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Exploring the Versatility of Starch Aerogels: A Critical Review and Future Trends Analysis

Karunakar Singh[1*], Usman Ahmed[1], Mahir Kumar[1]
[1]Department of Food Technology, Bhai Gurdas Institute of Engineering and Technology, Sangrur

Abstract: The aerogels are new groups of ultra-light materials that exhibit characteristics like high porosity, low density and excellent barrier properties. The development of aerogels had started in 1931, but commercial utilization was not possible until recent decades because of inefficient and riskier development methods. In recent decades, aerogels have mainly used for thermal insulation, but they have huge potentials to be used in various applications. Despite several source materials have been explored for the development of aerogels, silica based are the most used today. Starch is the most abundant, intensively utilized, low cost biopolymer and one of the source for production of aerogel. The development of starch based aerogels is ecofriendly, cheap, nontoxic and potentially can be used in various applications. Conclusively, the starch based aerogels have huge potential to be an advance material for various engineering applications.

General Terms: Starch, Aerogel, Supercritical Drying, Biodegradable, Gelatinization, Retrogradation

Keywords: Starch, Aerogel, Biodegradable, Supercritical Drying, Thermal Insulation, Drug Delivery, Absorbent.

Review Paper

***Corresponding Author:**
Karunakar Singh
Department of Food Technology, Bhai Gurdas Institute of Engineering and Technology, Sangrur

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1. INTRODUCTION

According to IUPAC, aerogel is defined as a gel comprised of a microporous solid in which the dispersed phase is a gas [1]. Basically, aerogel is synthetic ultra-light material with high porosity which is formed by replacing the liquid inside gel with a gas [2]. The high porosity of aerogel makes them extremely low in density, and gas inside them makes them very bad conductor of heat.

Starch is one of the most abundant and low cost biopolymer found in the leaves, seeds and tubers in the form of granules. The special phenomena of retrogradation re-arranges and re-associates the gelatinized starch molecules into ordered crystals at low temperature [3]. The solvent from the retrograded starch structure when removed, aerogels formed. Starch based aerogels are stable and biodegradable materials with low density (0.003–0.15 kg/m^3) and high specific surface area (500–1000 m^2 /g) [4, 5]. Moreover, they are non-toxic in nature as compared to inorganic aerogels. These specific properties are attracting interest from food, nutraceutical and pharmaceutical industries for various applications. Additionally, aerogels can be developed in the form of monoliths, powders and films, which further expand the field of their application. The present brief review will cover the history, application and future potentials of starch aerogel.

2. Historical Background

The father of aerogel "Samuel Stephens Kistler" developed aerogel for the first time in 1931 from jellies and his work was published by Nature [6]. Kistler also developed the first silica aerogel which is most commonly used aerogel in recent decades. The first commercial production of aerogels was started by Monsanto Corporation in 1940. But, Kistler's method of replacing the liquid with supercritical alcohol was more risky, time taking and expensive too. Later on, scientists found out a new method of supercritical drying by using a safer alkoxide compound. The introduction of supercritical carbon dioxide in place of supercritical alcohol reduces the time as well as hazards. This new method is well adapted in the current aerogel manufacturing process with some alternative methods like freeze drying.

3. Starch Based Aerogels

The inorganic aerogels made of silica graphene and metal oxide are most studied and successfully adopted commercially [7]. But, in last decades aerogels based on biopolymers have caught the interest of researchers to explore the potential of starch, cellulose, alginate, agar, chitin, κ-carrageenan, etc. in aerogels developments [8]. The biopolymers are rich in functional groups mainly, hydroxyl groups which play an integral role in the development of the structure of starch aerogel. Moreover, most of the biopolymer's sources are nontoxic, sustainable and biodegradable in nature.

Table 1: List of some starch based aerogels

Starch source	Properties analyzed	References
Potato, Pea, Corn	Bulk density, morphology, surface area, thermal conductivity and mechanical properties	[9]
Wheat	Surface area, pore size, and pore volume, morphology, water solubility and thermal stability	[10]
Potato, maize	Drug adsorption and drug release	[11]
Corn	Density, surface areas, crystallinity and morphology	[12]
Corn, Pea	Surface area, particle size distribution, morphology, adsorption and release active compound	[13]
Potato, maize, rice	Specific surface area, thermal decomposition, crystallinity, electrical conductivity	[14]
Maize	Solubility, adsorption, crystallinity, thermal properties, surface area	[15]

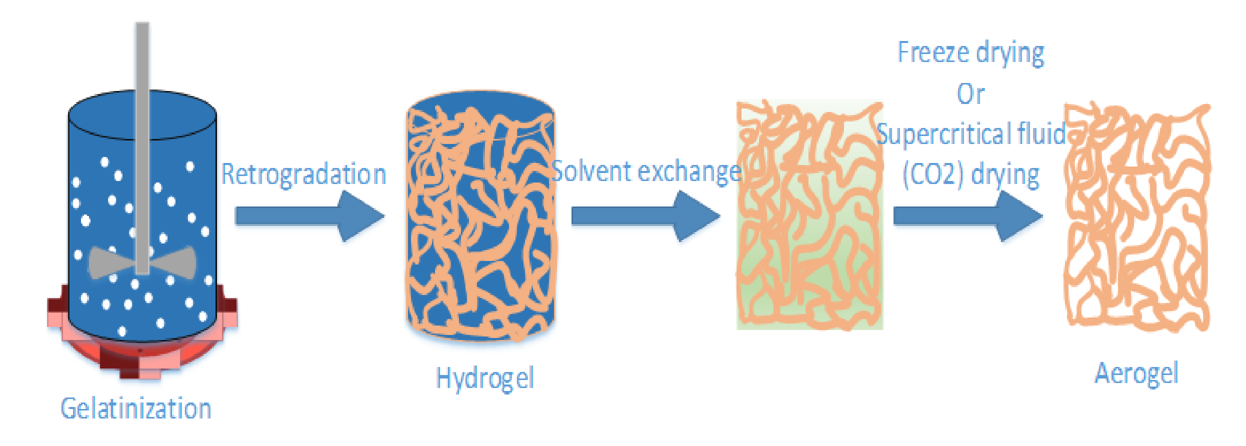

Figure 1: Process diagram for the development of aerogels from starch

The development of aerogels starts with the gelatinization of starch as presented in Figure 1. The gelatinized starch is then kept at low temperature for retrogradation in which starch molecules rearrange and reordered to form strong networks. The retrograded starch contains water, which is replaced by other volatile solvents without damaging the pores. In the final stage, either freeze drying or supercritical fluid drying is mainly used to remove remains of water without any shrinkage or disturbance of pores. Freeze drying can also be used to remove moisture by sublimation without affecting the structure of hydrogel. In general, freeze drying is a much simpler, more economical and environmentally friendly process than ambient pressure drying. However, some notable precautions such as long aging duration to stabilize the gel body, a solvent exchange to provide a low expansion coefficient and high sublimation pressure, and the addition of salts to achieve low freezing rates and freezing temperatures are considered while freeze drying. The starch based aerogels reported is presented in Table 1.

4. Properties of Aerogel

The aerogels have unique structural properties which contribute to their useful thermal, mechanical, electrical and chemical properties. Structural features like porosity, mass density, average pore size, pore size distribution, particle size, and surface area decide the aerogel's application based properties like thermal conductivity, acoustic barrier properties, mechanical strength, electrical properties, etc. Moreover, the morphological properties also decide the adsorption behavior and maximum adsorption of chemicals in the aerogel matrix [16]. It has been well reported that aerogels have ultrahigh porosity and ultralow density, very high surface area, ultralow thermal conductive, refractive index and dielectric constant [17]. These extreme physical characteristics make aerogels the excellent barrier of heat, light and sound. In addition to thermal and barrier applications, the biological use of aerogels depends on pore structure, biocompatibility and stability in liquids [18, 19]. In the case of the biosensor, properties like open porosity and surface functionalization to selectively target molecules are important [20, 21]. In drug delivery applications, high surface area, accessibility of the pores and affinity of aerogels to given the drugs are critical properties for delivery system design [22, 23]. In tissue engineering applications, the interaction of meso/ macro porosity and biocompatibility of aerogels are decisive properties [24, 25].

Furthermore, surface functionalization open porosity, hydrophobicity or oleophobicity decide the sorption properties of aerogels [26, 27]. The sorption characteristics of aerogels are used to absorb heavy metal ions, water treatment and oil spills. In bio-catalysis applications, properties like compatibility with various enzymes, the ability to adjust pore size to molecular size of particular reaction products and non-toxic nature of byproducts are considered [28]. In addition to structural characteristics discussed above, digestibility solubility, wetting property and crystallinity of starch aerogels are critical parameters to describe the specific application of starch aerogel. Lastly, it can be concluded that aerogels use are widely expanded and the different properties are still explored by researchers for the specific applications.

5. Applications

The applications of aerogels have been explored in recent decades for the specific purpose as shown in Figure 2. The aerogels from starch have been used for encapsulation and controlled release of bioactive compounds [10-31], biomedical uses and tissue engineering [32, 33], as packaging and thermal materials [34, 35], and as templates for the synthesis of novel functional materials [36, 37]. Moreover, aerogel can be utilized as superabsorbent [38], air filtration units due to the high number of pores [39-41]. More popularly, NASA has successfully used aerogels to trap space projectiles travelling with hypervelocity speed to protect the satellites and other similar objects. Also, they have been used as a thermal barrier in space suits due to porous, low density and light weight nature [42].

The starch based aerogels have also utilized as an active packaging material [43]. Moreover, the high amylose starch based carbon aerogel has been found to possess high electrical conductivity could be potentially used as a semiconductor material [44]. Though starch based aerogels have attracted the researchers due to biodegradable, nontoxic and risk-free development, commercial production and utilization are still rare as compared to silica based aerogel. For an insight, in India, organic aerogels have neither been intensively studied nor used for specific purpose. But, the application of aerogel based products like carbon aerogel (formed after pyrolysis of starch aerogels) have been explored by several researchers as heavy metal absorbent [45, 46].

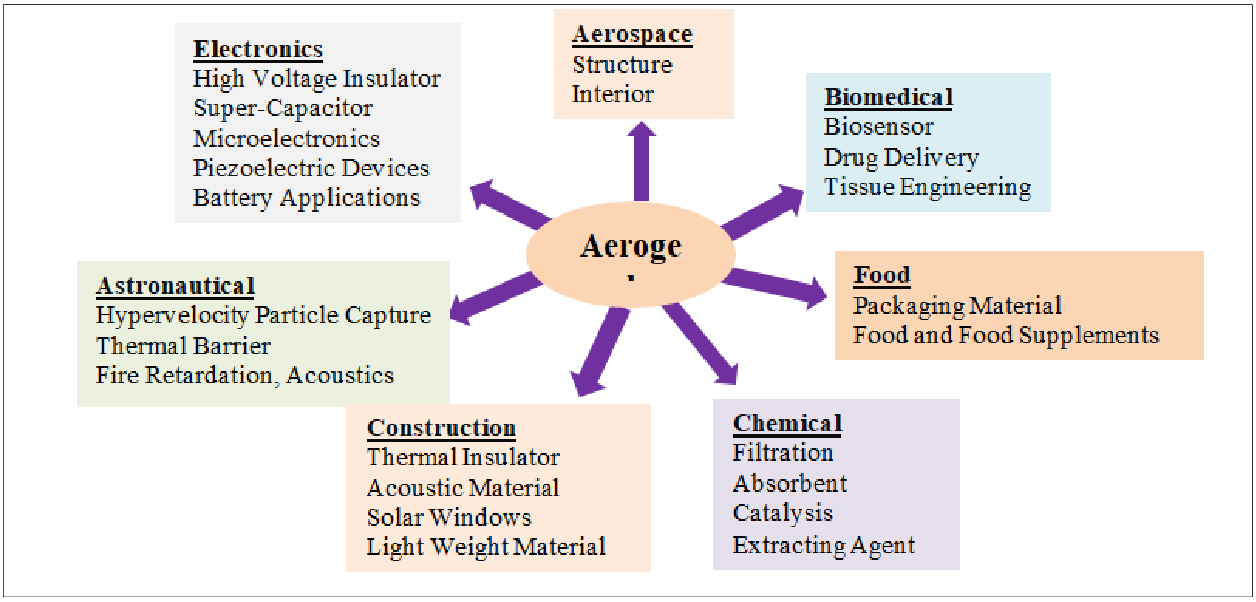

Figure 2: Wide range of applications of aerogels in the different technical fields.

6. Challenges and Future Trends

The studies in recent decades have successfully explored the structural and functional properties of starch aerogels. The major reason why starch aerogels are still not commercially-viable is their mechanical properties. The brittle nature of aerogels limits its applications [47]. Additionally, the hygroscopic nature of starch aerogels also limits the uses to the dry environment only. From the economical aspect, supercritical drying is the most expensive method for replacing the solvent inside the aerogel [48]. Due to these constraints, commercial applications of starch based aerogels are restricted to carbon, and some small amounts of organic aerogels.

The scientific studies on structural and functional properties of starch aerogels direct toward great potential in the future. The greatest advantage of using starch is its ability to change the structural, functional and morphological properties after different kinds of starch modifications. These properties of starch aerogels can easily be tuned using different preparation conditions like starch type, modification, the addition of other biopolymers, etc. after optimizing formulations and processing parameters. In biomedical applications, starch aerogels have a clear advantage over inorganic aerogels which are mechanical irritants to the eyes, skin, respiratory tract, and digestive system [49]. In the technical aspect, engineering properties of starch aerogels are comparable with alternative materials for the specific applications. Hence, the applications of starch aerogels will be more sustainable as compared to similar inorganic material and technically.

7. CONCLUSION

The aerogels are synthetic ultra-light material with high porosity currently being used in various applications due to their extreme properties. The aerogels are prepared from diverse types of inorganic as well as organic materials. The development of starch aerogels starts with gelatinization and retrogradation phenomena of starch and aerogel formed is ecofriendly and nontoxic. Though starch aerogel has been explored to use as thermal and acoustic insulators, packaging materials, drug delivery systems and others, commercial production and utilization are still rare due to expensive production and poor mechanical properties. The starch modification, addition of other additives like hydrocolloids can tune the properties of starch aerogels as per specific requirements. But, in this regard, studies are rare and have partially compared the properties of starch aerogels with alternatives materials. Hence, the optimization of additives and preparation methods need to be critically studied in the future to explore the other potential of starch aerogels.

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