



Revieu

Applications of Plant Polymer-Based Solid Foams: Current Trends in the Food Industry

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Abstract: Foams are a type of material of great importance, having an extensive range of applications due to a combination of several characteristics, such as ultra-low density, tunable porous architecture, and outstanding mechanical properties. The production of polymer foams worldwide is dominated by those based on synthetic polymers, which might be biodegradable or non-biodegradable. The latter is a great environmental concern and has become a major waste management problem. Foams derived from renewable resources have aroused the interest of researchers, solid foams made from plant polymers in particular. This review focuses on the development of plant polymer-based solid foams and their applications in the food industry over the last fifteen years, highlighting the relationship between their material and structural properties. The applications of these foams fall mainly into two categories: edible foams and packaging materials. Most plant polymers utilized for edible applications are protein-based, while starch and cellulose are commonly used to produce food packaging materials because of their ready availability and low cost. However, plant polymer-based solid foams exhibit some drawbacks related to their high water absorbency and poor mechanical properties. Most research has concentrated on improving these two physical properties, though few studies give a solid understanding and comprehension of the micro- to macrostructural modifications that would allow for the proper handling and design of foaming processes. There are, therefore, several challenges to be faced, the control of solid foam structural properties being the main one.

Keywords: foams; cellulose; natural fibers; mechanical properties; microstructure



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1. Introduction

Foams are a type of material of great importance with an extensive variety of applications due to their combining several characteristics, such as ultra-low density and tunable porous architecture and mechanical properties. Industrial applications include their being used in kinetic energy absorbers, biomedical scaffolds, thermal insulation, construction, separations, and devices for the storage and generation of energy [1].

The production of polymer foams worldwide is currently dominated by those based on synthetic polymers. They are mostly inexpensive and tailor-made to serve several purposes, having a wide range of applications where mechanical function is important, both in the food and non-food industries [2,3]. Synthetic polymers might be biodegradable (e.g., poly(glycolic acid) (PGA), poly(lactic acid) (PLA) and their copolymers) or non-biodegradable [4]. The latter is a great environmental concern, since non-biodegradable polymer based-foams have become a significant part of countries' solid waste, posing a major waste management challenge [5,6]. Commonly, non-biodegradable synthetic polymer-based foams are petroleum-derived, such as polyethylene (PE), polystyrene (PS), polyurethanes (PU), and polypropylene (PP) [6,7]. Biodegradable polymers decompose into CO₂, water, inorganic compounds, and biomasses that finally form humus [8], which recommends them as alternatives to non-biodegradable polymer foams [8,9].

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In this context of increased environmental concern, many researchers have developed foams from renewable resources, such as cellulosic materials, starch, proteins, and other biopolymers, for food, environmental, medical, and other applications [5,6]. Some of these have shown great short-term promise, particularly in medical and environmental contexts, and research into this area has been making great advances in the last decade. Due to the high number of them, not all the applications can be considered in this systematic review, which will restrict its focus to the development of solid foams produced from plant polymers with potential or direct applications in the food industry over the period from 2015 to 2021. A systematic literature search was performed across the Web of Science, Science Direct, and MDPI databases. The information is organized according to the main sources of the foaming agents, with a special emphasis on the foam structure—property relationships.

2. Food Industry Applications

Utilization of plant polymer-based solid foams in the food industry can be categorized into two main areas according to their final uses: (i) as an edible material, e.g., food matrix, or (ii) as packaging material. Although their final state is solid, solid foams start as wet foams before being solidified. They can be produced by different mechanical, physical, and chemical foaming processes [10]. In the wet stage, they are air-filled systems, in which foam structure stabilization is the result of molecules acting as surfactants or Pickering stabilizers. The transition from a wet to a solid state is usually accomplished by either cooling, heating, or curing the wet foam [11]. The processing techniques to solidify plant polymer-based foams may include baking, freeze-drying, extrusion, injection molding, or compression molding processes [12]. For packaging materials, supercritical fluids, such as carbon dioxide (CO_2) or nitrogen (N_2), can be used with molding techniques, producing stable foams that are lighter and of higher dimensions than their solid counterparts [10].

Edible solid foams constitute the fundamental basis of several food products, such as bread, meringue, and ice cream [13]. For a solid foam to be considered an edible material, the first consideration, obviously, is to be food grade. Additionally, some important properties to be evaluated are moisture adsorption capacity, mechanical and physical properties, sensory and organoleptic properties, cell morphology, digestibility, loading capacity, etc. The evaluation will depend on the targeted usage of the foam.

Some of the properties mentioned above will be relevant for foams intended to serve as a structural basis for packaging materials. However, certain mechanical and physical properties will be of special relevance to their suitability for this purpose. Thus, these foams must: (i) provide protection for fragile food products, (ii) show appropriate mechanical and barrier properties, (iii) be lightweight and (iv) non-toxic, and (v) have appropriate moisture adsorption capacity, amongst other things. In addition, the evaluated properties will depend on the food to be packaged, as well as other factors, such as shelf-life, storage conditions, etc. [14,15].

The present review article deals with the research and development of solid foams derived from plant polymers with potential or direct applications in the food industry over the last fifteen years. Additionally, this review will highlight details of the micro- and nanostructure of foam, the structure–property relationships between polymers, and the physicochemical characteristics elucidated in the studies consulted. It should be borne in mind that although the rheological properties before solidification are important for the physicochemical characteristics of solid foams, this matter will not be addressed in this review due to the depth of the matter and because it has already been touched upon in several other reviews. Readers are encouraged to seek out more detailed information in the articles by Dollet and Raufaste [16], Nastaj and Sołowiej [17] and Alavi et al. [18].

2.1. Plant Polymer-Based Foams as Edible Materials

Edible solid foams are of interest for a variety of applications in the food industries. Those produced from plant-derived compounds have been gaining in importance not only amongst vegan, vegetarian, and flexitarian consumers, but also amongst those who are

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concerned about carbon footprints. Despite the many deficiencies of early plant polymers, in terms of function, drawbacks or higher prices which limited their acceptance, the abundance of agricultural commodities and new regulations for material recycling and disposal have made them more desirable, as they are relatively inexpensive and ubiquitous [19]. Depending on the foaming agent, foam pore configuration, mechanical properties, and possible tunable structure, various edible plant polymer-based foams can be developed to serve different purposes. To describe those applications, the following information is organized according to the foaming agent, highlighting its role in the final product structure, and is summarized in Table 1, where further details about foam structure and polymer structure are given (for a list of some polymers, see Figure 1).

PLANT POLYMERS

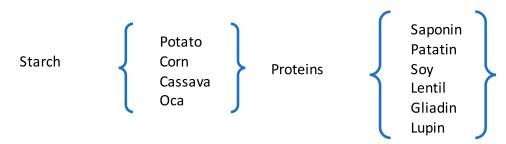


Figure 1. Examples of sources of plant polymers utilized to produce solid foams.

2.1.1. Saponins

Saponins (Figure 2) are amphiphilic glycosidic secondary metabolites produced by a wide variety of plants. Soapwort (*Saponaria officinalis*) is a natural source of saponins, which are known for their surface properties and capacity to form foams [20]. Jurado-Gonzalez and Sörensen [21] studied the chemical and physical properties of soapwort extract as well as its foaming properties under common food processing conditions, such as in the presence of sodium chloride and sucrose. The saponin extract exhibited high foaming capacity and stability. In addition, low pH did not significantly affect foam properties, while heating the extract improved the foaming capacity and stability. Testing the saponin extract at concentrations below 30% ethanol slowly lowered its foaming capacity. Meanwhile, heating increased foam capacity and stability. All these results confirm that the saponin extract from soapwort is a potential alternative foaming agent for use in several food systems, especially in hot food applications.

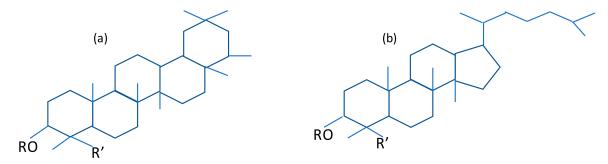


Figure 2. Saponin structure: (a) Triterpenoid type; and (b) Steroid type.

For example, the soapwort concentrate and extract powder enriched with saponin developed by Çam and Topuz [22] through optimized extraction, enrichment, and drying processes was used as a foaming agent in the production of traditional Turkish delight. The foams produced from saponin concentrate and extract powder showed good stability and

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resistance to heating process. In terms of chewiness, taste, and texture, they had similar results to commercial soapwort extract at the same soluble solid content, though these foams scored slightly lower than the latter. However, a positive aspect is that taste and odor problems caused by microbial proliferation, along with quality losses due to the lack of standardization in the extracting process, are less frequent than when commercial soapwort extract is used, which creates an opportunity for industrial production. Characterizations of the foam structure, which might help to improve the final product were not systematically conducted, thus further research is required for understanding the textural analysis results.

2.1.2. Potato Protein

Potato protein obtained as a by-product of starch production has several potential applications in the food industry. The most abundant protein fraction is patatin, which has shown good foaming properties, as demonstrated by Schmidt et al. [23]. The foaming capacity of patatin samples tested by Schmidt ranged from ~0.8–1.8 L/L, with the highest overrun value at pH 3 and reduced values at pH 5 and 7, respectively. Higher foam overrun at pH 3 is likely related to the unfolding of patatin at pH levels lower than 4.5. Foam stability of different potato protein fractions displayed a wide range of values. The relative foam stability was lowest at pH 3, ranging from 18–78% of the initial foam, while 67–80% was seen at pH 5 and 7. Descended stability value was especially pronounced for the patatin fraction, though the reason behind this is not known. It is suggested that phenolic compounds present in these fractions can alter the hydrophobic character of proteins. Thus, patatin fractions may show different stability values due to modifications in surface activity, foam height stability, and liquid drainage [23].

Ozcelik, Ambros, Morais, and Kulozik [24] examined the use of patatin as a foaming agent and pectin as a foam stabilizer to produce a snack from dried raspberry puree foam by freeze drying. They also compared the effects of using microwaves during freeze drying on the structure and on the storage behavior of the raspberry puree foam. The results showed that raspberry puree has a better storage stability under the foam structure during the long-term storage period at 37 $^{\circ}$ C. It was expected that the open porous structure could have increased the deterioration of the bioactives due to the higher surface area. However, by the end of the study, Ozcelik et al. hypothesized that hydrocolloids and potato protein produced a protective barrier as a dried lamella in the foam structure around the pores which resembles a glassy membrane structure and slows down the deterioration. The microwave-assisted freeze-drying process did not affect raspberry puree foam negatively during storage, as compared to the traditional freeze-drying technology used as a control. For example, there was no significant difference (p > 0.05) in the color among all samples by the end of storage. Furthermore, water activity was below 0.6 for all samples during the entire storage period; thus, microbiological stability was ensured.

2.1.3. Soy Protein

The quaternary and tertiary structures of native soy protein limit and hinder foaming properties for food applications because of the large size of the molecules and their compact tertiary structure. Thus, some treatments that modify structure, such as heating and hydrolysis, must be applied to allow soy protein to be used as a foaming agent [25].

Soy protein isolate (SPI) was utilized by Zhang et al. [26] to prepare a solid foam from freeze-dried O/W emulsions containing bacterial cellulose (BC) as Pickering particles. Using different oil fractions, the researchers modified pore size and density. Increasing the amount of oil, SPI–BC solid foams were produced, which exhibited uniform and smaller pores that displayed an open-cell structure with pore sizes of several dozen micrometers ($<50~\mu m$). This is likely because emulsion droplets gradually became smaller and more uniform, contributing to the construction of a denser network and increased viscosity to prevent droplet accumulation. Thus, the physical stability of the prepared emulsions was high before freeze-drying. Along with this tunable structure, SPI–BC solid foams showed

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improved mechanical properties, no cytotoxicity, and great biocompatibility, with potential for food industry applications [27].

Another way of using SPI as a foaming agent was tested by Thuwapanichayanan et al. [28] to produce a banana snack. SPI banana foam had a dense porous structure that was crispier than foams produced by fresh egg albumin (EA) or whey protein concentrate (WPC). It is probable that SPI could not be well dispersed in the banana puree during whipping and that the final interfacial tension at the air/liquid interface might not be low enough to produce a significant foaming of the banana puree. WPC and EA banana foams underwent less shrinkage because SPI-banana foam was less stable during drying, so its structure collapsed. Also, WPC and EA banana foams had fewer volatile substances due to shorter drying times.

A similar approach was attempted by Rajkumar et al. [29] using a combination of soy protein as a foaming agent and methyl cellulose as a stabilizer to produce a foamed mango pulp by the foam mat drying method. To obtain the same level of foam expansion, the optimum concentration of soy protein as foaming agent was 1% compared to 10% of egg albumin. Although biochemical and nutritional qualities in the final product were better when using egg albumin, the much lower concentration required for soy protein would be beneficial in terms of cost. It would be interesting to understand how the soy protein and methyl cellulose combination contributed to the positive results in foam expansion; however, this effect was not studied.

Similarly, blackcurrant berry pulp was foamed using SPI and carboxyl methyl cellulose (CMC) as foaming and stabilizer agents, respectively. In this study, Zheng, Liu, and Zhou [30] tested the effect of microwave-assisted foam mat drying on the vitamin C content, anthocyanin content, and moisture content of SPI blackcurrant foam. Several parameters of the microwave drying process, such as pulp load and drying time, had positive effects up to a certain level and then showed a negative effect on the content of both vitamin C and anthocyanin in blackcurrant pulp foam. At the lower pulp load condition, microwave power causes the temperature of blackcurrant pulp foam to rise, which resulted in vitamin C degradation. As for drying time, the longer the drying time, the greater the degradation of vitamin C in the blackcurrant pulp. The quality attributes in terms of color and appearance were better than in samples treated under traditional drying conditions.

2.1.4. Gliadin and Lupin

Ceresino et al. [31] studied the impact of glycerol (Gly), linoleic acid (LA), and transglutaminase (SB6) in two concentrations (1-TG-Glia and 2-TG-Glia) as plasticizers on the development of gliadin (Glia) solid edible foams. Nanomorphology, studied by SAXS, indicated that Gly impaired the unfolding of gliadin in the foam; however, no statistically significant impact of the glycerol on gliadin polymerization within the foam was observed. In addition, there was a notable variation regarding bubble size distribution and a weakening effect on foam stabilization. However, if small pore sizes are desired in aerated food, there is a potential use for glycerol as an alternative to sugar, as well as the use of glycerol as a co-surfactant.

The addition of linoleic acid (LA) in the foams caused the formation of an interrupted Glia network with large, sparsely located bubbles as revealed by X-ray tomograms. Overall, LA impacted gliadin polymerization and foam morphology by preventing the formation of S–S bonds and isopeptide bonds in the gliadin protein. The use of linolenic acid led to the formation of specific nanomorphologies in the foams, referred to as lamellar phases—a process that has been observed for the first time ever in this field of study. These processes suggest that the fortification of gliadin foam with linoleic acid, which is an essential fatty acid for humans, is possible in gliadin breakfast snack prototypes as a main ingredient to improve the nutritional profile of starch-rich foods, since those two components are "compatible" in structured foods.

However, comparison of the non-treated gliadin foam (0-Glia) with the 2-TG-Glia (1.17 U/g) showed that an increase in the size of the bubbles as well as improved bubble

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spatial homogeneity occurred after a great cross-linking and polymerization of gliadins in the foam. This resulted in a well-developed protein matrix and foam morphology, in comparison to the other sets of foams composed of food dispersants. The study also suggests that SB6 may have played a role in gliadin folding and unfolding, probably because of the deamidation reaction.

The results from this study showed that gliadin is a promising resource to create edible solid foams and has great foaming functionality.

In a similar study, Ceresino et al. [32] studied the impact of transglutaminases (TGs; SB6 and commercial), glycerol (Gly), soy lecithin (Lec) and linoleic acid (LA) on the microand nanostructure of solid foods for the creation of foams from LPI and fat blends that could be used to make aerated foods with an appealing texture. As in the previous study, 3-D tomographic images of LPI with TG revealed that SB6 contributed to an exceptional bubble spatial organization. Thus, SB6 significantly contributes to the foam's homogeneous periodic morphology. However, due to spray-drying preparation of Lupin, transglutaminases have limited influence on further cross-linking of the proteins. Nevertheless, the addition of lecithin promoted the formation of new hexagonal structures at the nanometric scale of the foam matrix, whereas linoleic acid contributed and led to the creation of lamellar structures and complex protein–lipid bonding at the nanometric and molecular range of the foam walls. Thus, both lecithin and linoleic acid generate less homogeneous foams.

Results suggest that hydrophobic interactions between lupin proteins, which favor the development of a stable cross-linked matrix and thick matrix walls due to protein bond rupture and rearrangements, promote the formation of a relatively continuous surface. It has also been noted that both LA and LPI are compatible in forming stable layers. This is a result of great significance which may lead to many applications in the confectionery industry.

As in the first study, glycerol produced a weakening effect on lupin foam stability, which might be associated with its effect on decreasing polymerization. Glycerol–Lupin foams were too brittle and unstable to withstand tomography and SEM analysis.

2.1.5. Starch

Starch is a low-cost, biodegradable, non-toxic, and readily available organic polysaccharide. As such, it is a valuable and convenient resource for the food industry. However, its use in edible solid foams is still not well explored.

One of the techniques that has been studied is that used in the production of extruded starch-based snacks. The extrusion process produces foam by the expansion of the ingredients' melted mixture. The expansion phenomenon occurs in different stages. The first stage is the expansion of the melt, which is often followed by a shrinkage phase before the melt solidifies. Then, the melt exits the die, followed by its expansion due to the sudden pressure drop. Internal moisture migrates quickly towards the surface, which drastically decreases the moisture content and temperature of the melt. The melt continues to expand until the melt temperature decreases below its glass transition temperature (Tg), where expansion ceases and the structure of the extrudate sets [33].

In Martínez-Sanz [34], foams were produced by extrusion cooking using Spirulina at 0, 1, 5, and 10 wt.% mixed with corn starch. During extrusion, starch granules are ruptured as they are subjected to high shear, pressure, and temperature. As a result, the crystalline regions of the granules are melted. A polymerization and rearrangement of amylose and amylopectin chains occurs before leaving the extruder die nozzle. Shorter amylose and amylopectin chains are associated by hydrogen bonds after exiting the nozzle if water or some other plasticizer is present [35]. The gelatinization of starch was produced during extrusion by raising the moisture content up to 30 wt.% and letting the samples equilibrate for 24 h before processing. As a result, starch foams were very amorphous, while Spirulina–starch foams showed a slightly more crystalline structure than the pure extruded starch, due to Spirulina complexation with amylose. Thus, Spirulina–starch foams showed more densely packed and well-connected porous structures, making the foam texture harder as Spirulina content increased. During storage, the free fatty acids

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from Spirulina re-crystallized and the resistant starch content in the 10% Spirulina foam rose. Nutritionally speaking, this result might be interesting for the food industry, which is always looking for a way to produce new healthy snacks.

Several extruded starch-based snacks have been studied in this category. For example, corn starch-based snacks with amaranth, quinoa and kañiwa [66]; rice starch and pea protein snacks [33]; and corn starch based-snacks with common bean [67]; among others. According to Zhang et al. [68], starch is suitable for this kind of application, since granule degradation by gelatinization allows the formation of a stable, expanded structure. Regarding proteins, during the extrusion process they are unfolded, realigned, hydrolysed, and can cross-link with other ingredients like starch. In addition, proteins affect extrudate expansion through their ability to influence the water distribution within the extruded melt. The presence of protein can disrupt the pore walls of the expanding melt, which results in reduced expansion and smaller sized, denser cell structures. On the other hand, protein content can increase the number of pores of starch-based extrudates at certain levels, as a result of a greater number of nucleation sites [34].

Table 1. Studies for food industry applications of plant polymesr-based solid foams.

Plant Polymer	Study	Type of Foam	Foam Characteristics	Polymer Characteristics
Proteins				
Saponin/Soapwort extract	Foaming agent in the production of traditional Turkish delight [22] Egg white replacement in sponge cake up to 75% [37]	Edible Edible	Good stability and resistance to heating process Good stability and resistance to heating process. Similar behavior to egg white in sponge cake elaboration	They are composed by an aglycone unit called sapogenin linked to one or more carbohydrate chains. The sapogenin unit consists of either a sterol or a triterpene unit, which is the more common. The carbohydrate side-chain is habitually attached to the 3 carbon of the sapogenin. The carbohydrate portion is water-soluble, whereas the sapogenin is fat-soluble; thus, saponins have surface-active properties [36]
• Patatin	Foaming agent to produce a snack from dried raspberry puree foam by freeze drying [24]	Edible	Foam structure is open and resembles a glassy membrane structure around the pores	Patatin belongs to a family of 40 – 42 kDa glycoproteins with isoelectric point values between 4.5 and 5.2 . It shows a secondary structure composed of 35% alpha-helixes, 45% beta-strands and 15% aperiodic. It has a denaturation temperature of 60 °C at pH 7.0 and a relatively low stability as a function of pH showing loss of structure at pH ≤ 4.5 [38]

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 Table 1. Cont.

Plant Polymer	Study	Type of Foam	Foam Characteristics	Polymer Characteristics
Proteins				
	 Preparation of a solid foam from O/W freeze-dried emulsions containing bacterial cellulose as Pickering particles. (Zhang et al. [26]) 	Edible and packaging material	Foams have a tunable structure, e.g., size and density tailoring. They also showed uniform and smaller pores with an open-cell structure and pore sizes of about <50 µm, as well as improved mechanical properties	
Soy protein isolate	• SPI-banana snack [28]	Edible	Foams with dense porous structure that renders a crispier texture	Soy protein is a globulin protein. Its polypeptide chains have a three-dimensional structure linked by disulfide and hydrogen bonds with a
	 Foamed mango-soy protein pulp [29] 	Edible	Good foam expansion. There is no link given by the authors for foaming properties and structure	molecular weight ranging from 300,000 to 600,000 KDa. Proportion of two major protein polymers in soy
	Foamed blackcurrant–soy protein pulp [30]	Edible	There is no link given by the authors for foaming properties and structure and there is no description of the latter	protein are 35% conglycinin (7S) and 52% glycinin (11S), giving about 80% of the total soy protein [39,40]
	 Replacement of eggs by soy protein isolate and mono- or diglycerides in yellow cake [41] 	Edible	SPI by itself cannot guarantee a suitable foam structure to form the cake. SPI–MDG foams produce batters with correct specific density and appropriate nanostructure, though fewer and larger porosities are observed	
Lentil protein concentrate	Replacement of eggs by lentil protein in angel food cake [42]	Edible	Lentil protein produced a foam that retains air bubbles due to strong networks around the air cells. The mean area of air cells is low, while the number of air cells per unit area is high	Lentil proteins are mainly comprised of albumins, (16%) and globulins (70%). Albumins have a molecular weight of about 20. Globulins contain both legumin- and vicilin-like proteins. The first group consists of six polypeptide pairs that interact noncovalently and have a molecular weight (Mw) of 320–380 kDa. Vicilins are trimers of glycosylated subunits with a Mw of 50–60 kDa [43]

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 Table 1. Cont.

Plant Polymer	Study	Type of Foam	Foam Characteristics	Polymer Characteristics
Polysaccharides	• Foam made from thermoplastic starch (TPS). TPS was made by acetylation and esterification with maleic anhydride of potato starch [44]	Packaging	TPS foam showed lower absorption with improved water resistance. The foam microstructure showed a sandwich-type structure, more or less dense outer layers, and a more compact cellular structure than pure TPS foam. Foams with more modified starch expanded more and became more porous	
	• Foam made from silylated starch [46]	Packaging	Foams show the typical sandwich structure, with denser outer layers with small cells and an inner layer with larger and more expanded cells. Silylated starch foams have a more compact structure with thicker outer layers than traditional starch foams. They become mechanically more resistant and have less water absorption capacity	Potato starch granules are on average shorter than sweet potato starch granules, while bigger than rice starch granules. Amylose content is
Potato Starch	Bioactive foams derived by thermopressing from sweet potato starch and essential oils [47]	Packaging	Foams with essential oils had small cracks and holes. They displayed a more irregular but denser surface due to starch-lipid complexes forming during the thermal process. Starch and essential oils also formed strong interactions, resulting in starch–essential oil complexes in the foam layers. Thus, essential oil drops were trapped within the starch granules. Foams presented a sandwich structure with two well-defined layers and the presence of air cells. Essential oil addition and type also affected the layer thickness and the air cell size between the foams.	lower than wheat and corn starch and higher than tapioca and sweet potato starch. It also has the highest molecular weight and the lowest degree of branching. Amylopectin of potato is much less densely branched than other starches, it has much longer chains, and it carries mono-phosphate ester groups [45]
	• Foam plates prepared by baking potato starch, corn fibers, and poly(vinyl alcohol) (PVA) [48]	Packaging	The foam has a sandwich type structure with dense outer skins containing small cells comprising the surface of the foam. The interior of the foam has large cells with thin walls. Adding over 50% corn fiber, foamed trays contain few small cells in their outer skin. In the interior the cells are smaller, and the foam becomes denser. Trays containing only potato and PVA had thinner skins and larger cells with thicker walls. The outer skin of trays containing corn fiber show compressed and bounded fibers	

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 Table 1. Cont.

Plant				
Polymer	Study	Type of Foam	Foam Characteristics	Polymer Characteristics
Corn Starch	 Foams produced by extrusion cooking using corn starch mixed with Spirulina [34] 	Edible	Starch foams were very amorphous. Spirulina–starch or hybrid foams showed a slightly more crystalline structure than the pure starch foam. Thus, hybrid foams showed more densely packed and well-connected porous structures, and foam texture is harder	Corn starch is, in general terms, similar to other cereal starches, and in specific properties has greatest similarity to its genetically closely related cousins, sorghum and the millets. Normal corn is composed of amylose and amylopectin. It is usually
	Glyoxal cross-linked starch-based foam without and with corn husk fiber, kaolin, and beeswax [51,52]	Packaging	Cross-linked starch foams had more expanded structures, and their cell walls were thinner than those of native foams. They showed areas of weak formation on the surface. The additives eliminated these zones. Addition of fiber, kaolin or beeswax increased the cell size in the center of the foams	composed of 27% amylose and 73% amylopectin [49]. However, this amylose/amylopectin ratio varies slightly with different corn varieties, environmental and soil conditions. Waxy maize consists of amylopectin only, and high amylose corn contains amylose as high
	 Cotton-fiber- reinforced cassava starch foams prepared by compression molding [53] 	Packaging	Foams showed a sandwich-type structure. The addition of cotton fibers, produced more dense structures, thicker cell walls, and lower area porosity	as 70% [50] Cassava starch granules are round with a granule size between 5 and 35 μm. The starch has an A-type X-ray
Cassava Starch	 Cassava starch foams added with sunflower proteins and cellulose fibers [55] 	Packaging	Foams exhibited a more compact, homogeneous, and dense microstructure. The cells were of moderate size, with fibers homogeneously spread throughout the whole material. Baked foams that included proteins were practically devoid of inner open cells Foams showed a sandwich-type	diffraction pattern, usually characteristic of cereals, and not the B type found in other root and tuber starches. The C-type spectrum, intermediate between A and B types, has also been reported. The nonglucosidic fraction of cassava starch is very low; the protein and lipid content are below 0.2%. There is
	 Cassava starch foams added with malt bagasse [56] 	Packaging	structure with dense outer skins that enclose small cells. The interior of the foams had large air cells with thin walls. They have a good distribution of the malt bagasse throughout the polymeric matrix and showed good expansion with large air cells	thus no formation of an amylose complex with lipids in native starch. Amylose contents of 8–28% have been reported, but most values lie within the range of 16–18%. The starch gelatinizes at relatively low temperatures. Initial and final gelatinization occurs at 60 °C and 80 °C,
	• Cassava starch foams added with sesame cake [57]	Packaging	Foams exhibited sandwich-type structure with denser outer skins that enclose small cells whereas inner structure is less dense with large cells. They also showed good expansion	respectively. The swelling power of the starch is also very high: 100 g of dry starch will absorb 120 g of water at 100 °C. At this temperature, over 50% of the starch is soluble [54]

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 Table 1. Cont.

Plant Polymer	Study	Type of Foam	Foam Characteristics	Polymer Characteristics
	Cassava starch foams added with grape stalks [58]	Packaging	Foams present dense and homogeneous external walls, with small, closed cell structure. The interior shows a structure with large open cells and a sandwichtype structure typical of thermoplastic starch-based materials obtained by thermal expansion	
	 Cassava starch foams added with pineapple shell [59] 	Packaging	Foams showed a good distribution of the pineapple shell fiber throughout the polymeric matrix and a semi-crystalline structure. They have a sandwich-type structure with dense outer skins and small cells comprising the surface of the foam and larger sized cells in the interior of the foam	
	 Cassava starch foams added with sugarcane bagasse [60] 	Packaging	Foams have filler fibers well incorporated into the starch matrix and well distributed, making the material homogeneous	
	• Cassava starch foams added with organically modified montmorillonite and sugarcane bagasse [61,62]	Packaging	Foams exhibited sandwich-type structure with denser outer skins that enclose small cells whereas the inner structure is less dense, with large cells. They also showed good expansion	
	Baked foams from citric acid modified cassava starch (CNS) and native cassava starch (NS) blends [63]	Packaging	SEM micrographs of foams showed that the cells formed were open with connectivity between cells. They had a sandwich-type structure composed of two layers. The outer layers had a smaller cell size but a denser structure, whereas the interior had a larger cell size and a more expanded structure. NS foam showed a thinner cell wall with a broad distribution of cell sizes. CNS foam, revealed a smaller cell size and a denser structure.	

Table 1. Cont.

Plant Polymer	Study	Type of Foam	Foam Characteristics	Polymer Characteristics
Oca Starch	Oca starch foams added with sugarcane bagasse (SB) and asparagus peel fiber (AP) [64]	Packaging	Foams with addition of fibers showed a less compact structure and with distribution no homogenous of poreswhen compared to the control. The fiber distribution through the cellulose matrix was dissimilar for both SB and AP fiber. Trays with SB fiber had larger cells arranged in a thinner layer than those with AP fiber. Both exhibited the typical sandwich structure	Oca starch has a phosphorus content ~60% lower than potato starch. Its amylose content is approximately 21% (lower than that of maize and potato starches). Amylopectin is similar to that of potato amylopectin, with some differences in the length of its internal chain and amount of fingerprint B-chains. Oca starch granules had a volume moment mean size of 34.5 µm and B-type polymorph [65]

2.1.6. Plant Polymer-Based Egg Protein Replacers

In aerated foods such as meringues, marshmallow, bread, cakes, and soufflés, foams are responsible for the appropriate textures and a particular mouthfeel because of the little air bubbles trapped in the food system [1]. This is a complex process, where different physicochemical interactions and processing conditions play crucial roles to achieve the appropriate foamy structure. Polymer functional properties (foaming capacity and stability, as well as emulsification) are critical to achieve a solid foam-like structure. That is why egg proteins are important ingredients in the bakery industry and the main goal when using other polymers as substitutes is to replicate their functionalities because replacers influence the textural and physical properties of the final product. Several studies have been carried out using whey protein to prepare meringue and there has been an extensive gain of knowledge in the understanding of its rheology and surface properties, as shown by the works of Nastaj and Sołowiej [17] and Nastaj, Sołowiej, Terpiłowski, Mleko [69,70].

However, in the field of plant polymers, finding substitutes for egg proteins as foaming agents is not an easy task, though some advances have been made. For example, soapwort extract can be used to partially replace egg white proteins (EWP) as a foaming agent in sponge cake formulations. Rheological and physical properties of cake batters and physical and sensory properties of sponge cakes were analyzed to determine the effects of soapwort extract addition. Different formulations were produced replacing egg white proteins with soapwort extract by 25%, 50%, and 75% on weight basis. Replacement of the protein source up to 75% did not have a significant effect on the specific gravity of batters (p > 0.05). Likewise, the flow behavior indices (n) and the consistency indices (k) of cake batters were not affected by the addition of soapwort extract. Saponin content in the soapwort extract and saponin chemical structure containing polar (water-soluble side chains) and nonpolar (sapogenin) molecules facilitate incorporation of air into the batter. Additionally, physical properties of sponge cakes were not altered either. Regarding the sensory properties of sponge cakes, the results were also favorable. Sponge cakes formulated with 50% and 75% soapwort extract on weight basis received significantly higher chewiness scores than control cakes (p < 0.05) [37].

Likewise, lentil protein can totally or partially substitute egg and milk protein as a foaming and stabilizer agent in angel food cake, resulting in products with satisfactory quality [42]. In this study, increasing the amount of lentil protein will increase the viscosity of the batter due to the more entangled lentil protein structure at higher protein concentrations, which might help air retention in the aerated system. Less air escaped from the lentil protein-based foamy batter than the control during baking, probably due to the formation of strong networks around the air cells that prevented microstructure collapse during gas expansion when the wet foam was transformed into solid foam. Additionally, the mean

area of air cells was reduced by the presence of lentil protein but the number of air cells per unit area increased; thus, the height of angel food cakes with lentil protein remained very close to that of the control formulations [42].

Likewise, yellow cake prepared from a mixture of soy protein isolate and 1% monoor diglycerides that replaced eggs as a foaming agent yielded a similar specific volume, specific gravity, firmness, and moisture content [41]. The authors of this study presented a detailed explanation of cake structure based on an analysis of the relationship between SPI secondary structure and different additives. β -sheet structures were dominant among the secondary structures in all control and eggless groups. The content of these structures increased after the addition of SPI, suggesting an increase in the intermolecular interactions in gliadins.

On the other hand, adding Xanthan gum into the cakes with SPI and soy lecithin reduced the β -sheets significantly and converted them to random coils and helical structures. This might be attributed to the slightly charged property of soy lecithin, as it binds to proteins via hydrophobic interactions and the remaining phosphate groups repel each other to loosen the molecules, leading to weakened intermolecular interactions arising from β -sheets and looser molecules being converted into coils. Gliadin is rich in proline; therefore, the β -turn conformation could be more highly favored. They also proposed a schematic model for the gluten formed in the presence of SPI. The model was based on the structural analyses of gliadin and glutenin after the addition of the protein and additives. Analysis of starch suggested the existence of new cross-linking with ester bonds, while an SPI analysis showed the presence of dominant gliadin aggregates in the size range of 100–200 nm and glutenin networking structures containing fewer but larger porosities. These results provide enough support to suggest using SPI in combination with 1% monoand diglycerides (MDG) as a substitute foaming agent for eggs in cakes.

2.2. Plant Polymer-Based Foams as Food Packaging Materials

The distribution chain of the food industry is heavily dependent on appropriate packaging materials. When considering the performance required for prolonging shelf life, the properties of most interest in packaging applications, and their relevance in use, can be classified as mechanical and optical properties, chemical stability, and moisture and gas barrier function [69].

For several years, conventional, non-biodegradable plastics have been the principal source of material for food packaging. Many already known reasons are responsible for the wide use of plastics, e.g., they are generally lighter in weight, more easily formed into different shapes, extremely versatile, and have a low cost of production [69]. However, severe concerns related to environmental catastrophe have set suitable conditions for the development of alternative eco-friendly materials derived from natural polymers for packaging [8].

A natural packaging material must fulfil the demands made by the food industry. For example, it should serve as a physical barrier and temperature controller—that is, it must have a high impact resistance and high thermal insulation. It also should act as a biochemical and microbiological preserver (e.g., gas exchange regulator). Equally important is that its production and disposability have a low carbon footprint, as well as low pollution risks and greenhouse gas emissions. Meeting these criteria, plant-derived biopolymers from agro-industrial sources that are renewable, abundant, and inexpensive would present a convenient and attractive alternative [55].

2.2.1. Starch

The low cost, availability, and compostability of starch make it of great significance for the packaging industry [70]. There are hundreds of studies utilizing starch as a replacement for synthetic packaging material. Nonetheless, and regardless of the fabrication method or starch source, all show the same drawback related to water absorption or water vapor

permeability [71,72] due to the hydrophilic nature of starch molecules. Therefore, this is one of the biggest problems to solve.

One strategy has been to modify the molecular structure of starch to make it more hydrophobic. In a study by Bergel et al. [44], potato starch was used to fabricate a thermoplastic starch (TPS) foam that was modified by two methods: (i) acetylation and (ii) esterification with maleic anhydride. Their results showed that non-modified TPS foams absorbed 75 g water/100 g solids, while foams with 13% acetylated starch (TPS–Ac) and 20% esterified starch (TPS–Es) presented lower water absorption (42 g and 45 g water/100 g solids, respectively), improving the foam water resistance. Analysis of pure TPS, TPS–Ac, and TPS–Es foam microstructure showed that they have a sandwich-type structure.

This kind of structure is typical in TPS foams produced by a mold compression process or baking process. They consist, roughly speaking, of two sets of layers—outer layers and interior layers. Outer layers have a denser structure, smaller cell size, and less voids than the interior layers which have larger cells and more expanded structures. Additionally, in this study, TPS—Ac presented more or less dense outer layers, depending on the acetylation degree, and a more compact cellular structure than pure TPS foam. Differences in viscosity values of foams might explain distinctive microstructures, as acetyl groups are related to a decline of intermolecular bonds between water and unmodified starch due to their hydrophobicity. If the pastes have low viscosity, they cannot hold vapor bubbles as effectively as more viscous ones during the baking process. Therefore, the lower the viscosity of the paste, the greater the paste expansion, which generates foams with a thinner outer layer and large inner cells.

Similarly, in another study by Bergel et al. [46], two silanes were used for potato starch silylation: 3-chloropropyl trimethoxysilane and methyltrimethoxysilane. The foams were made using modified starch, gelatinized starch, polyvinyl alcohol, and water. Microstructure analyses showed the typical sandwich structure with denser outer layers of small cells and an inner layer of larger and more expanded cells. This microstructure translates into a more compact structure and thicker outer layers, which can be explained by the higher viscosity of the silylated starch pastes applied to make these foams. High viscosity is caused by silane cross-linking. Additionally, mechanical tests showed that foams become more resistant to cracking and fracture with the addition of silylated starch. This may also be due to the cross-linking of silanes which make starch pastes more viscous. Meanwhile, the silylation modification yielded foams with less water absorption. The improved foam performances make them a potential packaging material for use in the food industry.

Cruz-Tirado et al. [47] utilized sweet potato starch and oregano (OEO) or thyme (TEO) essential oils to produce bioactive foams by thermopressing. The essential oils were used at two concentrations (7.5 and 10%). The foams were characterized according to microstructure, mechanical properties, antimicrobial properties, and structural properties. In terms of structure, SEM micrographs revealed that foams presented a sandwich-type structure with two well-defined layers and the presence of air cells. The foam thickness was not significantly affected by the essential oil type and concentration at any level, but the starch-lipid interactions resulted in the formation of amylose-essential oil complexes with lipids localized in the first layer. This structure of the foam may have prevented the essential oil from degrading under the thermoforming temperature. Regarding the solubility and mechanical properties, essential oil addition yielded starch foams with low water solubility but also lower mechanical resistance, especially for 10% OEO. Transversal section microstructure analysis showed that TEO-foams and OEO-foams have more compact structures and fewer porosities, which may have decreased water absorption, especially at the surface. Additionally, strong interactions between OEO and sweet potato starch molecules limited the interactions between chains of amylose-amylose, amylopectinamylopectin, or amylose-amylopectin, possibly weakening and destabilizing the starch structure. In addition, sweet potato starch and essential oil foams were more effective against Salmonella (Gram-negative bacteria) and L. monocytogenes (Gram-positive bacteria) Appl. Sci. 2021, 11, 9605 15 of 23

as the essential oil diffuses from inside the foams to the surface. According to the authors, the foam structure might influence essential oil diffusion strongly. The SEM micrographs showed that the essential oil was in the first layer of the foam and was later displaced by water vapor during thermoforming. The foams with 10% essential oil exerted a greater antimicrobial effect due to a greater amount of essential oil that diffused to the environment. The phenolic compounds present in the foam and probably responsible for microbial inhibition are carvacrol, thymol, therpinene, and p-cymene. Therefore, these foams showed good properties to be applied as bioactive food containers.

Another approach by Uslu and Polat [51] and Polat et al. [52], was to prepare glyoxal cross-linked baked corn starch foams with the addition of corn husk fiber, kaolin, and beeswax. Cross-linked starch foams had a more expanded structure, as shown by SEM micrographs. This is likely caused by a quicker gelatinization of the cross-linked starches at a lower temperature, and faster water evaporation during the baking process. In addition, the cell size increased with the cross-linkage addition amount, while cell walls of the cross-linked starch foams were thinner than those of the native foams. Both the tensile and flexural properties of the foams were significantly affected by cross-linking. Foams made from cross-linked starches were more flexible. Inclusion of the corn husk fiber resulted in increased water resistance of cross-linked corn starch foams. Addition of beeswax or kaolin increased the cell size in the center of the foams and decreased the tensile and flexural strength; however, these additives also reduced the water absorption of the foam trays. It is likely that both the physical and chemical properties of fibre contributed to the improvement of the tensile properties of the trays. For example, the long size of the fibre permitted the formation of hydrogen bonds with beeswax and a spreading of the fibre in the direction of tension.

A similar study was developed by Pornsuksomboon et al. [63] in which they obtained very similar results, though they used cassava starch and citric acid as a cross-linker. The citric acid-modified cassava starch foam (CNS) had a higher density, lower thickness, and denser structure than native cassava starch (NS). These differences in morphology are probably due to different viscosity values between the batters. As the viscosity of CNS batter was high compared to NS batter, NS foam was more expandable than CNS foam. On the other hand, the 50/50 NS/CNS ratio foam exhibited a uniform distribution of cell sizes with thinner cell walls than both the NS and CNS foams, also because of the different viscosity of the blended starch batters. In addition, the thermal stability of the blended starch foam was lower than NS foam, probably due to the presence of ester bonds with low thermal stability, while the stabilizing effect of the higher degree of cross-linking and strong hydrogen bonds in the citric acid-modified starch might explain the significantly slower water evaporation and decomposition rate of NS/CNS blend chains.

In the same vein, the morphology and the physical, flexural, and thermal properties of cassava starch foams for packaging applications were researched as a function of cotton fiber and concentrated natural rubber latex (CNRL) content [53]. The main objectives were to solve their two main weaknesses, i.e., lack of flexibility and sensitivity to moisture. Cotton fiber was principally added as a reinforcing material. A comparison among SEM micrographs of starch biofoams, both with and without cotton fiber, showed a sandwichtype structure. However, after the addition of cotton fibers, the foam exhibited denser structures, thicker cell walls, and a lower area porosity (43.37% compared to 52.60%). It seems that cotton fiber presence decreased the chain mobility of starch via hydrogen bonding, resulting in a high viscosity of the starch batter and less expansion of the foam. CNRL helped to control moisture into cassava starch foam. As CNRL content rose, the moisture adsorption capacity of the foam declined (-73.4% and -41.78% at 0 and 100% RH, respectively). This may be due to the hydrophobicity increment of the foam. Foam flexural properties were also tuned by regulating CNRL content. For example, with an amount of 2.5 phr of CNRL, the elongation of the biofoam improved by 24%, while the bending modulus decreased by 2.2%. An interesting study carried out by the same research group involved a soil burial test that assessed the biodegradability of the cotton-fiber-reinforced

cassava starch foam. They found that the degradation mainly progresses by hydrolysis and is delayed by the addition of CNRL.

Sunflower proteins and cellulose fibers were also added to cassava starch to produce biodegradable food packaging trays through a baking process [55]. The study was focused on the relationship between the proportions of these three components and their effect on microstructure, physicochemical and mechanical properties of the trays. The results showed that increasing the fiber concentration from 10% to 20% (w/w) raised the water absorption capacity of the material by at least 15%, while mechanical properties were improved. On the contrary, an increase in sunflower proteins up to 20% (w/w) reduced the water absorption capacity and the relative deformation of the trays to 43% and 21%, respectively. The formulation that exhibited a more compact, homogeneous, and dense microstructure, with maximal resistance (6.57 MPa) and 38% reduction in water absorption capacity, contained 20% fiber and 10% protein isolate. This optimized material presented the best mechanical properties, lower water absorption, a lower thickness, and a higher density. Likewise, Mello and Mali [56] used the baking process to produce biodegradable foam trays by mixing malt bagasse with cassava starch. The concentration of malt bagasse varied from 0–20% (w/w) and the microstructural, physical and mechanical properties of foams were assessed. The trays had an amorphous structure as a result of a good distribution of the malt bagasse throughout the polymeric matrix. Foams showed a sandwich-type structure with dense outer skins enclosing small cells. The interior of the foams had large air cells with thin walls. They showed good expansion with large air cells. Their mechanical properties were not affected by variation in the relative humidity (RH) from 33 to 58%. However, when the trays were stored at 90% RH, the stress at break decreased and the strain at break increased. This is likely due to the formation of hydrogen bonds with water favored by the hydrophilicity of starch molecules. Thus, the direct interactions and the proximity between starch chains reduced, while free volume between these molecules increased. Under tensile forces, movements of starch chains were facilitated, and this is reflected in the decrease of the mechanical strength of materials. The sorption isotherm data demonstrated that the inclusion of malt bagasse at 10% (w/w) resulted in a reduction in water absorption of starch foams. Cassava starch trays with malt bagasse might, therefore, be a fitting alternative for packing solid foods.

In another similar study, Machado et al. [57] added sesame cake to cassava starch to produce foams and evaluated the effects on the morphological, physical, and mechanical properties of the materials produced. The content of sesame cake added ranged from 0% to 40% (w/w). Cassava starch-based foams incorporated with sesame cake exhibited improved mechanical properties and reduced density and water capacity absorption when compared to starch control foams. Using sesame cake (SC) concentrations higher than 20% showed better mechanical properties than commercial expanded polystyrene (EPS). Foams produced in this study showed a decrease in flexural stress and modulus of elasticity with the addition of SC. The reduction of these properties correlates with their lower density and larger cells in inner structure in comparison to control foams. Large cells in the foam's inner structure and thinner walls can be associated with water evaporation and leakage through the mold, consequently causing cell rupture. Nevertheless, although enhancements in flexibility and moisture sensibility are still necessary, starch-based foams incorporated with sesame cake might be an alternative for packing solid foods and foods with low moisture content.

Another biodegradable cassava starch-based foam produced by thermal expansion was developed by Engel et al. [58], who incorporated grape stalks and evaluated the morphology (SEM), chemical structure (FTIR), crystallinity (XRD), biodegradability, and applicability for food storage. Foams exhibited sandwich-type structure with denser outer skins that enclose small cells, whereas the inner structure was less dense with large cells. The material also showed good expansion, which might be the result of the occurrence of hydrogen bond-like interactions between the components of the expanded structure during processing of the foam. Biodegradability tests demonstrated neither formation of

recalcitrant compounds nor structural alterations that would hinder foam degradation. Foams were completely biodegraded after seven weeks. Additionally, foams made with cassava starch with grape stalks added showed a promising application in the packaging of foods with a low moisture content.

Cassava starch, in combination with pineapple shell, was also utilized as a strengthening material to manufacture biodegradable foam trays by a compression molding process. The starch/fiber ratios were varied to modulate the foam, microstructure and physical and mechanical properties. The foams showed a good distribution of the pineapple shell fiber throughout the polymeric matrix and a semi-crystalline structure. Even though all reinforced foams showed high water absorption, foams produced at a starch/fiber ratio of 95/5 showed the lowest values of thickness and density (2.58 mm and 367 kg m⁻³, respectively) and the highest crystallinity index value. This starch/fiber ratio also led to foam trays with tensile strengths similar to those of expanded polystyrene samples. This is likely due to the reinforcing effect of the interfacial interaction between the fiber and the starch matrix. However, high proportions of fiber can interfere with the expansibility and produce discontinuity in the starch matrix. An increase in the fiber concentration weakened interactions among starch chains due to a lower proportion of starch in the composites. Based on the results above, the cassava starch-based foams might be a promising biodegradable material to be used for solid food packaging, and future research should focus on the improvement of their physicochemical and structural properties [59].

In the study by Ferreira et al. [60], new biodegradable trays were produced based on the blend of cassava starch with sugarcane bagasse. This mixture was then blended with different fibrous agro-industrial residues, such as cornhusk, malt bagasse, and orange bagasse. Trays produced from those mixtures presented high water sorption during storage under high or medium relative humidity. They were also more rigid and more susceptible to degradation than EPS trays. FTIR analysis revealed that hydrogen bonding between cassava starch and the other biodegradable tray components may have occurred during processing, as well as water interaction with other formulation components (starch, glycerol, and fibers). SEM micrographs showed that fibers of the residues were incorporated into the starch matrix and well distributed, making the material homogeneous, which contributed to good mechanical properties. As a result, the combination of cassava starch, sugarcane bagasse, and cornhusk was shown to be the better mix.

In the works by Matsuda et al. [61] and Vercelheze et al. [62], biodegradable trays were developed based on cassava starch and organically modified montmorillonite, called Cloisite®10A and 30B, using a baking process. They studied the changes on the microstructural and physicochemical properties of the trays when using the modified montmorillonite. Foams had the typical sandwich-type structure of the foams made by thermopressing. This structure includes dense outer skins that enclose small cells, similar to other foams made with cassava starch, as seen above. The interior of the foams had large cells with thin walls. Samples produced with the nanoclays showed larger air cells than the control sample. In the samples produced with sugarcane fiber, distribution of these fibers in the foam structure was homogeneous up to a concentration of 20 g fiber/100 g formulation. The density values were not affected by the addition of nanoclays. Probably, the addition of the nanoclays improved the foaming ability of starch pastes, resulting in the greater resistance of cell walls against collapse during the water evaporation that occurred during the baking process, as well as producing more thick trays. Results showed well-shaped foam trays with lower water absorption when using nanoclays in the formulations than using starch alone. The foam densities were between 0.2809 and 0.3075 g/cm³. There were no dimensional changes during storage in the trays at all RH conditions tested, but no explanation was given to this phenomenon. The trays potentially resulted in an alternative packaging option for foods with low water content.

Oca (Oxalis tuberosa) represents a novel starch source. In the work of Cruz-Tirado et al. [64], sugarcane bagasse (SB) and asparagus peel fiber (AP) were mixed with oca starch to produce baked foams. The structure of foams reinforced with SB fiber (starch/fiber ratio

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of 95/5), AP fiber (95/5) and without addition of fiber (100/0) was heterogeneous. The fiber distribution through the cellulose matrix was dissimilar for both SB and AP fiber. Trays with SB fiber had larger cells arranged in a thinner layer than those with AP fiber, which was probably due to less interference with starch expansion during thermoforming of the tray. Both exhibited the typical sandwich structure. Oca foams mixed with asparagus peel fiber exhibited higher rates of thermal degradation than the control but not to the point of affecting their applicability, while sugarcane bagasse fiber in high concentrations created more dense trays with lower water absorption (WAC) than the control because high SB concentrations decreased starch mass in the mixture, decreasing the foaming of starch, which created a more compact structure, whereas the addition of low SB fiber concentrations probably yielded trays that were more porous with larger diameters of cells that facilitated the entry of water. The density of the oca foams was reduced by lowering the fiber concentrations. Trays were made harder and more deformable by the addition of fiber, though it did not improve the flexural strength of the foams.

2.2.2. Cellulose

Cellulose materials are appropriate for the development of biopolymer-based foams due to their biodegradability and low environmental impact but also because of their low density, high aspect ratio, large surface area, and non-toxicity [7]. In general, cellulose nanofiber-based solid foams can be made using various procedures and these usually comprise three steps: (i) the preparation of a gel, (ii) the creation of the 3-D structure via foaming in the presence of surfactants, and (iii) the removal of the solvent. The subtraction of the solvent can be performed using several techniques, such as, supercritical drying, freeze-drying, oven-drying or ambient conditions. Varying the processing route will impact the nano- or macrostructure of the final product, which subsequently will have an effect on the properties of the solid foam, such as porosity and its mechanical and barrier properties [73].

Cellulose nano- and microfibrils, especially, have been utilized in the production of low-density porous materials that display high specific surface areas, low thermal conductivity, and low dielectric permittivity [70]. Because of their distinctive mechanical and morphological characteristics, the cellulose nano- and microfiber-based foams have attracted industrial interest over the last 20 years [1].

For example, Cervin et al. [74], created a lightweight and strong porous matrix by drying aqueous foams stabilized with surface-modified nanofibrillated cellulose (NFC). The innovation in that study was that they use cellulose as foam-stabilizing particles. As shown by confocal microscopy and high-speed video imaging, NFC nanoparticles stopped the air bubbles from collapsing or coalescing by arranging themselves at the air—liquid interface. Stability was achieved at a solids content around 1% by weight. Careful foam drying resulted in a cellulose-based porous matrix of high porosity (98%), low density (30 mg/cm³), and with a Young's modulus higher than porous cellulose-based materials made by freeze drying. The size of the pores was in the range of 300 to 500 μ m.

Similarly, Ghanbari et al. [75] reported the effect of cellulose nanofibers (CNFs) on thermoplastic starch (TPS) foamed composites. The analyses were focused on the thermal, dynamic mechanical analysis (DMA), density, and water uptake. The results revealed that thermal stability, storage modulus (E'), loss modulus (E''), and damping factor ($\tan \delta$) increased for all TPS/CNF samples compared to the pure TPS-foamed composites, while apparent density and water absorption of foams decreased when composed with CNF. Additionally, incorporation of CNFs caused an increase in the glass transition temperature (Tg) of the foams. Moreover, 1.5 (wt.%) CNF concentration gave superior resistance or stability with respect to heat compared to its counterparts. An interesting feature shown by the foams was revealed by SEM images of composite foams containing 1.0 or 1.5 (wt.%) CNF: the size of the cell decreased while density increased as a result of CNF acting as the nucleation agent. CNF favored the formation of the cell nucleation sites and the bubble heterogeneous nucleation during the foaming process.

In the study of Ago et al. [70], various types of isolated lignin-containing cellulosic nanofibrils (LCNF) were used to reinforce waxy corn starch-based biofoams. The addition of LCNF increased the Young's modulus and yielded stress in compression mode by a factor of 44 and 66, respectively. In addition, the water sorption of the foams was decreased by adding LCNF due to relatively lower hydrophilicity of residual lignin. The optimized foams exhibited mechanical properties similar to those of polystyrene foams. Based on the results, cellulose reinforced foams might potentially become a sustainable and biodegradable alternative for packaging and insulation materials.

Using similar components but a different approach, Hassan et al. [76] fabricated biodegradable starch/cellulose composite foams cross-linked with citric acid at 220 °C by compression molding. Increasing the concentration of citric acid made water absorption capacity decrease, while stiffness, tensile strength, flexural strength, and hydrophobicity of the starch/cellulose composite foams increased. For example, tensile strength, flexural modulus, and flexural strength increased from 1.76 MPa, 445 MPa, and 3.76 MPa, for 0 % citric acid to 2.25 MPa, 601.1 MPa, and 7.61 MPa, respectively, for the starch/cellulose composite foam cross-linked with 5% (w/w) citric acid. The foams also showed better thermal stability compared to the non-cross-linked composite foam, indicating that composite foams might be used as biodegradable alternatives to expanded polystyrene packaging.

In another study, lignin from bioethanol production was employed as a reinforcing filler by Luo et al. [77] to fabricate a soy-based polyurethane biofoam (BioPU) from two polyols (soybean oil-derived polyol SOPEP and petrochemical polyol Jeffol A-630) and poly(diphenylmethane diisocyanate) (pMDI). The results are similar to those obtained in other studies where different cellulose sources were used to reinforce lignin-induced cell structure modifications and thereby increase the density and improve the thermal properties of the foam. The mechanical properties were also improved with the presence of lignin, and the samples with 10% concentration had better mechanical properties over other treatments, with values of 0.46 MPa, 11.66 MPa, 0.87 MPa and 26.97 MPa for compressive strength, compressive modulus, flexural strength, and flexural modulus, respectively. According to the authors, the lignin-polyurethane mixtures are characterized by a complex super molecular architecture due to the specific properties of their components. Polyurethanes produced an interpenetrating polymer network (IPN) structure, whereas lignin acted as an emulsifier for polyurethane soft and hard segments because it was subtly dispersed and integrated into the polymer amorphous phase, thereby improving the mechanical properties of foams. The research assessed the potential utilization of lignin in polyurethane applications, such as fillers and coating.

Silva et al. [78], studied the use of different concentrations of cellulose fiber on rigid polyurethane foams (RPFs). Mechanical resistance and thermal stability of the composite foams were not significantly changed by the introduction of cellulose industrial residue fibers, whereas thermal conductivity displayed a minor reduction. Based on those results, cellulose–polyurethane composite foams are potentially useful for applications in thermal insulating areas. Interestingly, the composite foams showed a predisposition to fungal attack in wet environments due to the presence of cellulose fibers. However, in this case, this attribute is appropriate, as it decreases the environmental impact after disposal.

Due to the pressure of environmental concerns over the two last decades, considerable research and development in the area of nanocellulose-based materials have been extensively carried out. As a consequence, new products and applications of nanocellulose are steadily emerging as a range of applications of nanocellulose-based biodegradable polymers, thermoplastic polymers, and porous nanocomposites [1].

3. Conclusions

Applications of plant polymer-based solid foams in the food industry are mainly focused in two areas: edible foams and packaging materials. In these areas, there are many plant polymers that are utilized. However, most of the studies focused on the utilization of starch and cellulose, due to their availability and production costs. Still, it is observed

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that starch is not more widely studied in the field of edible foams, being a very common by-product of the agriculture and food industry. This is likely because pure starch makes weak and high water absorption foams, so starch must be modified, or other compounds must be incorporated, in order to strengthen the foams and reduce their water absorption. However, these increase the cost of the final product. In addition, a deep knowledge of starch behavior in the presence of other components is required to overcome some disadvantages, such as brittleness and high water absorption capacity.

In this context, most research aims to improve physical characteristics of solid foams, especially the mechanical and thermal properties which are generally impacted by the conditions of the foam process. However, creating a solid knowledge and comprehension of micro- to macrostructure modification will allow for more adequate management and design of processing conditions. Considering the above, there are two kinds of studies to perform. First, those in which researchers evaluate different properties or characteristics and link them to structural changes without further discussion. The second type goes beyond that and explains the changes based on phenomena produced by the several physical and chemical interactions among the components of the foams. This knowledge is crucial in order to tune the structural properties of solid foams through the control of the properties of the liquid foam (bubble size distribution, pore opening, foam density, etc.), which is a big challenge. However, research involving plant polymers in this area is still lacking.

Along with this, the successful application of solid foams depends on other aspects related to foam creation that are very challenging; for instance, the preservation of the liquid foam structure throughout the transition process from liquid to solid foam, and the timescale pairing between the stability of the liquid foam and the solidification. Thus, one of the major drawbacks is rooted in the internal structure of the plant polymer-based foams, which will probably collapse due to poor mechanical properties. Considering this, in the field of edible solid foams, the utilization of functional proteins as foaming agents, e.g., soy protein and lentil protein, helps keep internal structure to an extent. Still, stabilizers are needed, e.g., to act as Pickering particles or to increase viscosity. Other compounds also might help to reinforce the structure, e.g., cellulose, even though this has not been widely explored in this field. In another vein, the incorporation of natural fibers, such as cellulose nanofiber (CNF) or microfibrillated (CMF), has improved the mechanical properties of plant polymer-based solid foams, helping to overcome their natural lack of strength by reinforcing the structure to endure the foam drying process. Other serious limitations arise from the high hydrophilicity of plant polymer compounds in wet conditions and limited thermal resistance. These drawbacks are also addressed by adding cellulose fibers, especially lignin, which may provide the system with better water resistance.

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