

Review

Structural Features, Modification, and Functionalities of Beta-Glucan

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Abstract: B-glucan is a strongly hydrophilic non-starchy polysaccharide, which, when incorporated in food, is renowned for its ability to alter functional characteristics such as viscosity, rheology, texture, and sensory properties of the food product. The functional properties of β -glucans are directly linked to their origin/source, molecular weight, and structural features. The molecular weight and structural/conformational features are in turn influenced by method of extraction and modification of the β -glucan. For example, whereas physical modification techniques influence only the spatial structures, modification by chemical agents, enzyme hydrolysis, mechanical treatment, and irradiation affect both spatial conformation and primary structures of β -glucan. Consequently, β -glucan can be modified (via one or more of the aforementioned techniques) into forms that have desired morphological, rheological, and (bio)functional properties. This review describes how various modification techniques affect the structure, properties, and applications of β -glucans in the food industry.

Keywords: β -glucan; dietary fiber; modification; food functionality; health applications

1. Introduction

In the 21st century, an interest in food formulations containing complex polysaccharides continues to rise, owing to the bioactivities and health-promoting functions of these polysaccharides [1,2]. Polysaccharides are an indispensable component of many foods. Digestible polysaccharides are a good source of calories and glucose needed for normal metabolic processes in the body. Moreover, a large amount of indigestible dietary fiber exerts beneficial health activities in the body [3,4]. One of the widely known and documented bioactive polysaccharides is β -glucan. B-glucan is a non-starch polysaccharide composed of β -D-glucose monomer units holding a glycosidic linkage at β (1 \rightarrow 3), (1 \rightarrow 4), and/or (1 \rightarrow 6), either in a branched or in an unbranched manner [5]. A vast amount of literature asserts that the intake of β -glucan is associated with prebiotic effects and various beneficial health outcomes such as reduction in glycemic index and serum cholesterol; control of diabetes, cardiovascular diseases, cancer, and hypertension; immune-enhancing properties; antimicrobial (antibacterial, antiviral) properties; and wound healing activities, among others [6–15]. Consequently, research studies on β -glucan have continued to grow since the 1950s when studies on these biomolecules began to be published (see Figure 1). The US Food and Drug Administration recommends regular ingestion of 3 g of β -glucan from cereal sources, such as oats or barley, along with a low cholesterol diet, for reducing the risk of heart-related diseases [16].

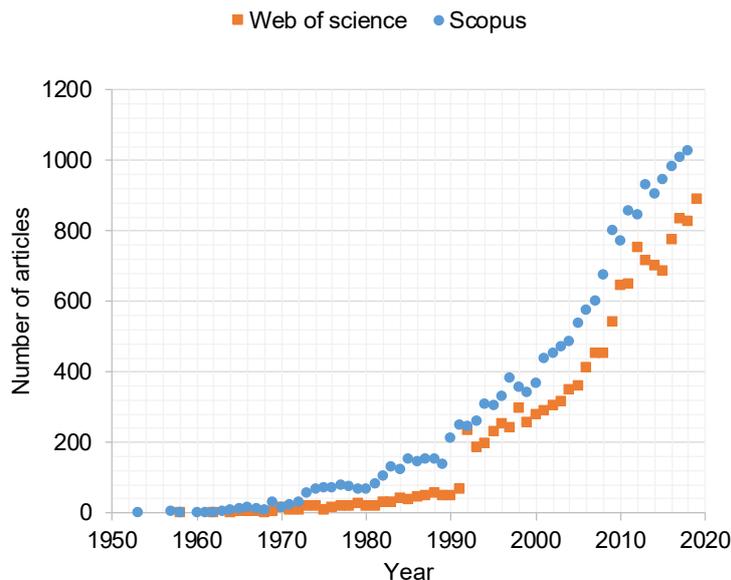


Figure 1. Number of published articles in Scopus (<http://www.scopus.com>), and Web of Science (<https://clarivate.com/products/web-of-science/>) from 1950–2018 using the term “ β -glucan” in article titles, abstracts, and key words.

β -glucans have several hydroxyl groups that help in bond formation with reactive groups of other compounds, leading to alterations in their water solubility, conformation, and ability to form aggregates. The position (i.e., whether β (1 \rightarrow 3), (1 \rightarrow 4), or (1 \rightarrow 6)), degree, and length of branching affect the molecular weight and alter the conformation (shape, size, and structure) of β -glucan. These properties are essential for carbohydrates to perform their various functional roles in food products [17], as well as biological activities in living body systems [14]. A growing number of research studies have explored new avenues to modify the conformation of β -glucan in order to exploit the activities and properties of β -glucan. Some of the well-known methods used to modify β -glucan are physical treatment (low or high temperature), chemical processes (e.g., use of acids, alkali, salts), enzymatic treatment (e.g., with enzymes such as glucanase, lichenase, etc.), and mechanical techniques (e.g., homogenization, sonication). Described in this review are different methods for the modification of β -glucan and how each modification technique affects the conformational and functional properties of β -glucan. Insights into the food and health applications of modified β -glucans are also given, together with comments on emerging/needed research in this area.

2. Sources, Chemical Structures, and Functionalities of β -Glucan

Historically, cereals have been the most well-known source of β -glucan. However, with the advancement in research, β -glucans have been identified and are extracted from microbial sources [5,18], as well as from some mushrooms, lichens, and seaweed/algae (Figure 2). β -glucan occurs widely in the cell wall of these microorganisms (bacteria, fungi, yeast) and in the endospermic and aleuronic walls of the cereal grains (oats, barley, rye, and millets) [19,20].

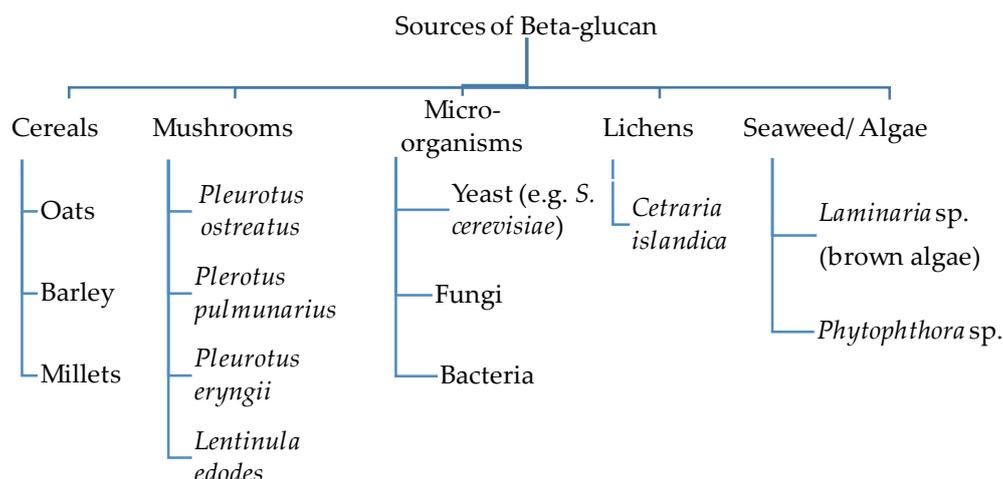


Figure 2. Sources of β -glucan.

Table 1 shows the content of β -glucan from different sources. β -glucan usually occurs in cereals at low concentration ($\sim 5\%$ *w/v*) [21,22]. The levels of these polymers vary quite widely in microorganisms. Optimized yields of β -glucan extracted from baker's yeast (*Saccharomyces cerevisiae*) gave only 5%–7%, but *Euglena* can accumulate β -glucan intracellularly to more than 90% [23]. The content of β -glucan from seaweeds mainly depends on the type. Stipes and holdfasts of *Durvillaea antarctica* contain 33% and $<5\%$ of β -glucan, respectively [24]. The β -glucan content of the mushrooms also varies widely, from about 3.1% to 46.5% [25].

Table 1. Content of β -glucan from different sources.

Food Source	Content	References
Oats	4.5%–5.5%	[21]
Barley	4.5%	[21]
Whole rye flour	1.0%–2.5%	[22]
<i>Saccharomyces cerevisiae</i>	5%–7%	[23]
<i>Euglena</i>	90%	[23]
Stipes of <i>Durvillaea antarctica</i>	33%	[24]
Holdfast of <i>Durvillaea antarctica</i>	$<5\%$	[24]
<i>Sparassis crispa</i>	43.6%	[26]
<i>Inonotus obliquus</i>	3.1%	[25]
<i>Gyrophora esculenta</i>	22.7%	[25]
<i>Coriolus versicolor</i>	46.5%	[25]

β -glucan isolated from the different sources varies in characteristics such as glycosidic linkages, degree of branching, molecular weight, and solubility. Cereal-derived β -glucans are predominantly mixtures of β (1 \rightarrow 3) and β (1 \rightarrow 4) glycosidic linkages without any β (1 \rightarrow 6) bonds [27–29]. β -glucans from yeasts (e.g., *Saccharomyces cerevisiae*) are mixtures of linear β (1 \rightarrow 3) backbones with 30-residue straight chains and connected to these are long branches attached via β (1 \rightarrow 6) linkages [30]. Fungal β -glucans are made of straight β (1 \rightarrow 3) glucan with short-branched chains connected through β (1 \rightarrow 6) [29–31]. Bacterial β -glucans (e.g., those from *Agrobacterium biovaris*) have straight and unbranched β (1 \rightarrow 3)-D-glucan backbones [32], while seaweed β -glucans (such as those found in brown kelp, laminaria) are species-dependent and may contain straight chain β (1 \rightarrow 3) residues or the straight chain backbone together with high levels of β (1 \rightarrow 6) branches [6,12]. The chemical structures of β -glucan from different sources are shown in Figure 3.

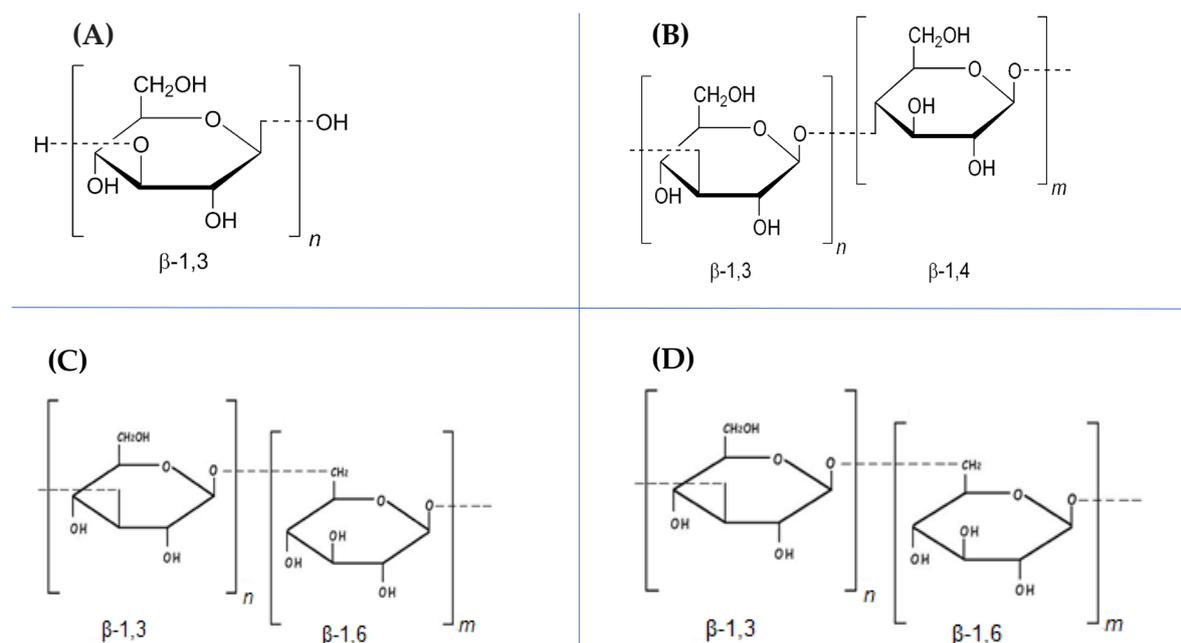


Figure 3. The chemical structure of β -glucan from different sources. (A) β -glucan from bacteria; linear β -1,3 backbone with no branches; (B) β -glucan from cereals, or lichens; linear β -1,3 or β -1,4 backbone with no branches; (C) β -glucan from some seaweeds (e.g. *Laminaria* spp); β -1,3 backbone with β -1,6 branches; (D) β -glucan from fungus or yeast; β -1,3 backbone with β -1,6 branches that are short (fungus) or long (yeast).

Based on origin and processing method used in their extraction and modification, β -glucans can exist in a range of conformations (see Figure 4). The most widely observed conformations are random coils [33], helices (single, double, or triple) [34], worm-like shapes [35], rod-like shapes [17], or aggregates [35,36]. The molecular weight (MW) of β -glucan ranges from 10^2 to 10^6 Da, depending on the source. For example, soluble β -glucans from two edible mushroom varieties maitake (*Grifolafrondosa*) and shiitake (*Lentinula edodes*) were estimated to have MW of about 400 kDa [37]. Cereal β -glucans are also soluble [38,39] and may reach MW of between 1.1 and 1.6 MDa (for oats) and around 49 MDa for barley [27,28].

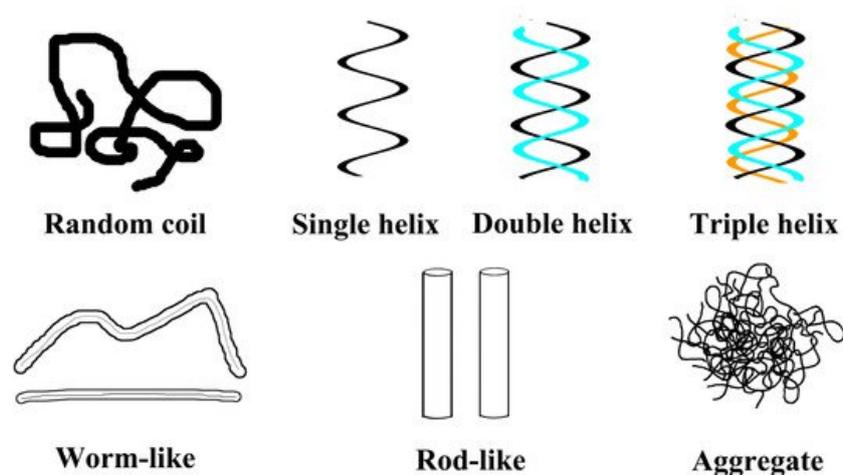


Figure 4. Schematic of typical conformations of β -glucan. Source: Wang et al. [15], reproduced under Creative Commons Attribution License (CC BY).

Aside from their purported nutritional value as a source of soluble dietary fiber, β -glucan has received huge interest in the food industry owing to its rheological characteristics. The molecular weight, water retention properties, and solubility of β -glucan have a huge impact on its viscosity and

flow behavior [40]. β -glucan is very hydrophilic due to the abundance of hydroxyl groups that participate in hydrogen bonding with water and give the molecule an ability to hold water in both soluble and insoluble forms [5,41]. Solubility also depends on the molecular weight, which, as stated earlier, is influenced by the chain length and degree of branching in the molecule. Two other phenomena that affect the molecular weight of β -glucan, namely self-association and aggregation, are dependent on certain physicochemical properties such as the conformation, the molar ratios of trimers and tetramers in the molecules, and the hydrodynamic radius [42].

The solubility profile of β -glucan is vital for the rheological, nutritional, and sensorial application of the molecules [43]. For example, viscosity is an indispensable parameter when β -glucan is to be used as thickening agent in food systems such as beverages, salad dressing, and dairy products [44–47]. In this context, long-chain β -glucans with high MW have the capability to form viscous gels and pseudo-plastic solutions, owing to the complex conformational arrangement of the chains [15,46]. Viscous β -glucan solutions are able to act as stabilizers or thickeners in food formulations. However, the knowledge that the microstructure of the food does affect the bioavailability of nutrients [48] and how some dietary fibers, at high levels, reduce the bioavailability of nutrients [49], means highly viscous β -glucan may exhibit an antinutritional effect in food formulations.

Degraded (or modified) β -glucan, on the other hand, has lower MW, which gives rise to softer gels at high concentrations. The lower viscosity of β -glucan is desired in beverage products to impart stability against phase separation without compromising other sensorial properties. Processing techniques that change the degree of branching and molecular weight of β -glucan could, therefore, be used to manipulate the functional properties of β -glucan to give formulations with desired visco-rheological properties that can be used in various food systems.

3. Extraction, Modification, and Their Effects on Structure and Properties of β -Glucan

The techniques for the extraction of β -glucan vary with sources. The five main extraction methods used are: Hot water extraction [50], alkali extraction [51], enzymatic extraction [52], solvent extraction [53], and ultrasound/microwave-assisted extraction [54,55]. These techniques can be used alone or in combination. The entire extraction process of β -glucan in lab scale and industrial scale is shown in Figure 5. Interested readers should refer to [56] or in depth information on the extraction and purification techniques of β -glucan from various sources.

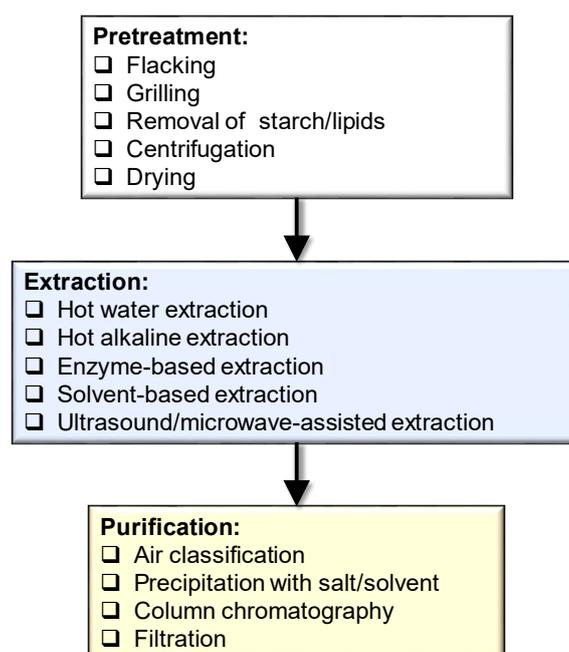


Figure 5. Schematic for the extraction and purification of β -glucans.

Although the acceptance of β -glucan as a functional ingredient has created new interests and use in various foods, the high molecular weight of this molecule presents challenges that hamper the full utilization of β -glucan in the functional food industry. Case in point, the high MW and high viscosity of native β -glucan make it difficult for the molecule to diffuse across cell membranes and act as an immune stimulator [57]. Food companies have a growing interest in utilizing modification techniques to alter the structure and conformation of β -glucan, with the aim of ameliorating the bio-functional properties of β -glucan. Some of the widely used techniques for the modification of β -glucan are shown in Figure 6. These techniques can have different effects on the characteristics, primary structure, and spatial conformation of β -glucan (as captured in Table 2).

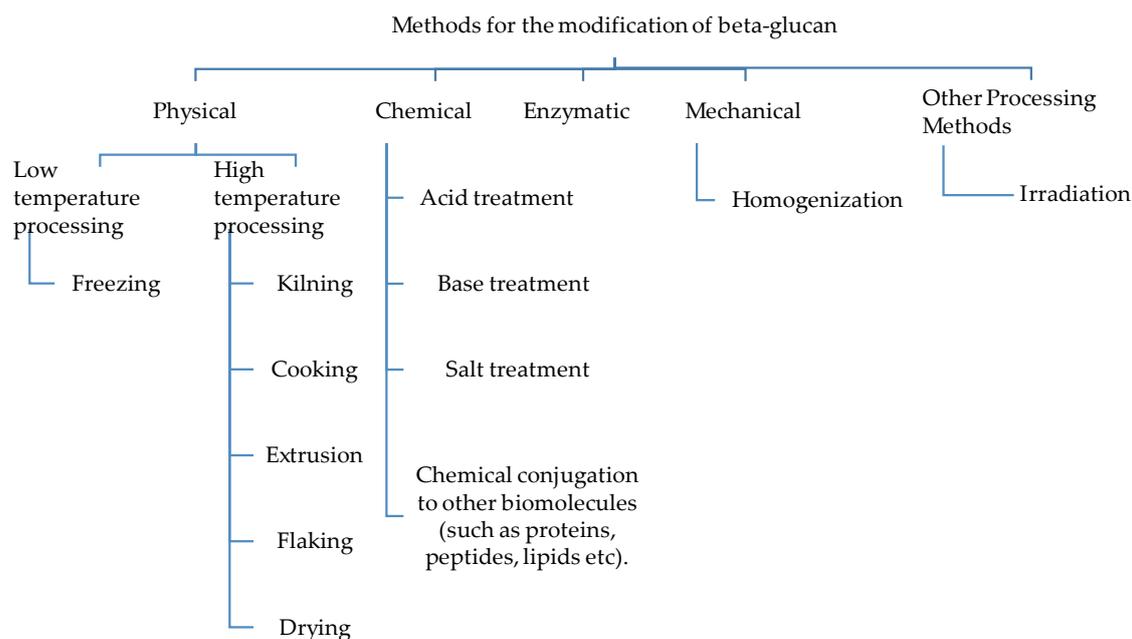


Figure 6. Some techniques the modification of β -glucan.

Table 2. Impact of various modification techniques on the properties of beta-glucan.

Sources of β -Glucan	Modification Method	Modification Condition(s)	Characterization Approach	Outcome of Modification	Reference
Edible fungus (<i>Pleurotusgeestanus</i>)	Physical	Thermal treatment	<ul style="list-style-type: none"> ▪ Rheological properties ▪ Microstructural features 	<ul style="list-style-type: none"> ▪ B-glucan showed two transitions at temperatures in the ranges of 8–12.5 °C and 25–60 °C, respectively ▪ Modified β-glucan had a degree of branching that differed from that found in other fungi 	[58]
Barley	Physical	Hydrothermal treatment (autoclave) in combination with different chemical treatments (50 mM CaCl ₂ , 70% ethanol, 100 mM HCl, and 2.5 mM NaOH)	<ul style="list-style-type: none"> ▪ Determination of the β-glucanase enzymatic activity ▪ Molecular weight characterization 	<ul style="list-style-type: none"> ▪ Reduced β-glucanase enzyme activity ▪ Produced high molecular weight β-glucan 	[59]
Oats	Physical	Constant drying at air temperatures of 25, 50, 75, and 100 °C	<ul style="list-style-type: none"> ▪ Water holding power ▪ Water retention power ▪ Capacity of displacement ▪ Gelation characteristics 	<ul style="list-style-type: none"> ▪ Reduction in water holding capacity at drying air temperature ≥ 25 °C ▪ Content and water retention power was influenced at temperatures ≥ 50 °C ▪ Increment in the gelation power was observed at drying air temperature ≥ 75 °C 	[60]
Oats	Physical	Constant drying at air temperatures of 25, 50, 75, and 100 °C	<ul style="list-style-type: none"> ▪ Water holding power ▪ Water retention power ▪ Capacity of displacement ▪ Gelation characteristics 	<ul style="list-style-type: none"> ▪ Reduction in water holding capacity at drying air temperature ≥ 25 °C ▪ Content and water retention power was influenced at temperatures ≥ 50 °C ▪ Increment in the gelation power was observed at drying air temperature ≥ 75 °C 	[60]
Brewer's yeast (<i>S. cerevisiae</i>)	Physical	Various drying methods (spray drying, air drying,	<ul style="list-style-type: none"> ▪ Microstructure characterization ▪ Stabilization study 	<ul style="list-style-type: none"> ▪ Air drying and lyophilization significantly affected microstructure and agglomeration properties 	[61]

			and lyophilization)	<ul style="list-style-type: none"> ▪ Spray drying and sonication retained the microstructure and exhibited reduced tendency for agglomeration 	
Yeast (<i>S. cerevisiae</i>)	Physical	Spray drying and lyophilization	<ul style="list-style-type: none"> ▪ Carrier to encapsulate Rifabutin (RB) drug ▪ Microstructural characterization 	<ul style="list-style-type: none"> ▪ Spray-dried β-glucan particles showed improved properties (e.g., smaller and uniform sizes, non-agglomeration capacity, high yield recovery) compared to non-spray dried β-glucan 	[62]
Oats	Physical	Steaming and flaking	<ul style="list-style-type: none"> ▪ Morphological ▪ Rheological, and ▪ Molecular mass characterization 	<ul style="list-style-type: none"> ▪ Reduced average and peak molecular weight (MW) of the β-glucan ▪ Reduced viscosity ▪ Changes in structural molecular properties 	[63]
Oat bran	Physical	Extrusion	<ul style="list-style-type: none"> ▪ Compositional ▪ Rheological characteristics 	<ul style="list-style-type: none"> ▪ Increased yield ▪ Larger average particle diameter ▪ Higher apparent viscosity and solubility ▪ Higher swelling power 	[64]
Oat bran	Physical	Extrusion	<ul style="list-style-type: none"> ▪ Physicochemical characterization ▪ Microstructural characterization ▪ Microscopic examination 	<ul style="list-style-type: none"> ▪ Depolymerization ▪ Changed MW and modified solubility ▪ Reduction of MW that impacted on hardness and density 	[65]
Oats	Physical	Freezing	<ul style="list-style-type: none"> ▪ MW distribution ▪ Solubility behavior ▪ Physicochemical characteristics ▪ Physiological effectiveness in reducing postprandial blood glucose response 	<ul style="list-style-type: none"> ▪ Reduced solubility of β-glucan as cycles of freeze-thaw increased ▪ Freeze-thaw-treated muffins remarkably increase blood glucose elevation than untreated muffins 	[66]

3.1. Physical Treatments

Physical treatments of β -glucan are used to modify the molecular, rheological, and morphological characteristics of the β -glucan. This technique involves both high and low temperature treatments used to modify the β -glucan, as shown in Table 1. High-temperature treatments (e.g., kilning, flaking, baking, cooking, and extrusion) constitute some of the most widely used techniques for the modification of β -glucan [8].

3.1.1. High-Temperature Processing

Kilning

The typical processing steps used for the industrial scale preparation of cereal products, such as flakes, flour, groats, and bran, often include a kilning step. Kilning is a hydro-thermal treatment performed primarily to inactivate lipases, thus controlling the generation of rancid products from lipids in the cereals. Kilning, therefore, helps prolong the shelf-life and quality of cereal products. Moreover, kilning inactivates β -glucanase and other enzymes responsible for the breakdown of β -glucan into short fragments [67,68]. Native structure and properties, such as strong gelling behavior, high molecular weight, and high viscosity of β -glucan, are retained in kiln-treated cereals [67].

Drying

The post-harvest drying of cereals has a remarkable impact on the quality of cereal grains [60]. Kumar and Kalita [69] studied the effect of drying on the quality parameters (i.e., water holding/retention power and capacity of displacement and gelation) of oat β -glucan extract. The β -glucan extracts were subjected to drying at different air temperatures of 25, 50, 75, and 100 °C until the moisture content reached 13%. It was observed that drying at air temperatures of 25 and 50 °C did not have any remarkable effect on the water retention capacity of β -glucan, but samples dried at air temperatures of between 75 and 100 °C observed a decline in the water holding capacity. Putatively, the high drying temperatures negatively affected the native structure of β -glucan, which consequently altered the gel-forming ability and water holding capacity of β -glucan. This suggests that drying can be used to alter the properties of β -glucan materials for various desired applications.

Aside from their effect on gelling behaviors, drying treatments can be used in combination with other treatments to get desired functionality from β -glucan. For example, Zechner-Krpan et al. [61] studied the effect of three drying methods (spray-drying, air drying, and lyophilization) on the microstructure and characteristics of β -glucan suspensions obtained from brewer's yeast (*Saccharomyces cerevisiae*). Sonication was used prevent agglomeration and improve the stability of the β -glucan extracts. They observed that air drying and lyophilization had significant effects on the microstructure and agglomeration properties of yeast β -glucan. Spray-drying, on the other hand, helped to retain the microstructure and exhibited no agglomeration phenomena.

Further, Upadhyay et al. [62] repaired and characterized encapsulated β -glucan particles containing a high amount of the antibiotic rifabutin (RB) for drug delivery applications. They extracted the β -glucan from yeast cells by using acidic and alkaline methods, followed by spray-drying or lyophilization to convert the extract into powder form. The spray-dried β -glucan particles showed improved properties such as smaller sizes, better uniformity, non-agglomeration capacity, high yield recovery, and high magnitude of drug delivery when compared with the lyophilized preparations. These characteristics also exhibited triple-helical conformation of β -1, 3/1, 6-attached glucans with higher thermal stability. The study, therefore, shows that β -glucan modified by spray drying has potential applications as dosage carrier to target and deliver more payloads for drugs.

Flaking

Flaking processes involve thermal and mechanical shear that may influence the molecular structural properties and interactions of β -glucan with the other components. In the case of cereals, a prior steaming is critical and helps inactivate enzymes (e.g., lipases and β -glucanase), and/or

facilitates the flaking process [70]. Liu [63] observed the impact of steaming and flaking on the morphology, rheological, and molecular mass of oat β -glucans. They observed that these two processes had no effect on the β -glucan concentration (implying there was no leaching of the β -glucans from the oat materials). However, there were reductions in the average molecular weight and peak molecular weight of the β -glucans. Further, they noted that the molar ration of tri- to tetramers (DP3/DP4) was enhanced, though the number of long cellulose-like oligomers (DP \geq 5) and the ratio of $\beta(1 \rightarrow 4)/\beta(1 \rightarrow 3)$ glycosidic linkages declined after processing. Consequently, the values of the peak viscosity and final viscosity of oat slurries were also decreased. Steaming and flaking, being hydrothermal and mechanical processes, respectively, may have changed the structural and molecular properties of the β -glucan, and exposed the β -glucan to interactions with other cereals' biomolecules such as starch and proteins.

Extrusion

Extrusion is a thermal/mechanical treatment that involves the application of high pressure and high shear to the uncooked mass, especially to starch-rich foods such as cereals [71]. Owing to the involvement of high temperature and pressure, extrusion results in a plethora of chemical changes, such as gelatinization of the starch, denaturation of proteins, and destruction or generation of flavors in the food product. Similarly, extrusion can modify the molecular mass and linkage distribution, functionality, morphological, thermal, and rheological characteristics of β -glucans. An investigation by Zhang et al. [64] examined the effect of extrusion on the composition, thermal properties, rheological characteristics, and functionality of the soluble fiber from oat bran. Their study demonstrated that soluble fiber from extruded oat bran improved yield, average particle diameter, higher apparent viscosity, swelling power, and solubility in contrast to soluble fiber from unextruded oat bran. This study reported that foam stability and functionalities in food preparations of soluble oat dietary fiber are improved by extrusion.

A different study by Tosh et al. [65] elucidated the effects of extrusion on the physicochemical characteristics of β -glucan. To achieve this, the authors extruded a series of oat bran cereals and further examined the effect of extruded cereal products (oat bran) on the viscosity of gut content after extraction under simulated gastric conditions at 37 °C. It was observed that extrusion caused changes in the molecular mass and solubility of the β -glucan. Moreover, microscopic examination revealed that harsher extrusion conditions caused depolymerization, disintegration of cell walls, and affected the distribution of β -glucan in the cereal. The reduction of MW of β -glucan had an impact on the hardness and density of the extruded cereals, and as MW reduced from around 1,930,000 to 251,000 g/mol, the apparent viscosity in the physiological extract also reduced significantly from 2900 to 131 m Pa.s (at 30 s⁻¹ shear rate).

Cooking

A number of studies have reported the effect of heat on the structure of microbial β -glucan. For example, Yiu et al. [72] studied the influence of cooking on β -glucan of rolled oats and observed that gradually cooked oatmeal had more solubilized (1,3)/(1,4)- β -D-glucan and starch and had a more viscous supernatant. Further, Knuckles and Chiu [59] have reported that high hydrothermal treatment (autoclaving) of barley varieties in the presence of different chemicals (e.g., calcium chloride, ethanol, hydrochloric acid, and sodium hydroxide) significantly reduces the activity of β -glucanase in barley, thus preserving the native structure and properties of the β -glucan therein. Also, highly branched $\beta - (1 \rightarrow 3)$ -D glucan has been shown to have triple helical structure and undergoes structural changes upon heating. Zhang [58] studied the influence of heating on the structure of purified $\beta - (1 \rightarrow 3)$ -D β -glucan obtained from edible fungus (*Pleurotus geestanus*). The finding was that when β -glucan is heated in the water it shows two transitions at two temperatures in the ranges of 8–12.5 °C and 25–60 °C. This phenomenon was attributed to the breakdown of the polymer bundles into small helical clusters in the first transition and dissociation of the helical strands to individual chains in the second transition. This feature, together with the unique bonding characteristics suggested that the conformation and viscosity of β -glucan from *P. geestanus* can be tuned by thermal

treatments, and has potential applications for the immobilization of cells, enzymes or therapeutic compounds in food and drug industries.

3.1.2. Low Temperature Processing

Freezing and Refrigeration

Low temperature treatment processes can reduce the molecular weight, solubility and/or extractability of cereal β -glucan. The reason is that freezing cannot deactivate the activity of β -glucanase enzymes responsible for the breakdown of β -glucan into low molecular weight moieties [67,68]. In their study, Lan-Pidhainy et al. [66] examined the effect of freezing on the physiochemical characteristics of β -glucan in oat bran muffins, as well as the effect of freeze-thaw cycles on the physiological effectiveness of β -glucan in reducing postprandial blood glucose response. They concluded that molecular weight and solubility of β -glucan decreased with increase in freeze-thaw cycles. Moreover, blood glucose elevation was markedly higher in freeze-thaw-treated muffins when compared to untreated muffins.

3.2. Chemical Modification

The process of chemical modification is primarily controlled by the presence of hydroxyl groups on β -glucan that act as points for the attachment of other functional groups. The attachment of the functional groups provides extended chemical derivatization and modified forms of β -glucan that are suitable for practical applications in food and health applications [73–75]. The structure and solubility of β -glucan depends on the source as well as the method of extraction, and poor solubility in β (1 \rightarrow 3)-D-glucan can affect health negatively by causing microembolization, granuloma creation, pain, and inflammation [76]. A number of chemical modification approaches such as sulfation, phosphorylation, and carboxymethylation are used to improve the functionality (especially solubility) of β -glucan as presented in Table 3.

Table 3. Impact of chemical modification techniques on the properties of β -glucan.

Sources of β -Glucan	Modification Method	Modification Condition(s)	Characterization Approach	Outcome of Modification	Reference
Cereal	Chemical	Addition of ascorbic acid (vitamin C) and dehydroascorbic acid to the pure cereal β -glucan (0.6%) in the presence of iron sulfate	<ul style="list-style-type: none"> ▪ Rheological characterization ▪ MW distribution 	<ul style="list-style-type: none"> ▪ Reduced solution viscosity and MW 	[77]
Cereals	Chemical	Addition of apple juice with high levels of ascorbic acid into barley porridge	<ul style="list-style-type: none"> ▪ Rheological characteristics ▪ Molecular properties 	<ul style="list-style-type: none"> ▪ Reduced MW and viscosity 	[68]
Fungus (<i>Poriacocos</i>)	Chemical	Carboxymethylated β -glucan developed by using chloroacetic acid in either 2-propyl alcohol or water at high pH ≥ 12	<ul style="list-style-type: none"> ▪ Solubility characteristics ▪ Anti-tumor bioactivity 	<ul style="list-style-type: none"> ▪ Carboxymethylated β-glucan exhibited good solubility ▪ Presence of anticancer activity against Sarcoma as well as gastric carcinoma cells in vivo and in vitro 	[78]
Mushroom (<i>Pleurotus tuber-regium</i>)	Chemical	Monochloroacetic acid in sodium hydroxide solution	<ul style="list-style-type: none"> ▪ Solubility characteristics ▪ Anti-tumor activity ▪ MW distribution 	<ul style="list-style-type: none"> ▪ Higher water solubility ▪ Higher anti-tumor activity ▪ Improved MW profile/distribution 	[79]
<i>S. cerevisiae</i>	Chemical	Carboxymethylated by using monochloroacetic acid	<ul style="list-style-type: none"> ▪ Microstructure characteristics 	<ul style="list-style-type: none"> ▪ Modified β-glucan had a degree of substitution of 0.8 and did not have any cytotoxic or genotoxic effects 	[80]
<i>Gonderma lucidum</i>	Chemical	Sulfation, carboxymethylation, hydroxypropylation, hydroxyethylation, and methylation	<ul style="list-style-type: none"> ▪ MW distribution ▪ Microstructural characteristics 	<ul style="list-style-type: none"> ▪ Native β-glucan had a compact coil structure in dimethyl sulfoxide while the derivatives had slightly expanded flexible chains after modifications ▪ Derivative produced using methylation process had higher MW 	[81]
<i>S. cerevisie</i>	Chemical	Carboxymethylation (double step alkalization and etherification with the monochloroacetic acid)	<ul style="list-style-type: none"> ▪ Rheological features ▪ Solubility characteristics 	<ul style="list-style-type: none"> ▪ Carboxymethylated β-glucan had higher degree of substitution, viscosity and solubility as compared to untreated β-glucan. 	[82]

<i>Lasiodiplodia theobromae</i>	Chemical	Sulfation by using solvent formaldehyde, catalytic reagent pyridines, and chlorosulfonic acid in the form of hydroxyl group donating compound	<ul style="list-style-type: none"> ▪ Microstructural characterization ▪ Physiological effectiveness in terms of anticoagulant power 	<ul style="list-style-type: none"> ▪ Creation of sulfonate or unsaturated bonds, with content and degree of substitution of 11.73% and 0.95, respectively ▪ Increased anticoagulant activity as with increase in dose of activated partial thromboplastin time (APTT) and thrombin time (TT) because of the insertion of sulfonate groups on the polysaccharides 	[83]
Baker's yeast source (<i>S. cerevisiae</i>).	Chemical	Sulfation by using dimethyl sulfoxide (DMSO)-containing urea	<ul style="list-style-type: none"> ▪ Anti-tumor activity ▪ Physicochemical characterization 	<ul style="list-style-type: none"> ▪ Activation of macrophages and aids in stimulation of bone marrow ▪ Higher antitumor activity 	[84]
Yeast	Chemical	Sulfation process by utilizing combination of sulfuric acid and n-propanol (1:4 molar ratio)	<ul style="list-style-type: none"> ▪ Elemental analysis ▪ Morphological analysis 	<ul style="list-style-type: none"> ▪ Derivative of β-glucan had 0.36 degree of sulfation ▪ Enhanced solubility 	[85]
Curdans	Chemical	Sulfation (sulfation of curdlans by various chemicals such as piperidine-N-sulfonic acid (PSA method), SO_3^- pyridine complex in pyridine (SPC method), and chlorosulfonic acid in pyridine (CSA method))	<ul style="list-style-type: none"> ▪ Physiological effectiveness on HIV infections ▪ Physiological effectiveness in terms of anticoagulant power 	<ul style="list-style-type: none"> ▪ Sulfated curdlans were proved effective against infection by AIDS virus strains ▪ Sulfated curdlans exhibited higher anticoagulation power than native 	[86]
Oats	Chemical	Non-enzymatic reactions (Maillard reaction)	<ul style="list-style-type: none"> ▪ Microstructure characterization ▪ Rheological analysis 	<ul style="list-style-type: none"> ▪ β-glucan-amino acid/peptide conjugate exhibited solid-like behavior, which is a required property in food product formulations 	[87]
Oat β -glucan	Chemical	Acetylation (using 4% and 6% acetic anhydride for 10 and 20 min)	<ul style="list-style-type: none"> ▪ Functional properties ▪ Thermal properties ▪ Morphological features ▪ Rheological properties 	<ul style="list-style-type: none"> ▪ Enhanced swelling capacity and bile acids binding capacity ▪ Decreased viscosity ▪ Promoted gel formation with a functional appeal and improved features 	[88]
Oats	Chemical	Reductive amination by using dimethyl sulfoxide	<ul style="list-style-type: none"> ▪ Microstructure characterization 	<ul style="list-style-type: none"> ▪ β-glucan derivative showed antibacterial (against <i>E. coli</i> and <i>Bacillus subtilis</i>) and 	[89]

(DMSO), sodium acetate and sodium cyanoborohydride reagents

▪ Physiological effectiveness in bile acid binding capacity in vitro studies

▪ enzyme inhibitory (angiotensin-converting enzymes, ACE) activities
▪ β -glucan derivative stimulated the creation of nitric oxide, an immune response modifier that plays an essential role in defense systems

3.2.1. Acid Treatment

Modification by Ascorbic Acid Treatment

Chemical agents, such as organic acids (e.g., ascorbic acid), mineral acids (e.g., phosphoric acid), transition metals (e.g., iron) and oxygen, have the ability to break glycosidic bonds in β -glucan, leading to modification in MW and changes in viscosity. Kivelä et al. [77] examined the effects of adding ascorbic acid (vitamin C) and its oxidation product (dehydroascorbic acid) to pure cereal β -glucan (0.6%) in the presence of iron sulfate. They observed a decrease in the viscosity and MW of the cereal β -glucan. Interestingly, the reduction in viscosity could be terminated by introducing a hydroxyl (OH) scavenger such as glucose or by limiting the concentration of oxygen in the solution.

The study concluded that common food additives and minor ingredients can be harmful for the stabilization of β -glucan in β -glucan-enriched food products. Another study by Ames et al. [67] showed that there is an increase in rheological and molecular properties of β -glucan when apple juice with high levels of ascorbic acid is added to food preparation such as barley porridge. Moreover, when coarsely ground barley was soaked for a whole night in apple juice containing ascorbic acid before cooking into porridge, there was a significant reduction in both the MW and viscosity of the cereal β -glucan in the final product. This has implications for β -glucan-fortified foods, and as such appropriate research is required to understand the potential food and health benefits/harm of incorporating β -glucan in organic acid-rich foods.

Modification by Carboxymethylation

Modification by carboxymethylation involves the etherifying the primary and or secondary alcohol groups in carbohydrates with the purpose of improving functionalities such as cold water solubility/dispersibility [79,90]. In this method chloroacetic acid in either 2-propyl alcohol or alkali water (pH > 12) is normally used for the carboxymethylation of β -glucan. The active sites for carboxymethylation can be C-2, C-4 and C-6 carbon atoms, and degree of substitution can be controlled by altering the ratio of sodium hydroxide to chloroacetic acid. As degree of substitution increases, structural transition is known to occur, and β -glucan changes from triple-helical structure through single helical to random structure [74,91].

Wang et al. [78] utilized carboxymethylation to produce water soluble β -glucan derivatives from *Poria cocos*, a wood decay fungus. The carboxymethylated β -glucan was separated into eight fractions by utilizing acetone as precipitant. They reported that the carboxymethylated β -glucan exhibited good solubility and anticancer activity against sarcoma as well as gastric carcinoma in both in vivo and in vitro studies. Moreover, Zhang et al. [79] prepared alkali hot water extracts of (1 \rightarrow 3)- β -D glucan from the mushroom *Pleurotus tuber-regium* and observed that after carboxymethylation, the MW of β -glucan increased from between 10,000 and 420,000 (initial) to between 20,800 and 53,200 (final). Compared to the native unmodified form, the carboxymethylated β -glucan also had higher water solubility and anti-tumor activity in vitro and in vivo. In a related study, Wang and Zhang [81] also studied the role of chemical derivatization on MW and conformation of β -glucan. They extracted water insoluble β -glucan from *Ganoderma lucidum* by using sodium hydroxide solution and further derivatized it chemically. They observed that modification by sulfation, carboxymethylation, hydroxypropylation, hydroxyethylation, and methylation resulted in β -glucan with MW values of 101,000, 63,000, 51,000, 72,000, and 141,000, respectively. Further, all derivatives had an improved water solubility profile. They also found that although native β -glucan had a compact coil structure, the derivatives produced from the five different chemical compounds had slightly expanded flexible chain conformations.

In some instances, prior treatment of the β -glucan before chemical derivatization improves the efficiency of the derivatization process. For example, Magnani et al. [80] extracted β -glucan from *Saccharomyces cerevisiae* by sonication and enzymatic treatment and further derivatized the extract by carboxymethylation. The modified β -glucan had a degree of substitution of around 0.8 and did not have any cytotoxic or genotoxic effects. Ding et al. [82] have also prepared carboxymethylated β -

glucan prepared with ball milling as pretreatment. The β -glucan was extracted from yeast (*Saccharomyces cerevisiae*) and modified by utilizing double step alkalization and etherification with monochloroacetic acid. The authors observed that the pretreatment step improved the degree of substitution, viscosity, and solubility of the modified β -glucan.

Modification by Sulfation

Sulfation or sulfurylation involves the addition of the sulfo hydrophilic groups ($-\text{S}(=\text{O})_2-\text{OH}$). This method involves the utilization of SO_3^- pyridine complex, chlorosulfonic acid in pyridine or direct sulfonation with concentrated sulfuric acid [74,84]. The produced sulfated β -glucan often has improved characteristics such as good water solubility, high yield, as well as bioactive traits such as anticoagulant, antithrombotic, antitumor, and immune-modifying characteristics [15,92,93]. In their study, Yoshida et al. [86] compared the effect of sulfation processes on curdlans by using three methods, i.e., piperidine-N-sulfonic acid (PSA method), SO_3^- pyridine complex in pyridine (SPC method), and chlorosulfonic acid in pyridine (CSA method). They examined the physiological effects of these derivatives and concluded that the sulfated curdlan derivatives had antiviral activities against human immunodeficiency virus (HIV). Moreover, the sulfated curdlan derivatives produced by using the method of SPC and CSA exhibited higher anticoagulation power than derivatives produced by using PSA. In another study, Wang et al. [85] modified the polarity and solubility of the β (1 \rightarrow 3) glucan extracted from yeast by using the sulfation process. To achieve this, they utilized a combination of sulfuric acid and n-propanol (1:4 molar ratio). This gave a yield and degree of sulfation of 37.4% (*w/w*) and 0.36, respectively. They postulated that on average, 36 sulfate groups were replaced on every 100 glucose subunits along the β -glucan polysaccharide. Vasconcelos et al. [83] studied the sulfation of exocellular β (1, 6) glucan isolated from *Lastodiplodia theobromae*. The amount of sulfur and degree of substitution of the sulfonated glucan were found to be 11.73% and 0.95, respectively, after sulfation. The sulfonated glucan also exhibited anticoagulant activity via an increase in activated partial thromboplastin time and thrombin time because of the inserted sulfonate groups on the polysaccharides.

Modification by Phosphorylation

Williams et al. [84] developed and characterized water soluble phosphorylated β -glucan from the insoluble β -glucan isolated from the baker's yeast (*Saccharomyces cerevisiae*). To derivatize the β -glucan, chemical modification was done by using dimethyl sulfoxide (DMSO) containing urea and then partially phosphorylated at 100 °C. This study concluded that the glucan phosphate was water soluble. It also activated macrophages and aided in the stimulation of bone marrow. Moreover, the produced β -glucan had antitumor therapeutic activity and immunoprophylaxis activity that has the potential to aid treatment of many infectious diseases.

3.2.2. Conjugation to other Biomolecules

β -glucan contains functional hydroxyl and aldehyde groups, which allows for modification through conjugation to other molecules. Various functional biomolecules, such as proteins, amino acids, organic acids (e.g., acetic acid), and polyphenols, have high affinity to bind with cereal β -glucan. Maillard is one of the chemical methods used to modify the β -glucan with proteins.

In their study, Sun et al. [87] found out that the viscoelastic nature of oat β -glucan changed after non enzymatic reaction (Maillard reaction), and the obtained β -glucan-amino acid/peptide conjugate exhibited solid-like behavior, which is a required property in many food product formulations, as well as for the encapsulation of biomolecules.

Conjugation by acetylation reactions with β -glucan involves the addition of acetyl groups (CH_3CO) to the β -glucan molecule, resulting in various enhanced functional characteristics. De Souza et al. [88] reported that oat β -glucan modified by the acetylation process has better functional properties, such as enhanced swelling capacity and bile acids binding capacity, compared to the

native β -glucan. Acetylated β -glucan could also be utilized in food applications because of its gel formation behavior and texture characteristics.

Shin et al. [89] conducted reductive amination of oat β -glucan and analyzed its physiological characteristics. The modified β -glucan had a degree of substitution of 0.48 and showed higher in vitro bile acid binding capacity than the native β -glucan. The β -glucan derivative also showed higher antibacterial activity against the *E. coli* and *Bacillus subtilis*, as well as ACE (angiotensin-converting enzymes) inhibition, in a dose-dependent manner. The β -glucan derivative also stimulated the creation of nitric oxide, an immune response modifier, and could therefore play an essential role in the host defense system.

3.3. Enzymatic Modification

In the food industry, enzymes play a key role to modify the functional characteristics of polysaccharides. In this regard, specific enzymes are employed for the purpose of depolymerization, debranching, and de-esterification. Depolymerization of β -glucan is essential to minimize the viscous characteristics that are apparent during processing/mashing of barley malt and/or during the production of the maltosaccharide syrup [94]. The enzyme β -glucanase acts on β -glucans and reduces the molecular weight, but it also enhances the solubility, bioactivity, and functionality of hydrolyzed β -glucan, as presented in Table 4. Roubroeks et al. [95] isolated β -glucan from oats and partially depolymerized the (1-4)- β -D-glucan by using lichenase (β -(1 \rightarrow 4)-D-glucan 4-glucanohydrolase). They examined the enzyme-treated β -glucan and found that molecular weight and intrinsic viscosity varied from 2200 to 213,900 g/mol and 7 to 316 mL/g, respectively. After depolymerization by enzymatic treatment, the structure of β -glucan had changed from semi-flexible chain to an extended random coil.

Table 4. Impact of enzymatic modification techniques on the properties of β -glucan.

Sources of β -Glucan	Modification Method	Modification Condition(s)	Characterization Approach	Outcome of Modification	Reference
Oats	Enzymatic	Enzymatic hydrolysis (Lichenase)	<ul style="list-style-type: none"> ▪ Microstructure characterization ▪ MW distribution ▪ Rheological 	<ul style="list-style-type: none"> ▪ Structure of β-glucan changed from semi-flexible chain to an extended random coil 	[95]
Yeast (<i>Trichoderma</i> strain <i>LE02</i>)	Enzymatic	Enzymatic hydrolysis (β -1,3 Glucanase)	<ul style="list-style-type: none"> ▪ Functional characterization 	<ul style="list-style-type: none"> ▪ Enhanced anti-tumor and antioxidant activities 	[15]
Oats	Enzymatic	Enzymatic hydrolysis (Cellulase)	<ul style="list-style-type: none"> ▪ Physicochemical characteristics ▪ Physiological effectiveness in reducing weight and cholesterol levels 	<ul style="list-style-type: none"> ▪ Reduction in MW of oat β-glucan ▪ Lowered body weight of the experimental mice 	[96]

Duan et al. [97] examined the effect of enzymatic hydrolysis by β -1,3 glucanase on β -(1, 3) glucan extracted from yeast (*Trichoderma strain* LE0₂). It was found out that fractions of β -glucan obtained after the enzymatic hydrolysis had molecular mass greater than 30 kDa and had improved water solubility. In addition to conformational modification, the enzymatic hydrolysis also improved the functional characteristics, such as antitumor and antioxidant activities, of the β -glucan. Moreover, Bae et al. [98] produced oat β -glucan hydrolysates with different molecular weights using enzymatic hydrolysis with the help of cellulase enzymes and examined their physicochemical as well as cholesterol- and weight-reducing properties. Cellulase treatment caused reduction in the molecular weight of oat β -glucan from 1450 to 370 kDa, which also affected the swelling power, and bile acid/fat binding power. They supplemented three hydrolysates (molecular masses 1450, 730, and 370 kDa, respectively) to high fat meal for mice study and reported that these hydrolysates remarkably lowered the body weight of the mice. In a follow up study, Bae et al. [96] reported that supplementation of β -glucan hydrolysates and native β -glucan both significantly lowered the LDL and VLDL cholesterol levels in the serum and further enhanced the liver lipid profile in mice. However, the hydrolysates were found to be more effective in enhancing the excretion of fecal cholesterol and triglyceride than the native β -glucans, which exhibited their effectiveness in improving the lipid profile. It follows therefore that incorporation of enzymatically produced β -glucan hydrolysates in food products and subsequent consumption can contribute to lowering the risk of cardiovascular diseases.

3.4. Mechanical Processing

Aside from enzymatic treatment, mechanical energy/forces can also be used to reduce the molecular weight of β -glucan and consequently enhance the functionality of the material. The outcomes of various mechanical modification treatments are given Table 5. Mechanical forces lead to the breakdown of glycosidic linkages in the β -glucan structure, which results in the reduction in molecular weight, which further alters water solubility and other related physiological functions. High-pressure homogenization is a mechanical treatment used to alter the molecular, functional, structural, and solubility-related characteristics of polysaccharides in food applications. Kivelä et al. [99] compared the impact of three homogenization techniques (a pilot scale colloid mill, a two stage high-pressure valve homogenizer, and a lab scale microfluidizer) on the structure and characteristics of oat β -glucan. The main emphasis of the study was to study the influence of mechanical energy input on the solution characteristics and molecular weight of the β -glucan. The authors observed a clear and irreversible decline in the molecular weight, viscosity, and shear thinning behavior of samples due to the application of high-pressure homogenization, while colloid mill did not affect these parameters. In the case of high-pressure homogenization, the reason behind the decrease in molecular weight might be the chain length scissoring and breakdown of aggregates or both. Owing to its ability to enhance the structural stability and mechanical fragmentation of β -glucan during storage, homogenization at elevated pressures is an efficient method for modification of β -glucan in solution.

In another study, Thammakiti et al. [100] examined how homogenization treatment influences the chemical composition, viscosity, and functional characteristics of β -glucan from yeast (*Sacchromyces cerevisiae*). The findings of that study were that β -glucan obtained after homogenization of yeast cells had higher levels of β -glucan, with higher apparent viscosity, as compared to the untreated yeast. It is likely that homogenization resulted in the fragmentation of the cell walls and improved release of the β -glucan from the yeast cells. Moreover, the β -glucan modified by homogenization process had higher apparent viscosity, water binding power, and emulsion stabilization characteristics than commercial β -glucan from yeast source.

Table 5. Impact of mechanical modification techniques on the properties of β -glucan.

Sources of β -Glucan	Modification Method	Modification Condition(s)	Characterization Approach	Outcome of Modification	Reference
Oat	Mechanical	Homogenization (colloid mill, high-pressure valve homogenizer, microfluidizer)	<ul style="list-style-type: none"> ▪ Solution characteristics ▪ MW distribution 	<ul style="list-style-type: none"> ▪ Reduced MW, viscosity, and shear thinning behavior of samples 	[77]
Microbial (<i>S. cerevisiae</i>)	Mechanical	Homogenization	<ul style="list-style-type: none"> ▪ Chemical composition ▪ Rheological features ▪ Functional characterization 	<ul style="list-style-type: none"> ▪ Increased apparent viscosity, water binding power, and emulsion stabilizing characteristics as compared to the commercial native β-glucan 	[100]
Brewer's yeast, (<i>S. cerevisiae</i>)	Mechanical	Mechanochemical Method	<ul style="list-style-type: none"> ▪ Physicochemical characterization ▪ Morphological characterization 	<ul style="list-style-type: none"> ▪ β-glucan phosphate up-regulated the functions mediated by the murine macrophage RAW264.7 and exerted immune stimulating activities 	[101]

It is worth mentioning that mechanochemical processing has been gaining prominence as an alternative to modifying β -glucan characteristics. It is a process in which mechanical energy is converted to internal energy in the milled polysaccharides (solids). As a result, there is the generation of many metastable active sites, which help the polysaccharides to react with other reagents. This innovative technique is utilized to modify morphological and structural features of the polysaccharides, such as cellulose, starch, and lignocelluloses, leading to improvements in their physicochemical characteristics [102–104]. For example, Shi et al. [101] utilized mechanochemical processes to phosphorylate and to make more soluble β -glucan extracted from brewer's yeast, *Saccharomyces cerevisiae*. The planetary ball mill successfully modified the native β -glucan to β -glucan phosphate by using sodium hexametaphosphate, and they reported that the modified β -glucan phosphate was more water soluble and observed a decline in peak molecular mass (6.6–10.0 kDa), degree of polymerization (17.6–33.7), and high degree of phosphate group substitution (0.77–2.09). The mechanical force caused the breakdown of the tight helical structure of the β -glucan molecules and increased the number of metastable sites to react with sodium hexametaphosphate. β -glucan phosphate was able to up-regulate the functions mediated by murine macrophage RAW264.7 cells, thus exerting immune-stimulating activities.

3.5. Other Processing Methods

3.5.1. Irradiation

Gamma radiations are ionic rays that are generally used for cold sterilization or non-thermal approaches to processing food to ensure safety. Recently, the technique has received tremendous attention because of its rapidity, ease of use, efficiency in leading to modification of food compounds, and as an efficient preservation method in food research and the application sector [57]. As presented in Table 6, β -glucan can be modified through gamma irradiation treatment by using electron beams, X-rays, or gamma rays to alter the molecular weight and in turn cause physicochemical changes in the structure.

Shah et al. [105] performed modification of cereal β -glucan with the help of gamma irradiation to enhance its antioxidant potential and reported that irradiation enhanced the free radical scavenging activity due to creation of new exposed functional groups ($-\text{COOH}$, $-\text{OH}$, and $-\text{CO}$). In addition, irradiation also elevated the antiproliferative potential of cereal β -glucan in human cells. FT-IR spectroscopy revealed that irradiation treatment shifted the carbonyl groups to lesser wave numbers, giving the material better chance to partake in hydrogen bonding. Consequently, irradiation produced β -glucan with modified antioxidant and antiproliferative activity, and this provides a functional ingredient with a variety of applications in food formulations.

In a study by Methacanon et al. [57], the influence of gamma ray modifications at varying doses (0–100 kGy) on the conformation of the β -glucan from microbial source (*Oppiocordyceps dipterigenia* BCC2073) was examined, together with how the molecular weight affected interleukin-8 (IL-8) stimulating activity. They reported that gamma irradiations did not affect the functional groups but significantly decreased the average molecular weight from 590 kDa to 5 kDa with increase in the irradiation dose up to 100 kGy.

Table 6. Impact of irradiation modification techniques on the properties of β -glucan.

Sources of β -Glucan	Modification Method	Modification Condition(s)	Characterization Approach	Outcome of Modification	Reference
Barley (<i>Hordeum vulgare</i> L.)	Irradiation	Gamma irradiation	<ul style="list-style-type: none"> ▪ Molecular characterization ▪ Rheological features ▪ Functional characterization 	<ul style="list-style-type: none"> ▪ Irradiation treatment shifted the carbonyl groups to the lesser wavenumber, implying that the treated β-glucan had better chance to partake in hydrogen bonding ▪ Modified antioxidant and antiproliferative activities 	[105]
Fungus (<i>Oppiocardyceps dipterigenia</i>) BCC2073	Irradiation	Gamma rays (various doses 0–100 kGy)	<ul style="list-style-type: none"> ▪ MW distribution ▪ Conformational characterization ▪ Physiological effectiveness in Interleukin 8 (IL-8) stimulating activity 	<ul style="list-style-type: none"> ▪ Reduced average MW ▪ β-glucan with low level of branching (α helix) was less active in stimulating the creation of IL-8 ▪ β-glucan with MW ~5 kDa showed maximum ability to induce IL-8 production 	[57]
Black yeast (<i>Aureobasidium Sp</i>)	Irradiation	Gamma radiations (Co-60 source and different doses of irradiations)	<ul style="list-style-type: none"> ▪ Physical features ▪ Microstructural characterization 	<ul style="list-style-type: none"> ▪ MW significantly reduced with increase in dose of irradiation ▪ Solubility of β-glucan improved due to radiolysis of glycosidic linkage ▪ Reduction in viscosity ▪ Deformation of the β-glucan into smaller granules 	[106]
Black yeast (<i>Aureobasidium Sp</i>).	Irradiation	Gamma Irradiation (dose 50 kGy)	<ul style="list-style-type: none"> ▪ Anticancer activity 	<ul style="list-style-type: none"> ▪ Low MW β-glucan elevated the proliferation of murine peritoneal macrophages and their creation of cancer necrosis factor and nitric oxide 	[107]
<i>Pleurotus tuber-regium</i>	Irradiation	Microwave (0.02 wt% aqueous sodium azide)	<ul style="list-style-type: none"> ▪ Solubility and shape characteristics 	<ul style="list-style-type: none"> ▪ β-glucan existed in the spherical shape in the aqueous sodium azide solution 	[108]

In a different study, Byun et al. [106] examined the effect of gamma irradiation on the physical and structural characteristics of β -glucan extracted from black yeast (*Aureobasidium sp.*). β -glucan solution (10% *w/v*) was treated with Co-60 radioactive isotope at different irradiations doses. The molecular weight of the modified β -glucan showed significant decrease with increase in dose of irradiation. Moreover, gamma radiation treatment improved the water solubility and reduced the viscosity of β -glucan, due to the radiolysis of the glycosidic linkage. Scanning electron microscopy confirmed that treatment with gamma irradiation caused the deformation of the β -glucan into smaller granules. Hence, this treatment can be used in the food industries to overcome the challenges encountered with highly high viscous and poorly water soluble β -glucan [106]. In a related study, Byun et al. [107] analyzed the anticancer activities of β -glucan produced by gamma irradiation dose of ~50 kGy to cause modification by reduction in β -glucan molecular weight. Anticancer activities were studied through in vitro and in vivo models. It was found that treatment with low molecular weight β -glucan (LMBG) elevated the proliferation of murine peritoneal macrophages and their production of tumor necrosis factor α and nitric oxide to a greater extent than treatment with high molecular weight β -glucan. It can be concluded that gamma radiations can be used as an effective modification method for the production of LMBG, which showed improved antitumor activity through immunomodulatory effects.

3.5.2. Microwave Energy

Microwave energy has also been known to change the conformation of β -glucan. This modification treatment increases the molecular chains of β -glucan, which results in enhanced physicochemical characteristics. Tao and Xu [108] developed modified β -glucan from water insoluble hyper-branched β -glucan (native) extracted from *Pleurotus tuber-regium* (king tuber mushroom) by using microwaves to enhance its water solubility. The microwave disintegration method (35 s at 765 W) resulted in the full dissolution of β -glucan when dissolved in sodium azide solution (0.02 wt%). Their findings using transmission electron microscopy confirmed that the β -glucan existed in a spherical shape in the aqueous solution.

4. Applications of Modified β -Glucan in Various Food Systems

β -glucan is well known for its good water retention, stabilization, and textural characteristics in food systems. These characteristics not only enhance the use of β -glucan in a range of food products for specialty purposes but also provide potential health advantages to consumers (see Figure 7). Owing to its solubility in water, β -glucan plays an important role in improving functional characteristics, such as rheology and texture-related properties, when used in food systems. Its ability to trap a large amount of water and intrinsic rheological characteristics make it an ideal thickener as it provides a better texture and desirable sensory properties to food products [57].

β -glucan and its derivatives can also be used as fat replacers/mimetics in food products such as baked goods and meats. Liu et al. [109] incorporated oat β -glucan and its hydrolyzed derivatives in meat balls as fat replacers to study the effects on the physicochemical parameters of the meat balls. They estimated the molecular weight of β -glucan with the help of high-performance size exclusion chromatography (HPSEC) and observed that the molecular weight of oat β -glucan treated by enzymatic hydrolysis (cellulase) ranged from 6600 kDa to 9400 kDa. Both the native and hydrolyzed β -glucan exhibited shear thinning behavior, while the hydrolyzed form had a minor decline in apparent viscosity as compared to native form. They observed a higher peak temperature and smoother surface for the hydrolysates-containing meatballs. This study concluded that oat β -glucan hydrolysates-containing meatballs had higher overall acceptability; hence, it is a very promising fat replacer in meat products. Similarly, in bakery products, cereals, being a rich source of β -glucan, can be used as fat replacers, and simultaneously impart positive health benefits in the form of dietary fiber. Some studies reported that Nutrim oat bran (OB) with 10% β -glucan content (dry basis) has a positive effect on human health by decreasing cholesterol level. Generally, it is utilized in food

formulations in the form of powder or gel to bind to and reduce the fat content and calorie value [110,111].

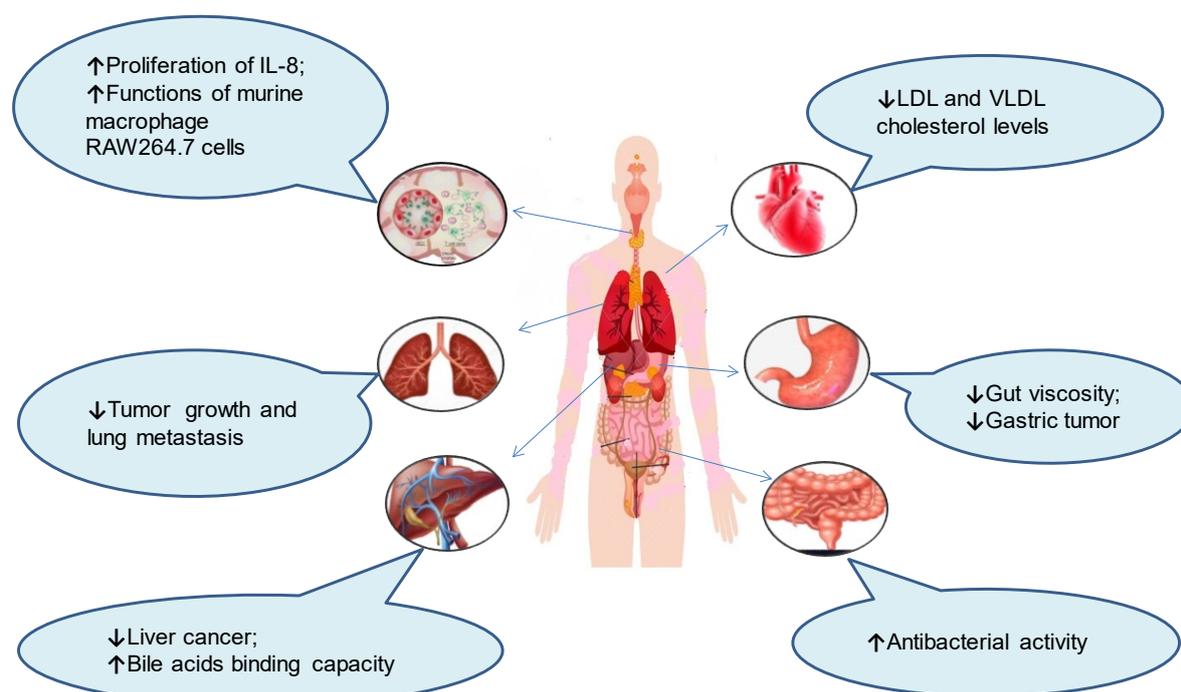


Figure 7. The effect of modified β -glucan on human physiology. IL-8, interleukin 8; LDL, low-density lipoprotein; VLDL, very low-density lipoprotein; Data from [57,65,78,79,88,89,96,98,101,107].

Lee and Inglett [112] successfully replaced different amounts of shortening (10%, 20%, and 30%) in cookies with modified β -glucan (20% jet-cooked oat bran (Nutrim OB)). They examined the effect of baking treatment on rheological and physical characteristics of cookies incorporated with β -glucan as compared to the control sample. The addition of Nutrim OB (as a fat replacer) caused reduction in diameter and increase in the height of cookies. The β -glucan-containing cooking also had more “elastic” characteristics. Therefore, replacement of fat with β -glucan can help to control calorie intake and the attendant health hazards caused by the excessive intake of fat.

It is important to note that in some cases the addition of β -glucan into baked products (e.g., bread) can cause undesirable physicochemical changes, such as lowered dough extensibility, reduced loaf volume/height, and undesired changes in crumb texture, which ultimately lowers consumer acceptability. Literature on the mechanistic understanding behind this phenomenon is limited. However, it is likely due to the enhanced water absorption capacity and viscosity of β -glucan, which in turn is related to the molecular mass. Cleary et al. [113] documented that incorporation of high and low molecular weight β -glucan (barley) in white bread preparation caused stiffer dough and reduced loaf volume and height. The bread prepared from high molecular weight β -glucan had higher levels of dough loss and degradation of bread quality during preparation. These limiting changes in bread quality can be overcome by using modified β -glucan with lower molecular weight range [113,114].

5. Conclusions and Future Outlook

Nowadays, research focusing on functional ingredients, which helps to provide nutrients as well as to promote health benefits, is of utmost interest. β -glucan is a polysaccharide with β -glycosidic linkages and is widely abundant and found in a variety of sources such as bacteria, fungi, algae, and plants. Recently, β -glucan as a food ingredient is gaining increasing research attention owing to its functional properties (in foods) and biological properties that rely on its structural conformation and molecular weight. β -glucan extracted from different sources, but with similar basic structure, shows different functional and biological activities. Because of its low solubility, the basic structure of β -

glucan can be modified to improve its bio-functional properties through changes in the molecular weight and structural conformation. Combination of modification methods such as physicochemical, chemo-enzymatic, mechano-physical or mechanochemical processes can significantly alter the bio-functional characteristics of β -glucan. However, these modification strategies can change the functional properties of β -glucan both negatively and positively, depending on the modification method. Studies on the influence of β -glucan modification on its bio-functional characteristics are widely abundant, but the mechanistic understanding of how the modification methods affect the molecular conformation and aggregation behavior of β -glucan is largely lacking. Unraveling the structural features of β -glucan is time-consuming and complicated because of the wide size range, high degree of polydispersity, and complex structural arrangement (e.g., helices) of the molecule. However, advancement in carbohydrate chemistry; separation techniques; and advanced analytical techniques, such as field flow fractionation, multi-angle light scattering (MALS), differential refractive index (dRI) detection, small-angle X-ray scattering (SAXS), and cryo-transmission electron microscopy (cryo-TEM), are proving promising. A systematic study into how various processing techniques affect the conformation and aggregation behavior of β -glucans will provide better understanding that can guide tailored modification of β -glucans for specific purposes, be it to improve their use in food products, or to enhance their in vivo health-promoting properties.

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