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Review

Potential use of Janus structures in food applications

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ABSTRACT

Janus surfaces present technological opportunities both for research and industry in which different chemical, physical and/or structural components need to coexist for a single purpose such as chemistry, textile and material science. Varying inorganic and organic (polymer-based) materials are conventionally used however, utilizing nature-derived polymers to fabricate Janus structures is a recent and attractive trend which makes them more applicable for bio-based treatments with environmental concerns. Particularly, promising applications of Janus structures as being surfactants, drug delivery and micro/nano encapsulation vehicles for biomedical purposes successfully forward the interest on Janus concept to the food related practices. Producing Janus structures from nature-derived and food grade polymers such as alginate, cellulose, chitosan, lipid nanocrystals, zein and some plant-proteins and their usage stronger emulsions with higher stabilities, biosensing or antimicrobial practices as well as bioactive delivery and release control might be considered as a new era for food processing industry.

1. INTRODUCTION

Janus structures are unique surfaces composing of different chemical, physical and/or structural components in one single particle, customized for a specific purpose [1]. Janus structures, mainly Janus particles (JP) are produced and utilized in order to obtain advanced interfacial surfaces with improved processing and technological properties. Their asymmetric and complex architectures enable to work with different materials having varying surface activities and combining them to fabricate a novel surface which could either be a particle, fiber, film, gel network, or surface with varying geometries such as spherical, cylindrical, disc shapes, snowman, dumbbell, various capsules and vehicles [2]. Due to their unique functional potentials having tunable forms and size (Figure 1), Janus surfaces have been used in varying research and application fields such as chemistry, textile and material science since the early 90's from the date that they were discovered [3]. Depending on the materials, they might be classified into three groups as inorganic, organic (polymer-based) and hybrid (polymer/inorganic) Janus structures [4]. For this purpose, a wide range of compounds have high potential to be fabricated as Janus structures such as inorganic compounds; Au–Fe_3O_4, $Cu_2(OH)_2CO_3$–CuS, Au–SiO_2, Ag–SiO_2, Fe_3O_4–SiO_2, and polymeric compounds; poly(methyl methacrylate), poly(styrene-2-(2-bromoisobutyryloxy)ethyl methacrylate), PS-b-polybutadiene(PB)-b-PMMA, poly(2-vinylpyridine-co-styrene), poly (N-isopropylacrylamide) and so on, for varying purposes [5]. However, associated with the increase of environmental concerns, comprising the green and sustainable production with lower carbon footprint, nature-derived polymers have been started to be investigated in terms of their fabrication potential for Janus structures, in the last two decades. Furthermore, the controllable and tunable properties of those nature-derived compounds with external inductions such as light, pH, temperature or ionic strength increased the attention on these polymers, not only for traditional usage in chemistry, textile and material science but also for biomedical applications [6]. Recently, the applications of bio-compatible nature-derived polymers as Janus structures for bio-based applications might be listed as solid surfactants, micro/nano motors, biosensing, drug delivery, bioimaging, cancer therapy and theragnostic [7]. In addition to bio-based applications of nature-derived and bio-compatible Janus structures, the potential of food-grade polymers to be processed into a Janus form were of great interest, lately [1, 8, 9]. Despite the relative abundance of the studies investigating the potential applications of Janus structures produced from food-grade polymers (with/without the assistance of other organic and inorganic compounds) for distinctive bio-applications, the studies are very rare for actual food systems.

Throughout this study, it was aimed to review the recent Janus structure applications which were produced from food-grade

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polymers/compounds both for real food matrices and other bio-based systems having a potential to be adapted into food materials. Basic properties of produced Janus structures, their components, production methods and their application potentials were covered and criticized in order to develop a promising perspective for future food processing.

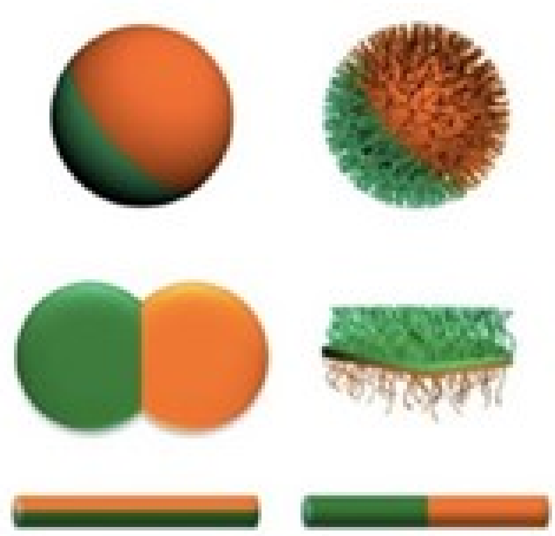

Figure 1 Representation of Janus concepts, having different materials and surfaces as one individual particle [6].

2. BIO-BASED POLYMERS TO FABRICATE JANUS STRUCTURES

Biologically compatible synthetic polymers such as poly lactic-co-glycolic acid (PLGA), polycaprolactone (PCL) and/or poly ethylene glycol (PEG) are highly efficient compounds to fabricate JPs for controlled released drug delivery which are appropriate to be produced with encapsulation, emulsification or electrohydrodynamic methods [6, 10, 11]. The JPs produced from these synthetic polymers, which were used even for cancer treatment studies, might also be applied for food matrices. However, utilization of these types of polymers for the areas such as food industry would require to use extensive and abundant amounts more than that of for pharmaceutics. For this reason, using potential synthetic polymers to produce JPs for food matrices might induce economic, environmental, regulatory and toxicity concerns [12]. Apart from artificially synthesized inorganic materials to be used for JPs production, the research interest was focused on organic, sustainable and even revalorized substances for a greener strategy. Polysaccharides such as starch, chitosan, cellulose; proteins like whey, soy, zein; and some fat crystals have potentials to be utilized as solid particles for interfacial stabilization in food matrices [1]. Possibility to be processed as solid components might enable them to be used for JP production however, there are only few studies in which some of those materials were used to produce JPs and further handled to stabilize model food interfaces as emulsifiers [12, 13]. On the other hand, another question raised is the possibility to use biocompatible natural/nature derived JPs which were produced for biomedical applications in food systems. Since delivery of a bioactive compound, biosensing and/or bioimaging are common purposes of food and biomedical research areas, possibilities for using similar/identical JPs in both areas should be discussed [4]. Some selected studies that used natural/nature derived polymers to fabricate Janus structures for direct food and food-adaptable practices are briefly presented in Table 1.

2.1. Food applications of nature- derived JPs

JPs are being used for biomedical applications like targeted delivery, imaging, cancer therapy, and/or biosensing with a growing interest in the last decade, yet still in-depth studies are required. Furthermore, investigating natural/nature derived substances having potential to be used for JP fabrication is one of the most recent trends, mainly for varying bio-applications but the studies associated directly for food systems are rare. The research history of nature-derived, food-grade JPs does not date back a long time. Amphiphilic hydrogel-solid based JPs were produced from shellac and alginate (3:2, wt) crosslinked by calcium cations within a monodisperse single emulsion system (oil-in-water) using a flow-focusing PDMS microfluidic device [14]. These monodisperse food grade particles had an average size of 25 x 20 μm and were proposed to be used in emulsions as both oil-in-water and water-in-oil food matrices however, real food application was not conducted. In another study, silver and chitosan based JPs were produced in order to be used as antimicrobial agents against *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli*, *Salmonella choleraesuis*, and *Botrytis cinerea* [13]. Composite formation was induced by high temperature (95 °C) and pH (10.0) conditions under vigorous stirring. Produced JPs were used as coating material for fresh blueberries and at the end of 4-day of artificial inoculation period, it was reported that silver/chitosan-based JPs performed a significantly higher suppression for growth and germination against mentioned organisms reducing the minimum inhibition and bactericidal concentration by 95% and 80-100%, respectively. For *Botrytis cinerea*, spore germination inhibition was reported as 100% when 0.2 mg/mL silver/chitosan-based JPs were applied. In another study, it was accomplished to fabricate only-starch based JPs [12]. Using a spin-coating spray method, two different JP types were produced with the assistance of (enzymatic and esterification) different natural compounds. Large (12.2 μm), half porous and waxy JPs with alpha-amylase and small (1.2 μm), half hydrophobic amaranth JP with octenyl succinic anhydride were able to be obtained. Those produced particles were not tested in a mimetic food system however, they were proposed to be used as texture improvers and/or surface-active agents in foods due to significant increase in absorption rates of half and fully porous waxy cornstarch JPs by 250-400% compared to non-porous sample. Same research group conducted another study in which microcapsules were produced following the esterification of maltodextrin and octenyl succinic anhydride [15]. Crosslinking of these branched polymers in the presence of calcium ions were found to be sufficient for stable encapsulation of plant based (corn, lemon, lavender and peppermint) emulsion, particularly with a loading ratio of 75% when the stoichiometric ratio was applied as 1:3 of maltodextrin-octenyl succinic anhydride and calcium ions. This study exhibited how high the esterified maltodextrin has the potential to be fabricated as JP for utilization as a promising emulsifier. In a comprehensive review, nature derived JPs were proposed as potential and promising stabilizers for food-grade Pickering emulsions which are thermodynamically unstable and easily tend to destabilize [1]. It is possible for a JP to increase the stability of a Pickering emulsion by tuning the oil/water interface and optimizing the hydrophilic/hydrophobic ratio of the surface-active agents.

Among the actual food grade Janus surface applications, to the best of our knowledge, there are no studies investigating the improvement of foaming properties in food systems. However, designing the interfacial properties at the air/water interface at microstructure level is critically promising to improve aeration capacity and stability for soft-solid materials like food systems [16]. Janus surfaces might act as a key for improved foam structures lasting much longer. In a study, Janus particles produced from polystyrene grafted gold-silica material was determined to avoid foam coalescence at the air/water interface for more than a month [17]. The used materials (polystyrene, gold and silica) might be food grade and recently nominated as non-toxic and safe to consume [18]. Considering the consumer demands, adapting natural/nature-derived components for the same purpose instead of microplastics is beyond comparison. Further researches are needed to fabricate Janus surfaces from more natural/nature-derived and food grade materials to be used as foam stabilizers.

So far, consumption was considered as the main redline in order to choose the origin of compound to fabricate Janus surface. However, in some cases, such as their applications in food safety, JPs may be used without the necessity of being produced from biocompatible, natural/nature-derived materials. In a study, a Janus emulsion agglutination assay was developed based on carbohydrate-lectin binding principle, in order to detect *E.coli*, in a model system (Figure 2) [19]. Janus emulsions were fabricated using many organic chemicals such as hexane, FC770, D-(+)-mannose, concanavalin A. The agglutination occurs specifically for *E.coli* at a concentration of 10^4 cfu/mL and could be analyzed quantitatively with a QR code, in assistance with image analysis and an application software.

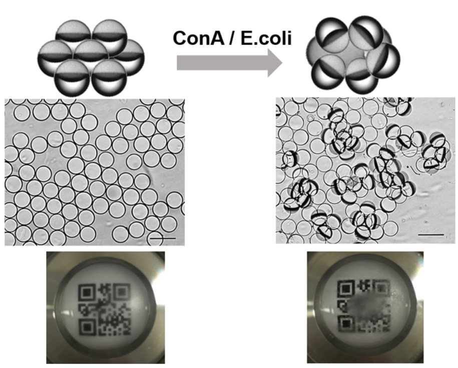

Figure 2 Agglutination of Janus emulsions in the presence of *E.coli* and their optical signal detection by a QR code [19].

Similar to the previous study, Fe_3O_4 based fluorescent magnetic Janus mesoporous silica nanoparticles were used to detect *E.coli* in the milk samples with a detection limit of 10^4 cfu/mL [20] and a non-spectroscopic signaling JP probe in order to detect *Salmonella typhimurium* based on a loop-mediated isothermal gene amplification method, with a detection limit of 10^2 cfu/mL [21]. Other types of food control approaches are also conductible such as tracing and monitoring the food adulterant components like formalin, histamine and hydrogen peroxide using Janus surfaces produced from transition metal chalcogenides and metal oxides [22].

Briefly, utilization of Janus structures could be considered for two major purposes; first one is using them in order to improve/stabilize structural properties which urges Janus structures built from biocompatible and natural/nature-derived materials. So far, only limited number of studies were run in order to examine the effect of Janus surfaces on functional properties and none of them were applied in a real food system. The other one is using Janus structure aiming to trace and/or monitor a particular metabolite of microorganisms for food safety aspects. This approach does not require JPs to be produced from biocompatible and natural/nature-derived materials. However, further studies are required to indicate the potential of JPs to be applied in food materials in order to reveal and adapt the benefits of Janus structures in the service of food industry.

2.2. Other potential food applications of nature-derived JPs

JPs that were specifically produced for bio-applications might be produced in three different ways which are soft particles consisting of organic/polymeric-based compounds, hard particles consisting of inorganic/metallic compounds, and hybrid particles consisting of both polymeric/organic and inorganic materials [3]. These different types of JPs are produced for bio-applications using different techniques and approaches, mainly dependent on their physico-chemical properties such as self-assembling, phase separation, seed-mediated polymerization, microfluidic synthesis, nucleation growth and/or masking methods (Figure 3) [7]. However, they were frequently reported in order to fabricate JPs made from synthetic polymers with/without metallic compounds as soft and hybrid particles but information on the production method for JP from natural-based materials are limited [4]. However, among all these well-known JP production methodologies, microfluidic device based fabrication (most of the time combined with liposome, encapsulation based emulsions) is one of the most popular technique to obtain nature-derived JPs [9].

2.2.1. Pectin based structures

Biopolymer based natural-derived Janus microbeads were first demonstrated in 2012, composing of pectin and alginate polymers (1:1, wt) using a flow-focusing PDMS microfluidic device by in-situ gelation [23]. Produced hetero Janus microbeads had an average diameter of 92 μm and were proposed to be used as emulsion stabilizers for food industry together with pharma and cosmetic applications. This combination might end up with limited application due to the hydrophilic nature of both pectin and alginate polymers. Later on, capillary flow based PDMS microfluidic devices were used to produce homo (pectin-pectin) and hetero

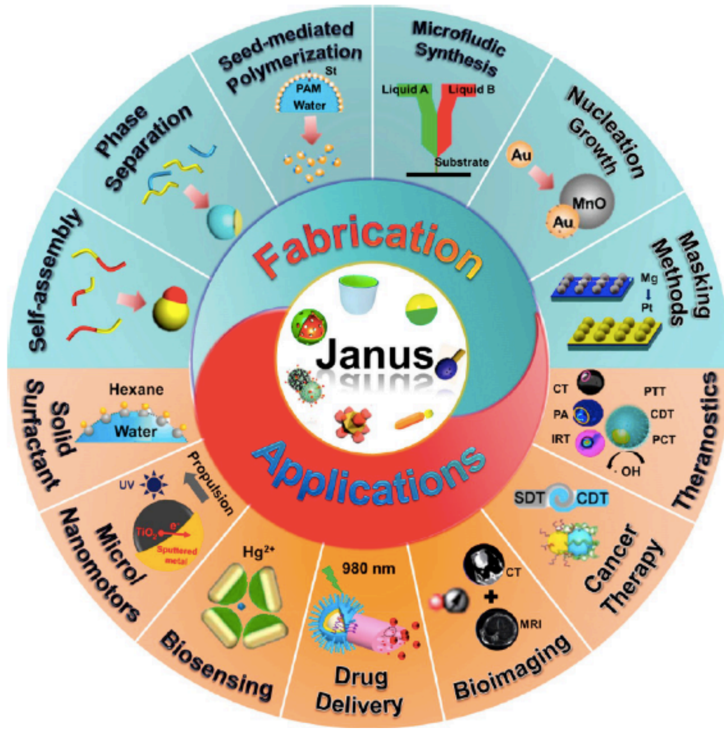

Figure 3 Representation of types, used materials, fabrication methods and utilization areas of Janus surfaces [7].

(pectin-alginate) pectin JPs as innovative polysaccharide based hydrogel microbeads in assistance with $CaCl_2$ and $CaCO_3$ [24]. Due to varying specific interactions between these two polymers, gelation phenomena of pectin as on-chip and off-chip, and the presence/absence of crosslinking agents, the sizes and shapes were able to be tuned as desired like sphere, doughnut-like, oblate ellipsoid or mushroom-like morphologies. The produced homo and hetero JPs were proposed to be used for release control applications at liquid/liquid interfaces for food, medicine and cosmetic purposes (Figure 4). In another study, JPs were fabricated from pectin polymers in assistance with folic acid, silver and/or gold nanoparticles using a dropwise addition self-assembling methodology by vigorous stirring at 24 °C for 5 h in ice bath [25]. For each 0.2% wt pectin and 1 mM folic acid quantity, 1 mM Au or Ag were added into the reaction. Eventually, JPs were obtained in a size range of 4-25 and 2-13 nm for Ag and Ag-Au combined particles, respectively with concentration correlated antioxidant activities based on % DPPH inhibitions.

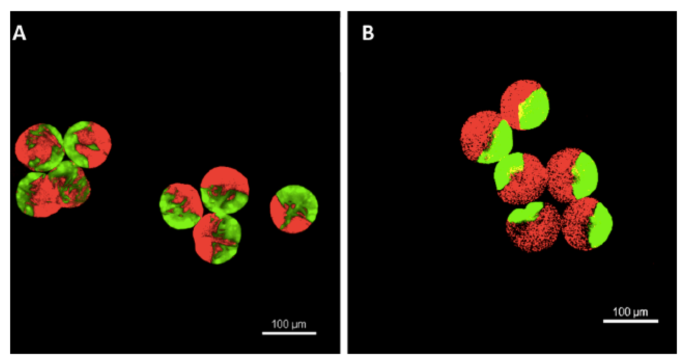

Figure 4 Fluorescence confocal microscopy images for Bodipy-pectin homo Janus (A) and hetero Janus (B) hydrogel microparticles with fluoresceinamine coupled pectin and alginate, respectively [24].

2.2.2. Alginate based structures

In order to fabricate a clean-labelled signal generator JP, sensory polydiacetylene liposomes and magnetic nanoparticle phases that were dissolved in alginate solution were crosslinked by calcium ions and Janus alginate beads were produced [26]. Alginate solution (4 %, wt) carried 1mM polydiacetylene liposomes while other alginate solution with the same concentration were mixed with the surface modified Fe_3O_4 magnetic nanoparticle solution with a volumetric ratio of 1:2. Unique JPs performed a sensitive detection and proper removal of lead (II) ions as well as being convenient for easy manipulation and magnetic field application for washing, solvent exchange and stirring which are the key elements of an enhanced sensitivity and fast detection for environmental and waste-water applications. Nature-derived biopolymers such as alginate, cellulose and chitosan were overviewed to be used for biosensing and electrochemical detection purposes as processed into JPs and their recent application potentials for biological applications were discussed [27]. In another study, alginate polymers were used to fabricate complex structures, not as a particle but fibers, that had Janus morphologies to be utilized as controlled delivery vehicles [28]. With the assistance of carboxymethyl cellulose (CMC) and sodium as the functioning element, alginate-based Janus fibers were produced using a method called "one-pot", which is a kind of simultaneous co-jetting and self-assembling approach. Co-jetted Na-alginate and Na-CMC phases which contains varying concentrations of malachite green and minocycline hydrochloride as model drugs, were pumped through a nozzle to create Janus fibers, transferred into a $CaCl_2$ solution (10%, v/v) to fulfill the gelation, then collected and sterilized with UV radiation. Fabricated drug loaded Janus fibers with different diameters, load amounts and alginate-CMC ratios were tested for release control and their antibacterial efficiencies and it was indicated that this production system allows tuning the properties and structure of Janus fibers depending on the desired variables. This system would be promising for encapsulation of bioactive compounds for food and medicine applications.

2.2.3. Cellulose based structures

Cellulose nanocrystals that were produced from hydrolyzed cellulose chains and fibers might be oxidized and transformed into a partially amorphous crystalline structure that could act as a Janus-like nanoparticles having a needle-shape sandwiched body. This Janus-like hairy cellulose nanocrystals phenomenon were reviewed and criticized comprehensively in a study by Sheikhi and van de Ven [29]. It was indicated that cellulose nanocrystals were compatible for sol-gel processing and convenient to produce colloids, film structures, hydrogel and aerogels mostly by self-assembling which are very adaptable and promising applications for food matrices. Similarly, the oxidized crystalline nanocellulose (prepared from cotton by hydrolysis with H_2SO_4, 65%) with a degree of 81.3% oxidation was induced to form self-standing films by casting or periodate-oxidation [30]. The produced self-standing films (with an average thickness of 9.4 and 64.5 μm, respectively) were tuned with a side-specific function due to having an aldehyde and a carboxyl sides applying the ozone treatment which also provided an elasticity to the Janus films, and proposed to be used for varying biomaterial engineering applications and/or separation technologies. These cellulose based Janus films also have potentials to be used in food application for similar purposes. Bacterial nanocellulose, microcrystalline cellulose pellicle (laboratory based), hardwood and bamboo derived bleached cellulose samples were used to fabricate cellulose nanofibrils via aqueous counter collision method [31]. Samples were prepared to be processed with counter collusion system, then nano-pulverized throughout a nozzle with 160 μm diameter with 60 cycle under 200 MPa ejection pressure. It was indicated that, aqueous counter collision method was sufficiently able to produce an amphiphilic Janus-type surface from varying cellulose nanofibrils with both a hydrophobic and a hydrophilic side structure. These amphiphilic Janus-type surfaces might be utilized in distinctive areas of food industry, particularly as structure stabilizers for varying liquid interfaces. In another study, cellulose nanofibrils were used to produce double sided amphiphilic nanofibrils by aqueous counter collision method, with localized surface acetylation and thereafter applied through a Pickering emulsion system [32]. Similar to the above-mentioned study, bacterial cellulose pellicles were defibrillated with aqueous counter collision treatment by 60 cycle under 200 MPa ejection pressure. Produced acetylated nanofibrils were applied to a heterogenous dispersion system (15 mL with 0.1%, wt nanofibrils) to build Pickering emulsion with an oil phase (14 mL toluene, 50 mg-0.41 mmol DMAP, 5 - 1500 μm-0.53 – 15.87 mmol Ac_2O). Acetylation was successfully achieved keeping the crystallinity and fibrous morphology of the nanofibers and produced film casts (1.8 mm x 1.8 mm) from acetylated cellulose nanofibrils, membrane-like Janus structures with anisotropic surfaces . In another study, chitosan grafted (2%, v/v) bacterial cellulose was utilized to produce an antimicrobial composite membrane with asymmetric wetting properties for potential usage as surface sanitary materials [33]. Chitosan grafted bacterial cellulose suspension (5 mL of 0.44%, wt) was sprayed layer-by-layer onto a polypropylene nonwoven fabric (10 cm x 10 cm). The produced Janus-like surface was reported to have significant antibacterial efficiency against *S. aureus* and *E. coli*.

Electrohydrodynamic methods have been recently applied to produce different cellulose-based Janus structures for varying purposes such as encapsulation of bioactive compounds and drug delivery applications. For instance, ethyl cellulose in assistance with polyvinylpyrrolidone (PVP) polymers was processed into a Janus nanofiber using side-by-side electrospinning technique [34]. With this approach, two monolithic and four Janus-type fibers (0.8 and 1.4 g/mL PVP and ethyl cellulose, respectively) were produced of which ciprofloxacin and silver nanoparticles were loaded with varying amounts (0.08 and 0.5 g/mL ciprofloxacin and silver nanoparticles, respectively). The monolithic nanofibers had an average diameter of around 0.78 μm while the average diameters of fibers were in the range of 0.73 – 0.84 μm. Particularly, it was reported that over the 90% of ciprofloxacin was released within the first 30 min, and performed a significant bactericidal activity against *S. aureus* and *E. coli*. This study was conducted as a wound dressing practice, however it has also an important potential to be applied in food industry for membrane production or novel packaging alternatives. Using a very similar approach as side-by-side electrospinning fabrication, ethyl cellulose (0.7 g/10 mL) in assistance with PVP polymers (0.4-0.8 g/10 mL) was processed as JPs, beads-on-a-string, and Janus nanofibers in order to load ketoprofen (0.2 g) and methylene blue (50 mg/10 mL) as a double drug loading study, recently [35]. The average diameters of the three different types of Janus structures changed in a range of 0.12 – 2.16 μm. A faster release of methylene blue and slower-sustained release for ketoprofen were able to be observed with Janus beads-on-a-string nanostructures which was nominated as very promising for double-drugs release purposes. It can be also considered as promising for bioactive compounds delivery systems in food matrices such as functional food products.

Recently, an intelligent packaging study was conducted in order to track the freshness status of packaged chicken meat [36]. For this purpose, a two faced (5 cm diameter with 600 μm thickness) Janus-like metachromatic label was produced using a film consisting of cellulose acetate, black carrot anthocyanin and plasticizer with a ratio of 12:1:1, and a pH dependent (transition around pH 6.2) color masked adhesive top layer. The label was fabricated using wire-bar printing process. The produced structure might not be a JP however, leaning on the same principle, it could be nominated as Janus-like structured film formation which could be simply used to detect the freshness of packed food products.

Apart from these studies, water remediation, filtration and waste effluent treatments might be also considered to be related with food industry, not only for environmental issues but also for revalorization of recovered by-products. Some recent studies examining the cellulose-based Janus nanoparticles and nanofibers that are produced and used to this manner are of importance. Cellulose-based and magnetic responsive (Fe_3O_4) JPs were produced by sequential adsorption approach to be used for phase separation of oil from waste water and/or crude emulsions ad water-in-oil [37]. Another study was conducted to produce a cellulose-based hybrid Janus-nanofiber structure for oil-water separation which was called as "Janus sponge" [38]. Cellulose nanofibers were separately crosslinked in aqueous media with methyltrimethoxysilane, and 3-glycidoxypropyltrimethoxysilane and cured in dry basis together at 120 °C for 1 h. Final hybrid Janus sponge had an asymmetric wettability as well as satisfying mechanical properties.

2.2.4. Chitosan based structures

Chitosan is one of the most favorable natural biopolymer being utilized as a clean-labelled and biocompatible material to produce bio-based Janus particles for varying purposes such as cancerous cell inhibiting drug loaded beads or being incorporated to the bioactive loaded fabrics aiming for the wound dressing [39, 40]. From a more "food-related" perspective, the study which covered the water-propulsion potential of Janus micromotors that were produced mainly from chitosan in assistance with Mg microparticles, poly(lactic-co-glycolic acid) and alginate focused on effective water remediation (waste water, seawater, etc.) strategy [41]. As another different Janus-based approach, glycol chitosan polymers were used to produce high-barrier, biodegradable and flexible Janus-like packaging material which was extremely resistant for harsh conditions such as 75% relative humidity and 0.17 cm^3/m^2 bar oxygen transmission rate per day [42]. Polylactic acid foils was coated with a clay-chitosan liquid crystalline suspension (1%, wt) with a thickness of 1.4 μm, yielded up a packaging material with an overall thickness of 27.5 μm, and was indicated to avoid bacterial growth (barrier side) as well as biodegradability (uncoated PLA side). This composite packaging material was highly recommended to be applied for real food matrices. Lately, alternative production methods like electrohydrodynamic approaches have been applied to produce soft/polymer based JPs due to the high efficiency and enable to produce well-controlled and tailored properties for obtained particles [10]. Usage of metallic nanoparticles is favorable in assistance with electrohydrodynamic methods due to the working principle of the applied technique, however, it is not obligatory. In a study, materials produced from chitosan in assistance with some other natural carbohydrates, proteins and synthetic polymers as soft/polymer and hybrid particles like JPs with electrospraying for different biomedical applications were reviewed and criticized in details [8]. It is very promising as being a milestone to exhibit the potential usage of chitosan as JP for possible food applications, using electrospraying or other electrohydrodynamic methods.

2.2.5. Protein based structures

In their experimental study, de Vries et al. emphasized that the natural amphiphilic proteins might be used as a building blocks to create a 3D (tri-block) Janus particle and/or structure [43]. They practiced a specific aggregation mechanism on zein in order to produce a thermo-responsive gel structure to be used as a JP polymer. For this purpose, addition of hydrophobic particles into the varying concentrations of zein solution (0.5, 1.25, and 2.5%) forced the rectangular tri-blocks of protein assembling into a 3-dimentional network structure. The collapsed 3D zein network were used to produce JP in assembling with the glycerol and the rheological behaviors could be tuned with changing temperature, which makes this structure to be used in many bio-applications as well as in food matrices. Recently, the production of Pickering emulsions using acrylate rapeseed protein isolate nanogels was found to induce the formation of anisotropic JPs as a promising bio-based interfacial applications [44]. Briefly, nanogels which are suitable to be reformed as JPs were obtained by heating the acrylate rapeseed protein isolate solution (1 mg/mL) to 90 °C for 30 min at pH 5.6, then followed by a sharp cooling to room temperature. Nanogels (0.1 – 1%) were further processed into Pickering emulsions (oil fractions as 0.1 – 0.5, v/v) with rapeseed oil mixing at 20000 rpm for 2 min. This food grade Pickering emulsion JPs were of great importance for their highly adaptable and utilization potential in food industry. Other researchers also investigated the JPs composing of zein and polyvinylpyrrolidone (PVP) fabricated using a side-by-side electrospinning technique in order to be used as a drug carrier vehicle with a desired release control ability [45] . Folic acid was chosen as the model drug and prepared as solutions with both components as PVP-folic acid (20-4 g) in 100 mL ethanol and zein-folic acid (28-6 g) in 100 mL ethanol-acetic acid (3:1) mixture. Zein-PVP Janus fibers were indicated to have an average diameter of 570 nm with a crooked surface with a fine release control for folic acid. This study was proposed as very promising to be applied in many other food hydrocolloids requiring further investigations and applications.

2.2.6. Lipid based structures

As another natural-derived compound, soybean oil was used to produce a scalable amphiphilic JP with a single-emulsion polymerization method [46]. The soybean oil-epoxidized acrylate, which was a commercial derivative of soybean oil, was induced to polymerize within a single-emulsion droplet of butyl acetate and ethyl cellulose in order to yield a dumbbell shaped JP composing of soybean oil polymers and ethyl cellulose. Using a glass-silicon (PDMS) microfluidic device, large scaled production of this soybean/ethyl cellulose (1:1, wt) was accomplished to be produced with high uniformity (25-80 μm) and high stability even under flowing conditions (2 L/h, dispersion phase). In another study, temperature responsive wax-based JPs were produced as dumbbell shaped through a capillary flow-based microfluidic device [47]. Molten wax was injected to the capillary in assistance with ETPTA. This inner phase also contained a crosslinking agent, photoinitiator (2-hydroxy-2-methylpropiophenone, 2.5 %, wt), and the crosslinking was induced by UV illuminations for 3 s at the outlet tip of the capillary. The produced JPs had an excellent coalescence stability at the water/oil interface even above a desired temperature, allowing highly stable emulsions to be potentially used for drug-delivery and controlled release systems.

In the last decade, the interest to fabricate Janus structures from not only biocompatible but also natural/nature derived materials has been increasing in order to use them for distinctive purposes. Mainly, carbohydrate, protein and lipid varieties have been successfully used to produce Janus surfaces for many bio-based applications including drug delivery, encapsulation, controlled release, stable emulsions or microfiltration however, not that prevalently for direct food applications. In any case, using nature

Table 1 Janus structures produced from nature-derived polymers and promising food-grade applications

Material	Production Method	Assistive Compounds	Structure	Purpose	Application Potential	
Starch	Spin coat spraying	Alpha-amylase or octenyl succinic anhydride	Janus particles	-	Texture improvement and surface-active agent	[12]
Chitosan	Self-assembling (Vigorous stirring at 95 °C and pH 10.0)	Silver nanoparticles	Janus particles	Suppressing microbial growth	Coating material production (biofilms)	[13]
Alginate	Capillary flow-based approach	Shellac and calcium cations for crosslinking	Janus particles	Emulsion stabilization (oil-in-water)	Stable emulsions in food industry	[14]
Pectin-alginate	Capillary flow-based approach	-	Janus microbeads	Emulsion stabilization	Stable emulsions in food, pharma and cosmetic industries	[23]
Pectin-alginate	Capillary flow-based approach (on-chip or off-chip)	$CaCl_2$ or $CaCO_3$	Janus microbeads	Release control at liquid-liquid interface	In food, pharma and cosmetic industries	[24]
Pectin	Self-assembling (Vigorous stirring at 24 °C for 5 h)	Folic acid with Gold and/or silver nanoparticles	Janus particles	Antioxidative surface for anti-cancer, anti-aging, wound dressing, etc. applications	Antioxidative biofilm and coating materials for food applications	[25]
Alginate	Self-assembling followed by injection	Polydiacetylene liposomes and Fe_3O_4 magnetic nanoparticles	Janus microbeads	Enhanced sensitivity and fast detection for biosensing	Environmental and waste-water, effluent treatments.	[26]
Alginate	"one-pot", (simultaneous co-jetting and self-assembling)	Carboxymethyl cellulose and sodium	Janus nanofibers	Drug release	Controlled released for food and medicine applications	[28]
Cellulose	Aqueous counter collision	Acetic anhydride (also toluene, DMAP, and Ac_2O for Pickering emulsion)	Janus nanofibers	Membrane-like Janus structures with anisotropic surfaces	Stable interfaces in food, pharma and cosmetic industries	[32]
Cellulose (ethyl)	Side-by-side electrospinning	Polyvinylpyrrolidone (PVP)	Janus nanofibers	Bactericidal surface loaded with ciprofloxacin and silver nanoparticles (wound dressing)	Customized membrane production or novel packaging alternatives in food industry	[34]
Cellulose (ethyl)	Side-by-side electrospinning	Polyvinylpyrrolidone (PVP)	Janus particles, Janus beads-on-a-string, and Janus nanofibers	Double drug delivery for ketoprofen and methylene blue	Bioactive delivery systems for novel functional foods	[35]
Chitosan (glycol)	Spray coating	Polylactic acid and clay	Janus-like surface	-	High-barrier, biodegradable and flexible packaging material	[42]
Rapeseed protein	Self-assembling with high temperature	Acrylate	Janus particles	Emulsion stabilization	Stable emulsions in food, pharma and cosmetic industries	[44]
Zein	side-by-side electrospinning	Polyvinylpyrrolidone (PVP)	Janus nanofibers	Drug release	Controlled released for food hydrocolloids	[45]
Wax (molten)	Capillary flow-based approach	ETPTA and photoinitiator (2-hydroxy-2-methylpropiophenone	Janus particles	Excellent stability at oil/water interface	Stable emulsions for drug delivery and controlled release	[47]

derived carbohydrate, protein and lipid materials for external bio-based applications efficiently, exhibits the potential and promising applications of JPs in food matrices.

3. CONCLUSION

Improving the technological properties of food matrices using sustainable, clean-labelled and green methodologies is considered as crucial techniques in recent years. For this purpose, engineering the Janus structures as particles, beads, fibers and/or surfaces produced from nature-derived and food grade compounds to be applied in food matrices might be one of the most promising alternative applications. Particularly, utilization potentials as solid surface-active agents for higher emulsion capacity and stability, intelligent packaging element, biosensors to detect any specified compounds and microorganisms, drug/bioactive compound carriers for controlled release issues make Janus structure applications in food systems noteworthy and promising. However, studies directly focusing on food systems are very limited so far and still there are plenty of materials and mechanisms to be explained, optimized and applied in order to obtain high quality processed and/or functionalized foods with longer stabilities and shelf life. Considering that the sustainability, energy efficiency and other environmental issues are also as remarkable as the production of optimized products, Janus structures might be one of the key tools for designing foods of near future.

4. CONFLICT OF INTEREST

The authors declare no conflict of interest.

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