available data suggest that aerogels would be able to protect sensitive compounds. For instance, entrapping plant extracts into cellulose aerogels was shown to highly maintain their antioxidant activity (De Oliveira et al., 2020). Aerogel coating seems to be critical to decrease oxygen susceptibility of loaded oil. To this regard, Ahmadi et al. (2016) showed that fish oil entrapped in whey protein aerogels coated with zein presented about 60 % lower peroxide value than oil impregnated without coating.

The peculiar physical properties of aerogels are also expected to modify the bioavailability of loaded molecules. To this regard, in vitro bioavailability of phytosterols loaded into starch aerogels resulted significantly higher (35 %) than that of the crude phytosterols (3 %).
recycling routes. Importantly, consumer experience and user (active packaging) (Dobrucka 2010). Packaging materials are selected based on their capacity to pacts, including origin of raw materials, sustainability of processing, and maximization of the interactions among proteins (Tang, Wei, & Guo, 2014). Due to this water insolubility, the release of loaded materials is generally delayed (Betz et al., 2012). As an example, fish oil loaded in protein aerogels was mainly released during intestinal digestion, whereas only a small amount was released during oral and gastric digestion (Kleemann et al., 2020).

3.3. Fat replacers

According to their open pore structure and large surface area, aerogels quickly uptake large amounts of oil. This capacity is particularly interesting for the preparation of oleogels, which are mainly proposed as fat substitutes to obtain healthier foods with reduced content of saturated/trans fatty acids (Patel & Dewettinck, 2016; Stortz, Zetl, Barbut, Cattaruzza, & Marangoni, 2012). According to this application, the oil fraction is driven into the pores of aerogel particles by capillary forces and held at the aerogel surface by surface-oil interactions. For this reason, large amounts of oil closely stick onto the aerogel surface both inside the pores and outside the aerogel particle, which loses the typical dry appearance. The presence of oil at the surface of the hydrophilic particles favors particle-particle interactions, due to intense hydrogen bonding in a nonpolar environment (De Vries, Lopez Gomez, Jansen, van der Linden, & Scholten, 2017). This mechanism allows the formation of a strong particle network, where protein particles behave like building blocks able to embed oil within pores as well as to hold it tightly in the interparticle space (Plazzotta et al., 2020). Absorbed oil is generally higher than 2 g per g of aerogel, regardless of the chemical nature of the aerogel (Table 2). In the case of oleogels obtained from aggregation of whey protein aerogels, the oil content exceeded 5 times the weight of the aerogel particles. The obtained material did not lose any oil upon centrifugation and presented the typical plastic behavior of commercial solid fats (Plazzotta et al., 2020).

4. Applications of aerogels in food packaging

Packaging materials have multiple purposes, being the most important to protect the packed product against mechanical stress, gases and vapors, moisture, light, temperature, microbes, and dirt (Robertson, 2010). Packaging materials are selected based on their capacity to provide this protection, taking into account the other functions that a packaging material may perform, including containing, transporting, serving, presenting the product, and providing information to consumers. Packaging materials can be used as primary packaging, i.e. consumer packaging, or secondary packaging which contains a defined number of primary packages. Secondary packaging units can also be gathered in a tertiary packaging for better transport and storage. The concept of packaging materials also includes a variety of components that can be inserted in the primary packaging to provide further information of the product quality and shelf-life (intelligent packaging), or to extend the shelf-life by adsorbing or releasing functional components (active packaging) (Dobrucka & Przekop, 2019). Other important criteria for packaging materials are their price and environmental impacts, including origin of raw materials, sustainability of processing, and recycling routes. Importantly, consumer experience and user friendliness determine the market potential of packaging materials.

The most important and unique property of aerogels for food packaging is their porous structure, leading to low weight and high specific surface area. This provides interesting opportunities for mechanical protection, thermal insulation, or active packaging materials capable of adsorbing or releasing specific compounds. Aerogel structures also offer an inspiring basis for designers to develop and construct material shapes (Michaloudis & Dann, 2017), which is essential in packaging design.

The mechanical properties of aerogels are determined by their porous morphology (Gnafar et al., 2017). Reinforcing components, such as nanoparticles or fibers can be added to increase the aerogel strength. A practical illustration of the aerogel strength is the weight an aerogel can withstand on it. For example, a chitin-based aerogel square weighing 60 mg and having ~5.6 cm² apparent volume withstand an object of 100 g without any shape distortion (Yan et al., 2020). Such strong materials could provide efficient protection to packed food against mechanical stress that could occur during transport or handling. Moisture can alter material properties, especially of materials derived from bio-based polymers. Repeated (minimum five cycles) mechanical milling followed by freezing in liquid nitrogen and thawing partially separated micro- and nanosized fibrils from cellulose fibers, and enabled preparation of dimensionally stable aerogels that retained their shapes and geometric sizes in solutions (Khelebikov, Postnova, Chen, & Shchupunov, 2020). This is a highly useful property with materials in contact with moist substances, like many foods.

A bio-based thermal insulator, such as aerogel, could be a sustainable replacement for expanded polystyrene used widely to pack products that need either cold storage, such as fish, or maintaining the temperature of hot contents, such as ready-made meals or hot beverages (Mikkonen et al., 2013). Pectin-TiO2 nanocomposite aerogels were proposed for the storage of temperature-sensitive food and prepared via a sol-gel process (Nesić et al., 2018). The thermal conductivity of these aerogels was 0.022–0.025 W/m K, being lower than the thermal conductivity of air (0.024–0.032 W/m K). The thermal conductivity of pectin aerogels followed the aerogel density within a U-shaped curve, where the density depended on preparation conditions, such as cross-linking degree and pH of the solvent (Groutl & Budtova, 2018). Pectin aerogels with thermal conductivity as low as 0.0147 ± 0.0002 W/m K were obtained with the optimized preparation method. The conjunction of the thermal insulation and the lightweight is especially attractive for specialized food service conditions like aircraft meal services or crewed spacecraft food, where solutions with reduced fuel consumption is a must.

An active aerogel component was developed to be used to extend the shelf-life of fresh fruit and vegetables (Lehtonen et al., 2020). This innovation was based on in situ production and release of a volatile compound (hexanal), which affects plant metabolism by decreasing ethylene production, and prevents growth of spoilage microbes. The concept was tested with blueberries, where less mold growth was observed, and cherry tomatoes, which maintained their firmness longer when packed with the hexanal-releasing active component in comparision with control samples.

5. Aerogels within EU food regulation

The use of aerogels in foods is not mentioned in current regulation. To this regard, not only the criticisms of production but also the safety issues of the final aerogels require some considerations. Among the advantages of aerogels, literature indicate the absence of hazardous chemicals in the material preparation. Nevertheless, attention should be paid to the use of ethanol in water substitution step. The operation must be performed using ethanol without any denaturant, and considering that volatile residues could remain selectively adsorbed on the high surface area of the aerogel. This might lead to consumption limitations for specific consumers, such as children or people with religious dietary restrictions.

As regards aerogel safety under EU regulation, the question is
whether these novel materials can be examined under the current Novel Foods Regulation (EU Regulation 2015/2283, 2015). Based on this regulation, ‘novel food’ means any food that was not used for human consumption within the European Union before 1997, and that falls under a defined list of categories. Among the latter, specific mention is made to food with a new or intentionally modified molecular structure as well as food resulting from technological interventions not previously used. Although not yet used for human consumption, most biopolymer aerogels seem not to fall under this category since they are made with polymers with a long history of safe food use and obtained by drying technologies which have long been used in the food sector.

Nevertheless, in aerogel production, unit operations are combined according to a novel process, in order to intentionally modify the physical structure. The large specific surface area and the pore sizes than come thereof is regarded as a property characteristic of the nanoscale (EU Regulation 2015/2283, 2015). In other words, even if aerogel monoliths or particles have sizes well above the order of 100 nm, their large surface area would account for specific physico-chemical properties that are different from those of the non-nanostructured form of the same polymer. In this sense, aerogels could be considered as engineered nanomaterials.

The debate on aerogels within food regulation is also open to other considerations, including the fact that the surface area of commercial foods obtained by freeze drying and supercritical extraction can fall in the same magnitude range of aerogels. However, in this case, there is a conceptual difference since the large surface area of aerogels is intentionally exploited to functionalise the material and improve its performance. Research on food aerogels is still in its embryonic phase and hence has not yet risen the attention of legislators. More information is certainly needed to distinguish aerogels that can be inserted in the diet from those that will require a specific authorisation.

As regards the use of aerogel as packaging materials, mention should be made to the general principles of safety and inertness for all Food Contact Materials, defined in the Commission Regulation (EC) No 1935/2004. This regulation states that the materials shall not release their constituents into food at levels harmful to human health or that change food composition, taste and odour in an unacceptable way. This should be ensured when aerogels are developed as packaging materials. Active and intelligent materials are considered under specified rules in Commission Regulation (EC) No 450/2009, as by their design they are not inert. Such materials may for example absorb substances from food packaging interior such as liquid and oxygen, release substances into the food such as preservatives, or indicate expiry of food through labelling that changes colour when maximum shelf life or storage temperature is exceeded. Substances permitted for the manufacture of active and intelligent materials are listed in the regulation. New packaging materials, including aerogel delivery systems, must go through safety evaluation as defined in the European Food Safety Authority guidelines (https://efsanetlibrary.wiley.com/doi/epdf/10.2903/j.efsa.2008.211). One possible solution is to coat the aerogel packaging surface with a barrier layer.

6. Future trends and research needs

An obvious concern with use of aerogels relates to their costs. Bio-based aerogels are typically obtained using highly purified molecules which are costly and produced with considerable waste generation. On the contrary, to allow valorization of industrial discards, which typically represent an environmental and economic burden, aerogels can be prepared according to virtues cycles of circular economy (Budnova et al., 2020). The production of cellulose-based aerogels has been explored using aqueous suspensions of cellulosic fractions of waste biomass, including cane bagasse, lupin hull, corn bracts, rice and oat husks, and spent coffee grounds (Ciftci et al., 2017; De Oliveira et al., 2019, 2020; Fontes-Candia, Erboz, Martinez-Abad, Lopez-Rubio, & Martinez-Sanz, 2019; Jing et al., 2019; Liu, Li, Zhang, Zhu, & Qiu, 2020; Zhang, Kwek, Li, Tan, & Duong, 2019). A further option is based on directly turning cellulose-rich vegetable waste into aerogels with the advantage of simplifying production process (Plazzotta et al., 2018b). Similarly, an increasing number of recent publications explore the possibility to upgrade low-value side streams to obtain aerogels for packaging applications from renewable resources (Alakalhunmaa et al., 2016). Thus the cost contribution of raw materials for aerogel preparation may be low but, on the other hand, a multiple step production process that requires the use of high amounts of solvents, such as supercritical CO2, is costly. Minimization of fresh solvent and continuous CO2 drying process could facilitate aerogel production and reduce costs in industrial scale compared to batch production (Miffl¨undt et al., 2020).

Research about aerogel structure in the context of its relationship with molecular composition, processing techniques and potential functionality in food is currently being studied at laboratory level. By contrast, the fate of aerogel ingredients within food materials is almost unknown. Aerogel particles were inserted into two food products, namely, granola bars and puddings, without any specific processing issue, and provided circumstantial evidence that aerogels can be successfully implemented in food formulations (Ubeyitogullari & Ciftci, 2019). Nevertheless, the specific physical properties of aerogels suggest the need for proper adjustments of formulation, processing and storage conditions of aerogel-containing foods. The latter should be then submitted to in vitro studies to clearly highlight their fate in human gut as well as to studies evaluating consumer attitude towards aerogels and market acceptance potentiality.

When considering aerogels for food packaging, two main challenges should be addressed by the aerogel community. Firstly, transparency of bio-based aerogels should be improved. The visual appearance of packaging materials is significant for consumer experience, with transparent materials being often preferred to allow visibility of the packed food. Highly transparent aerogels from oxidized cellulose were recently developed (Pappert et al., 2017) and lead the way to broadening the properties and application range of aerogels. Secondly, after use, packaging materials can be recycled back to material production, burnt for energy, composted, or discarded to landfill. The aerogel composition and its eventual assembling into multicomponent materials will strictly condition the potential recycling options.

Finally, the main issue to be tackled in aerogel technology to become a mainstream solution for food applications is a clear definition of the conditions for their safe use for human consumption and food contact. Testing aerogels with nanostructured properties is not a trivial task, especially when they are inserted in foods, and will require the availability of methods designed to clearly define nature and kinetics of their interaction with biological tissues.

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