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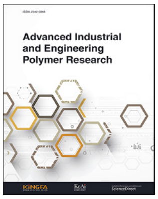

Starch-based biodegradable materials: Challenges and opportunities

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ABSTRACT

This paper reviews the recent development of starch-based materials, including both fundamental and application researches. In order to overcome the weakness of pure starch-based materials, such as lower mechanical properties found in natural polymers and moisture sensitivity, various blends and composites have been developed in the last two decades. In practical, incorporation of any additives is sensitive in developing fully biodegradable starch-based materials. Furthermore, safety issues will be considered as priority regarding any additives for food packaging applications. Based on these concerns, various natural filler and edible reinforce agents, such as natural fibers, starch or cellulous crystals, and laver, have been used in starch-based materials. So-called self-reinforced techniques, reinforcing starch matrix by modified starch particles, have also been used in developing starch-based composites. During developing starch-based foams the unique function of water, acts as both plasticizer and blow agent for starch-based foam, has been systematically studied. So far, various conventional processing techniques such as extrusion, injection, compression molding, casting and foaming, as well as some new techniques such as reactive extrusion, have been adapted for processing starch-based polymeric materials. Various starch-based products have been developed and commercialized.

1. Introduction

Starch is one of the most promising natural polymers because of its inherent biodegradability, overwhelming abundance and annual renewability. Starches offer a very attractive low cost base for new biodegradable polymers due to their low material cost and ability to be processed with conventional plastic processing equipment [1–5]. Development and applications of biodegradable starch-based materials has attracted increasingly attention since the well recognized issues of oil shortage and the growing interest in easing the environmental burden due to extensive use of petrochemically-derived polymers. Currently more and more countries have introduced regulations and lows of banning disposable plastics. Fig. 1 shows the photos of some commercialized starch-based products, which are not only fully biodegradable but also can be used to feed animals or even edible.

On other hand, the study of the unique microstructures of different starches and their multiphase transitions during thermal processing have increased fundamental knowledge of polymeric science, in particular to understand the structure–processing–property relationships in polymers [4–9].

1.1. *Microstructures of starch and phase transitions*

It is well known that techniques of synthetic polymers have been developed to the point where microstructures can be designed, and molecular weight and molecular weight distribution can be controlled. However, the microstructure of a starch granule has evolved to meet a plant's own needs and is therefore much more complex. Starch is a polysaccharide produced by plants as a means of storing energy. It is stored intracellularly in the form of spherical granules, with 2–100 μm in diameter. Most commercially available starches are isolated from grains such as corn, rice and wheat, or from tubers such as potato and cassava (tapioca).

From review of chemical, starch is a carbohydrate polymer consisting of anhydroglucose units linked together primarily through α-*d*-($1 \rightarrow 4$) glucosidic bonds [6,10–12]. Previous studies have showed that starch is a heterogeneous material containing two kinds of microstructures: linear and branched. Linear structure is called as amylose with a linear structure of α-1,4 linked glucose units,

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Fig. 1. Photos of commercialized starch-based products.

and branched structure is called as amylopectin with a highly branched structure of short α-1,4 chains linked by α-1,6 bonds. Some long-branched structure starches have been detected, such as in tapioca starch etc. Fig. 2 represents the chemical structure and a schematic representation of amylose and amylopectin starches. The molecular weight of amylose is about $\times 10^6$, which is 10 times higher than conventional synthetic polymers, such as PE, PP and PS, while amylopectin has molecular weight is much greater than amylose. Based on the light-scattering measurements, molecular weights of amylopectin could achieve millions. The linear structure of amylose has showed behavior more closely to that of conventional synthetic polymers. Since amylopectin has much higher molecular weight than conventional synthetic polymers that reduce the mobility of the polymer chains, which results in very high viscosity.

From review of physical, most native starches are semi-crystalline. The crystallinity of starched is about 20–45% [6,13–15] depending on resource. The short-branched chains in the amylopectin contribute mainly the crystalline regain and presents in the form of double helices with a length of ~5 nm. The amylopectin segments in the crystalline regions are all parallel to the axis of the large helix.

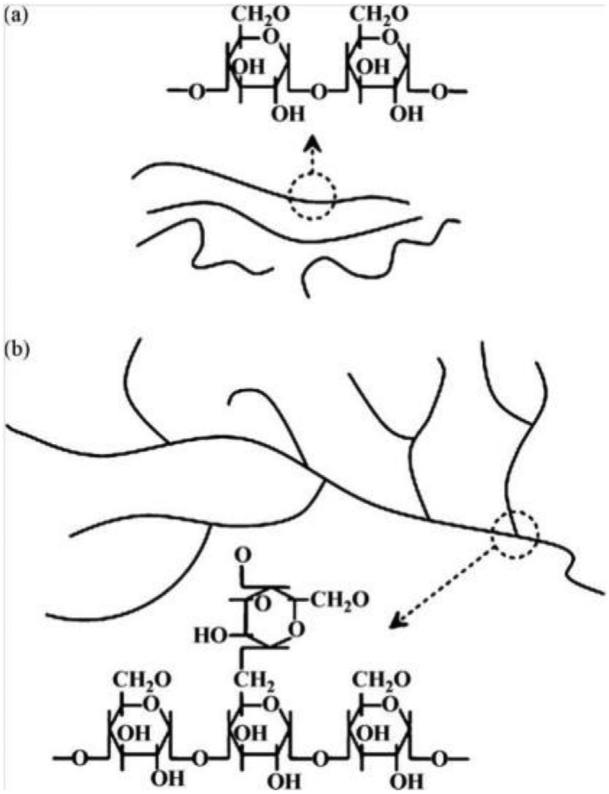


Fig. 2. Chemical structures and physical schematic representation of (a) amylose starch and (b) amylopectin starch.

The amylose/amylopectin ratio mainly depends upon the resource and age of the starch, and it can also be controlled by the thermal processing process employed.

Since the unique microstructures, in particular high molecular weight and hydrogen bonds, thermal processing of a starch involves multiple chemical and physical reactions, e.g. water diffusion, granule expansion, gelatinization, decomposition, melting and crystallization. In which the gelatinization is unique and is the most important because it is closely related to the others. Before the gelatinization, the decomposition temperature of starch is lower than its melting temperature. So you cannot thermally process starch-based materials using conventional plastic equipment, in particular extruder. So-called thermal plastic starch (TPS) is a gelatinized starch-based material. The well-accepted concept of "gelatinization" is to destroy the crystalline structure in starch granules, which is an irreversible process. The gelatinization processing involves granular swelling, native crystalline melting and molecular solubilization [10,16–27]. The multistage process of gelatinization can be detected by various techniques, such as XRD, polarized microscope, NMR etc, but most popular one is differential scanning calorimetry (DSC) [28–34].

Gelatinized starches can be retrogradation or re-crystallization during storing or annealing, but the crystal structures may be different. A schematic representation of the phase transition of starch during gelatinization and retrogradation is represented in Fig. 3. It is seen that the crystalline structure of the starch granules is destroyed during heating in water (Fig. 3a and b). Previous researches [35,36] have shown that amylose and amylopectin are partly separated during gelatinization because they are incompatible [9,37,38]. Both water and shear stress may enhance this separation. However, during extrusion processing with less water content, most of the amylose still remains in the amylopectin [4]. Although the double-helical crystalline structure formed by the short-branched chains in amylopectin can be torn apart during gelatinization, the chains remain in a regular pattern and keep a certain "memory". After the crystalline part being destroyed during gelatinization, the short-branched chains can form gel-balls [39] in the end of the chains. The gel balls mainly contain the chains from same sub-main chain (Fig. 3b). The molecular entanglements between gel-balls and super-globes are much less than those between linear polymer chains due to the size and length of the chains (only 4–6 glucose). During annealing or storing, the gelatinized starch can re-crystallize or retrogradation. Initially, V-type single helix crystals (Fig. 3c) have been found to form from amylose. Gelatinized amylopectin initially remains in an amorphous state, but with increasing time the crystallinity of the V-type crystals (contributed mainly by amylopectin) increased (Fig. 3d).

1.2. Extrusion processing of starch

Extrusion is one of the most popular techniques used for processing of polymeric materials, which mainly involves melting-solidification. However, during extrusion processing, starch granules undergo multiple and complicated phase changes, including starch swelling, loss of birefringence, melting and solubilization

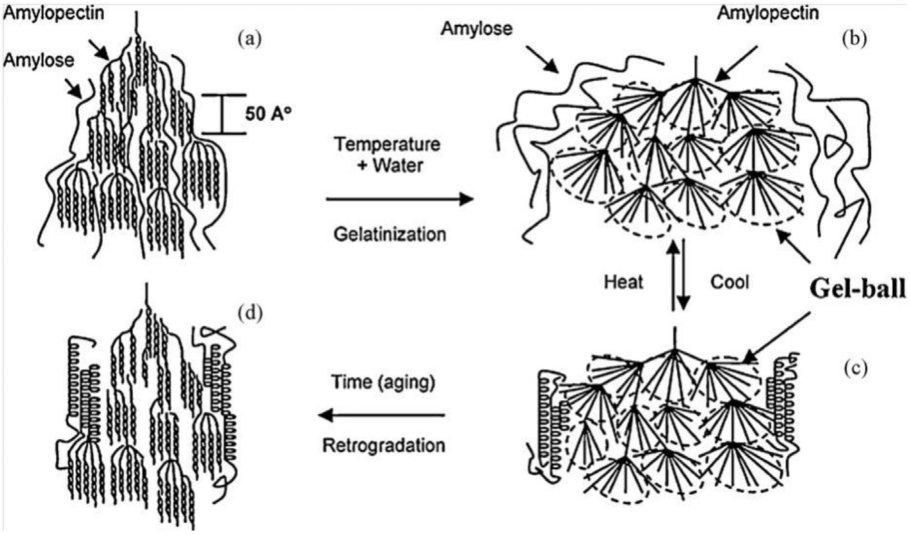


Fig. 3. Schematic representation of the phase transitions of starch during thermal processing and aging [Reproduced from Ref. [4] with permission].

[4,40–48]. Without shear stress, the thermal process of gelatinization is controlled mainly by water content and temperature [49]. When the temperature is lower than 50°C, the starch granular structure remains stable, with the constituent molecules held together in spherulites by van der Waals forces or hydrogen bonds [50] due to their largely intact crystalline components. When starch granules is heated beyond its gelatinization temperature, hydrogen bonding will be disrupted and water molecules become attached to the hydroxyl groups in the starch molecules, resulting in greater swelling and the dissolution of crystallites [50,51].

Due to extrusion processing introduces high-shear and high-pressure conditions, gelatinization can be achieved at low water content, since the shear forces physically can tear apart the starch granules, allowing faster transfer of water into the interior molecules [52,53]. Actually, during extrusion at low moisture conditions, small amounts of gelatinized and melted starch, as well as starch fragmentation (from degradation or decomposition), exist simultaneously [53–55]. Davidson at al [56]. Have reported that the extent of amylopectin fragmentation decreased with decreasing screw speed, and increasing temperature (121–177 °C) or moisture content (20–25%). Similar results were observed by Wen et al. [53] and Willet et al. [57]. Other study [58] showed that glycerol can reduce starch degradation under shear stress.

Due to the multiphase transitions of starch during extrusion, the microstructures and mechanical properties of starch-based materials strongly depend on the processing techniques and conditions. For example, Balta Calleja et al. [59] have reported that compression molding leaded relatively brittle materials, since the amylopectin crystals in the native powder remained largely preserved. While coasting films from aqueous gels resulted the formation of a new semi-crystalline structure, The products from injection molding has higher mechanical properties since amorphous phase was increased.

Actually, extrusion processing has also been widely used to modify starch, such as grafting and pre-gelatinization [60–66]. The high efficiency and accelerated rates at which modification reactions were carried out in the extruder, compared to batch processes, is particularly noteworthy.

2. Improving performances and decreasing cost

Improving performance and decreasing cost are two never stop strategies for all kinds of materials. Similar as polymeric materials from oil-based products, the materials from renewable resources are also rarely used singly. Actually, the history of composites from renewable resources is far longer than the conventional polymeric materials. In the biblical Book of Exodus, Moses's mother built the ark from rushes, pitch and slime: a kind of fiber-reinforced composite, according to the modern classification of material. During the opium war more than 100 years ago, the Chinese built their castles to defend invaders using a kind of mineral particle-reinforced composite made from gluten rice, sugar, calcium carbonate and sand.

Polymer blending and compositing are well-used techniques whenever modification of properties is required, because it uses conventional technology at low cost. The usual objective for preparing a novel blend of two or more polymers is not to change the properties of the components drastically, but to capitalize on the maximum possible performance of the blend. In principle, the properties of starch-based materials can be significantly improved by blending with synthetic polymers. Actually, during the 1970s–1980s, various starch-based blends with different polyolefins have been developed. However, these blends were not fully biodegradable, and thus the advantage of using a biodegradable starch was lost. In this paper, polymer blends and composites only from natural raw materials are discussed.

2.1. *Reinforcement by natural fillers*

Reinforcement by fiber has been widely used in developing polymeric composites and has successfully proven their value due to their excellent specific properties, e.g. high strength and stiffness, and low weight. The composites reinforced by fiber have been widely reported and even reviewed by many authors previously. In aspect of biodegradable materials, natural fibers are of particular interest since they not only have the functional capability to substitute the widely applications, but they also have advantages, such as lower density, and fiber-matrix adhesion, specifically with polar natural matrixes, such as starches and proteins. The natural fibers have showed good potential for application in waste management due to their biodegradability and their much lower production of ash during incineration.

Starch reinforced by cellulose fiber is a typical example of natural polymer composites. The reinforced composites have the advantages of being renewable, biodegradable, abundantly available and inexpensive. Such composites have attracted great attention in the last two decades. Generally, improving mechanical properties is one of the major driving forces to reinforce starch based materials using cellulose fibers. It has been reported [67] that tensile properties of thermoplastic wheat starch were increased four times after reinforced by cellulose fibers. Various natural cellulosic fibers, such as sisal, cotton, bamboo, jute, straw, kenaf and wood have been used to improved mechanical properties of starch-based materials. Compared to inorganic fillers, composites based on nature fibers offer a number of benefits including a renewable nature, a wide variety of fillers available throughout the world, low energy consumption, low cost, low density, high specific strength and modulus, high sound attenuation, comparatively easy processability, and a relatively reactive surface [68]. Various techniques and products have been developed and reviewed in details [4].

Recently, Amjad et al. reported starch-based composite films reinforced by corn/wheat hulls [69], and apricot and walnut shells [70], which are by-products of rigid particles from natural food resources. Fig. 4 shows the photos of wheat and corn hulls used in this work and their images under SEM. Both hulls are yellow-brown color particles. Wheat hull looks more like cellulose particles with irregular shape, while corn hull is flat in shape. Fig. 5 shows the granulated wheat and corn hull particles observed under optical microscope with normal and polarized lights. Both wheat and corn hull particles are irregular in shape and the crystalline particles can be clearly observed under polarized lights. Results showed that the materials became stronger after addition of these rigid fillers as expected. The gas barrier properties of the starch films were also improved by adding the hulls with higher density and higher crystallinity, especially the corn hull because of its flat structure. EM observations indicated that the compatibility between starch and the two hulls were quite good, which was expected since all the components are hydrophilic and exhibits polar behavior.

More recently, Chen et al. [71] reported starch/laver composites, in which the gas permeability of starch film was improved significantly by adding laver. It was interesting to find that when the laver was added into cold starch suspension, the laver flack (fiber) simply acted as reinforcing agent to improve the mechanical properties of the starch matrix, which results in increasing modulus and tensile strength. However, when the laver was added into hot starch suspension and mixed under shear stress, the protein containing in laver released out and mix with starch, which results in a starch-protein-laver fiber hybrid composites. In the hybrids system, fiber improves the mechanical properties of the starch-based film about 25%, while the protein reduces the moisture sensitivity and gas permeability about 45%. Scanning electron microscopic observation indicated good compatibility between starch matrix and laver. Since all the components used in this work are from food sources, the prepared films are safe for food packaging and application as edible films. Fig. 6 shows the photos of flavor bags from starch film reinforced by laver.

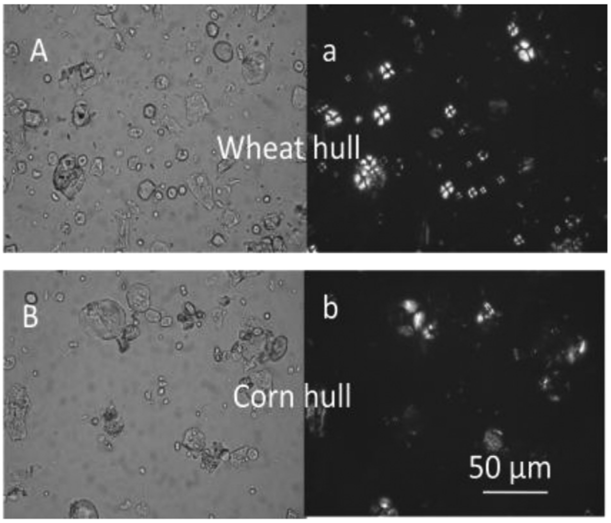


Fig. 5. Granulated wheat (A,a) and corn (B,b) husk particles observed under optical microscope with normal and polarized lights. [Reproduced from Ref. [69] with permission].

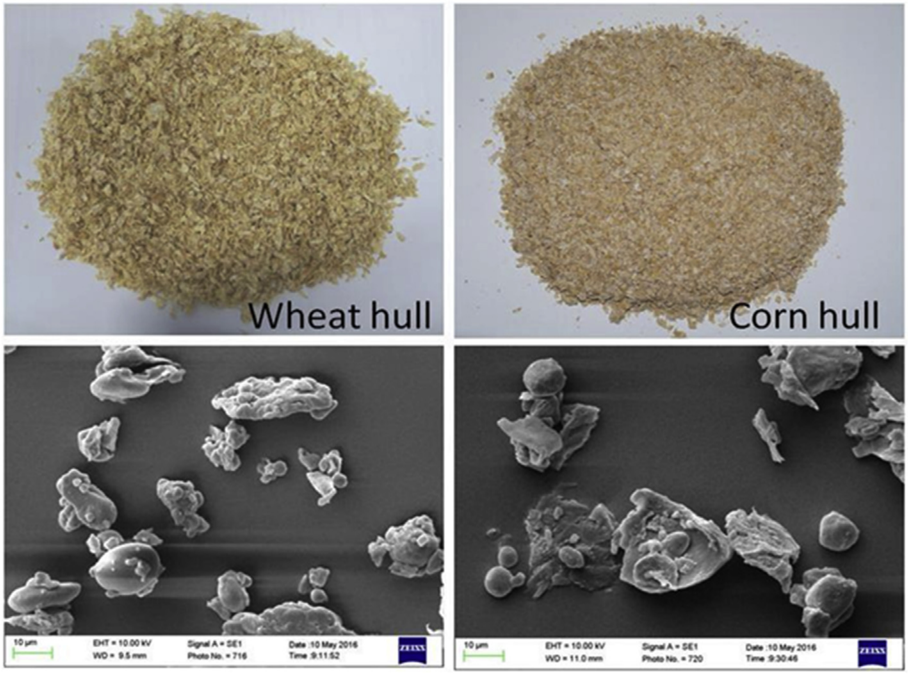


Fig. 4. Photos of wheat and corn husks, and their images under SEM [Reproduced from Ref. [69] with permission].

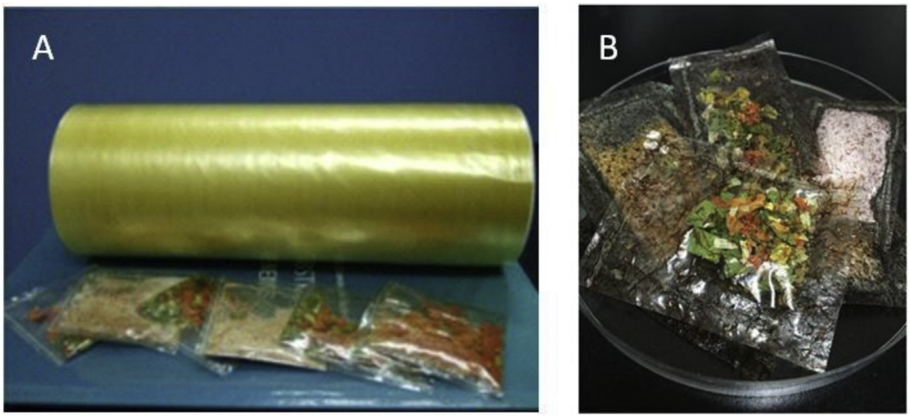


Fig. 6. Photo of starch-based film with developed flavor bags for easy muddle (A) and laver reinforced the products (B). [Reproduced from Ref. [71] with permission].

2.2. Starch-based nano-composites

The starch based nano-composites have continuously attracted attentions, and have been successfully developed and commercialized. One of the challenges using nano-clay is to exfoliate it since the strong boundary between layers by iron. Another issue is to improve the hydrophilic surface of clay with hydrophobic surface of most conventional polymers, especially polyolefin. These two challenges can be simply solved in starch-based materials. Firstly, the hydrophilic water is a very efficient chemical to delaminate clay with the enhancement by ultrasonic [72–79]. Secondly, starch itself is a hydrophilic polymer that can be well compatible with clay and water. Actually water is a plasticizer for starch-based materials.

Recently, polysaccharide-based crystals, particularly at nano-scale, have attracted huge attention used to improve the mechanical properties of starch-based materials since they have naturally perfect interface and all the components are edible [80–83]. Both cellulose and starch nano-crystals have been used to improve tensile strength as-well-as Young's modulus of starch-based materials [84–88]. For examples, it has reported [88] that cellulose nano-fibrils could increase the creep resistance and reduce the creep recovery rate of starch film. Other research [89] showed that starch films reinforced by 7% cellulose nano-crystals could achieve the strength and stiffness close to that of polyolefins.

More recently, Amjad et al. [90] reported the starch based edible films, which was reinforced by starch and cellulous macro-crystals. The films were transparent with smooth surface. Both crystals increased the Young's modulus and tensile strength of but slightly decreased elongation at break. SEM (see Fig. 7) clearly showed very good compatibility between starch matrix and the two crystals due to same chemical unit (glucose). Cellulose crystals have higher thermal stability, which provide better processibility and superior mechanical properties to starch films. On the other hand, starch films filled with starch crystals demonstrated higher protection against UV radiation. These films are not only biodegradable, but also safe for food packaging and can also be used to develop edible films and medicinal capsules since all the components used in this film belong to food sources.

2.3. Self-reinforce composites

Self-reinforced composites (SRCs), or single-polymer composites, in which a polymer matrix is reinforced with oriented fibers and tapes, or particles of the same polymer, are an interesting concept. The advantages of SRC systems include the ability to achieve perfect interfaces between composite components, their pure chemical functionality, and their higher value as recyclable products due to their relative homogeneity compared to composites composed of different classes of components [91–96]. This homogeneity is particularly important in biomaterials applications, since any additives composed of different chemicals could affect biocompatibility and biodegradability.

Typical starch-based SCR was reported by Lan et al. [97]. The unique technique of designing and preparing self-reinforced starch-based films was developed using a cornstarch that was chemically modified in different ways. Hydroxypropylation was used to decrease the gelatinization temperature and to improve processability. Lowering the processing temperature by reducing the gelatinization temperature was due mainly to the presence of the substituted group, which weakened or strained the internal bond structure holding the granules together [98]. The reinforcing component consisted of crosslinked starch granules, where the crosslinking increased granular thermal stability and moisture resistance.

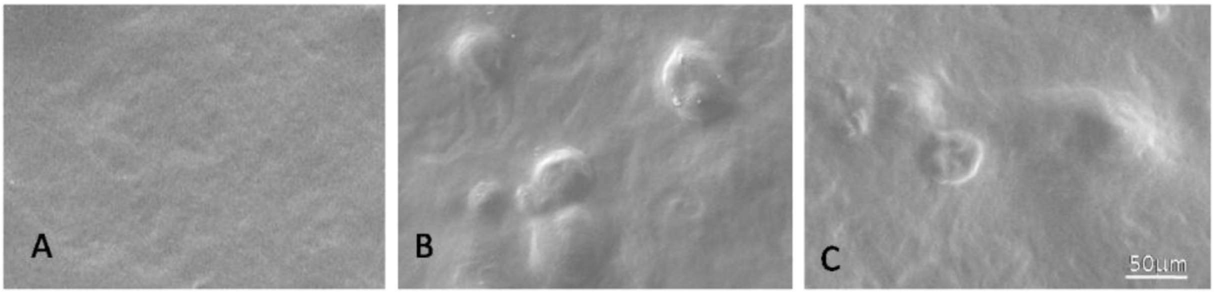


Fig. 7. Surface SEM images of starch film (A: pure starch film; B: containing starch crystals; C: containing cellulous crystals) [Reproduced from Ref. [90] with permission].

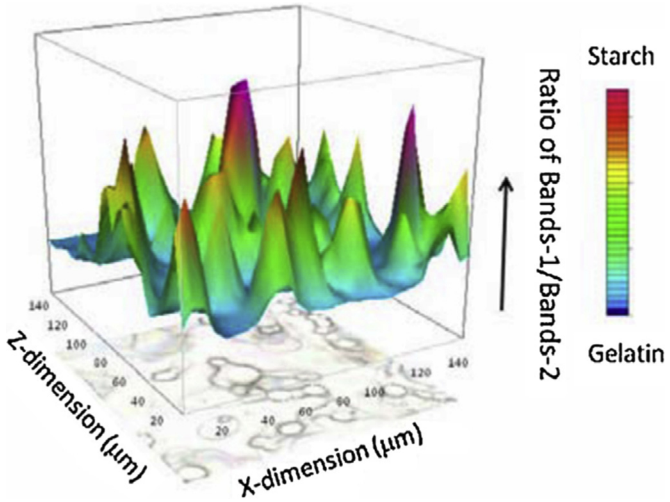


Fig. 8. Variation of the ratio of the area of the Bands-1 (starch)/Bands-2 (gelatin) plotted as 2D and3D contour maps for starch–gelatin (60:40) blend [Reproduced from Ref. [100] with permission].

Many starch materials reinforced by polysaccharide-based crystals can also be classified as a kind of SRCs since they basically have similar chemical components [80–90].

2.4. Blending with other natural polymers

Starch has also been used to improving processibility and reducing cost of other natural polymers. In this aspect, the discussion will focus on the blends of hydrogels. For example, the blended films of polysaccharides and proteins have showed unique properties, such as better gas barrier than any pure film [2,102,103]. Previous researches have shown that gelatin and starch are immiscible, however, their morphologies and compatibility are affected by various factors, such as processing time, temperature, pH value and solid concentration.

Zhang et al. [99–101] has reported the edible films developed by blending starch with gelatin. The well recognized complex issue of compatibility between starch and gelatin was investigated based on their interface and phase composition using synchrotron FTIR micro-spectroscope. Investigation of composition and interface of ablend using FTIR micro-spectroscopy enables unique insight into the interface and morphologies of the system since it is based on chemical contrast between constituents. A typical FTIR count contour map for starch–gelatin 40:60 blend is showed in Fig. 8. The image was generated from a single measurement set by allocating a color to each pixel based on the ratio of starch (Bands-1) and gelatin (Bands-2), which was used to identify the starch–gelatin content. The red peak in the scale denotes a high value of starch while the blue bottom line denotes a high value of gelatin. It can be seen that in this blending ratio the starch phase (Bands-1) presented as a dispersed phase, while gelatin (Bands-2) was a continuous phase. It is interesting to find that Bands-1 showed as sharp peak, not the column, which indicates there are certain chain diffusions on the interface of starch domains. That means there is still certain compatibility in the scale of polymer chains and total separation of starch and gelatin domains did not occur.

Another example is the blends of hydroxypropyl methylcellulose (HPMC) and hydroxypropyl starch (HPS) [104–107], which are receiving increasing attention due to their unique thermal/cooling gel systems and wide applicability. The researches for this system have both scientific and commercial importance. Scientifically, the blend system provides a good scientific model to investigate the thermal/cooling gel system, based on the rheological characteristics, phase transitions, morphologies, compatibility, etc. Commercially the blends have been widely used from food packaging and medicine capsules to cartilage tissue engineering applications. The relative advantageous properties of the two components were partially combined in such blends, which presented quite good processibility, mechanical properties, and barrier properties to oxygen and water vapor.

The viscosities of HPMC/PHS solution with different ratios under same shear rate and at different temperatures was showed in Fig. 9. It can be seen that viscosity of the starch HPS was much higher that of HPMC and the viscosity of the blends is increased gradually with increasing HPS content under different temperatures. As expected, the viscosity of pure HPS decreased with increasing temperature. However, the viscosity of pure HPMC decreased with increasing temperature at lower temperature (<50 °C) then increased in the range between 50 and 75 °C. The acceptable mechanism of thermal gelation of HPMC is the sufficient energy results in the outer layers of water molecules are driven from the cellulose ether chains, and the chains lock and the solution is transformed into a gel. It has been noted that the effect of HPS on the viscosity of HPMC is not linear. When the HPS content is lower than 70%, the viscosity peak of HPMC still exists and the peak temperatures are almost same, which provide an operation window for making capsule under similar conditions as pure HPMC. When the HPS is higher than 70%, there is no viscosity peak was observed but just a shoulder was detected.

2.5. Functionalized composites

In order to add some functions and meet market requirement, some functionalized starch-based materials have been developed. For example, Amjad et al. [108] have reported that application of pomegranate peel (PGP) as an antimicrobial agent as well as a reinforcing agent in developing starch-based films. Previous studies have shown that pomegranate peel extract demonstrate positive results against microbes [109,110]. However, there is no report before about the incorporation of pomegranate peel as filler in starch based films to develop antimicrobial materials. The advantages of directly using pomegranate peel include cheaper and improving mechanical properties at same time. Results showed that PGP inhibited the growth of both gram-positive (S. aureus) and gram-negative (Salmonella) bacteria. Meanwhile, PGP also increased Young's modulus, tensile strength and stiffness of the starch-based films. Studies on their interface showed there were reasonably good compatibility between starch and PGP particles. It is expected

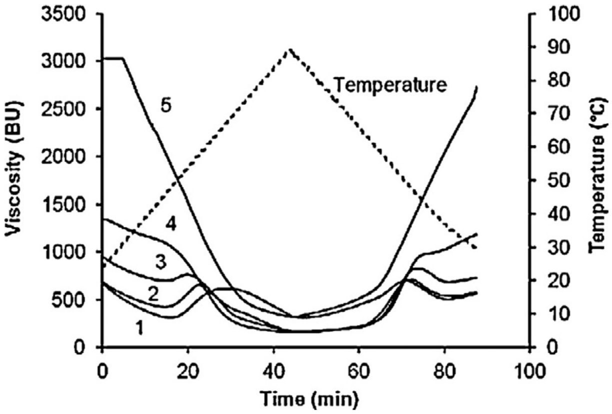


Fig. 9. Effect of temperature on the viscosity of HPMC/HPS blends: (1) 100/0; (2)70/30; (3) 50/50; (4) 30/70; and (5) 0/100. [Reproduced from Ref. [107] with permission].

since cellulous based pomegranate peel can be compatible with starch. It is expected that the developed material can be used as an edible film and food grade packaging material since all the components are food ingredients.

3. Reducing moisture sensitivity

The well recognized weakness of starch-based materials is their moisture sensitivity. The hydroxyl groups in starch contribute its hydrophilic nature, resulting in inadequate performance. The starch film showed higher water vapor permeability and lower tensile strength under higher moisture conditions. In order to decrease the moisture sensitivity and increase mechanical properties of starch-based materials, various blending and compositing techniques have been developed [111–116]. However, a blend containing starch cannot become hydrophobic until starch content is low enough to form a separate domain phase in a hydrophobic polymer matrix, in which case starch only acts as filler. Other techniques to reduce the moisture sensitivity is surface coating and crosslinking, which have many advangates include ease of processing, lower cost, flexibility to control thickness, maximizing natural properties of matrix, etc.

Starch crosslinking is a common approach to improve the performance of starch for various applications. Various crosslinking agents, such as phosphorus oxychloride, sodium trimetaphosphate, sodium tripolyphosphate, epichlorohydrin and 1,2,3,4-diepoxybutane, citric acid have been used to improve the mechanical and moisture stability properties of starch-based materials [117–122]. However, most of the crosslinking agents have to be added to a starch solution during film casting. This method is not suitable for industrial manufacture since starch film or sheet is mainly produced by extrusion casting. Coating or crosslinking on surface should be more suitable for post-treatment.

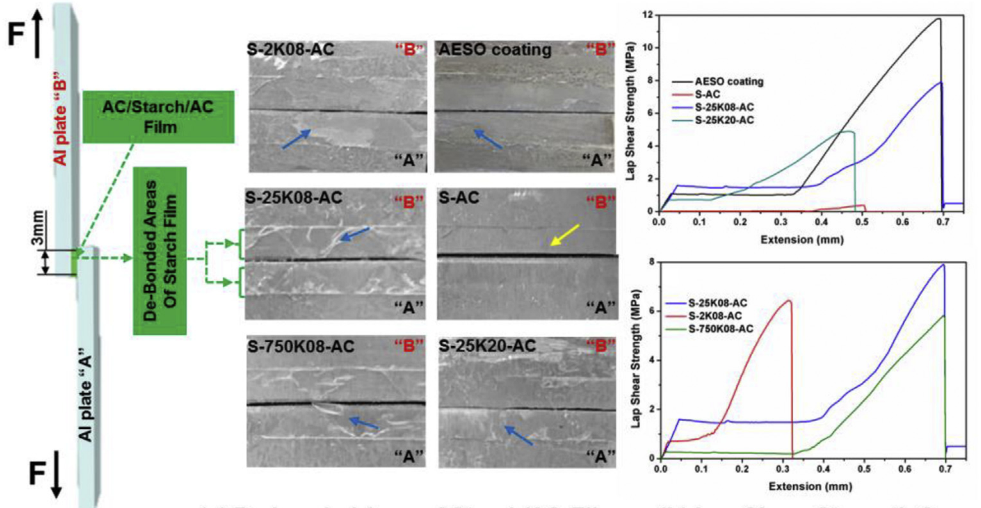
Recently, Ge et al. [123] developed an acrylated epoxidized soybean oil (AESO)-based coating to reduce the moisture sensitivity and improve the gas permeability of starch-based film. The starch based films was firstly dipped in AESO-based solutions, followed by crosslinking with ultraviolet (UV) light. The results showed that moisture permeability was decreased more than 10 times after the coating, which results in decreasing the moisture sensitivity of the starch-based films significantly. Observably, the AESO coating acted as a hydrophobic layer for starch film. It was found that the crosslinking density acted as one of the key factors, so even a very thin layer of AESO could achieve good water resistance. Since soybean oil also comes from renewable resource like starch, the film has showed great environment beneficent.

In order to improve the surface adhesion between starch and AESO coating and further improve the moisture sensitivity, Meng et al. [124] used polyethylenimine (PEI) to improve the interface between hydrophilic starch and hydrophobic coatings of AESO. The results from NMR, FTIR and XPS clearly indicated that PEI could react effectively with starch films through hydrogen bonding, and chemically react with AESO through the Michael addition reaction. The bonding forces between starch matrix and AESO coating was evaluated by shear adhesion testing. The results showed that the interfacial adhesion was significantly improved after surface treatment with PEI. The starch-based film treated with PEI almost maintained its original mechanical strength after water soaking for more than 3 h. The promised results demonstrated the new waterproof materials based on renewable and environmental friendly starch and AESO has been successfully developed.

A typical testing curve and the shear strength were showed in Fig. 10. It is seen that the failure for the coated starch films occurred at the interface between starch film and AESO coating or within starch itself, rather than at the starch adhesive/coating interface. The gap between starch and the coating was reduced significantly after PEI treatment. The shear strength between the starch matrix and the AESO coating was increased significantly after PEI treatment.

4. Starch-based foaming

Applications of starch foam have been spurred due to new regulation of banning disposable plastics announced by more and more countries in the world. Starch-based foam can simply replace many traditional plastic types of foam, such as from PS, PE and PU etc. Recently, Meng et al. [125] have studied the relationship between phase transition and foaming behavior of starch-based material. Through investigating the effects of water content on melting temperature (Tm), crystallinity, foaming process, cell structure as well as mechanical properties the mechanism of how water acting as both plasticizer and blow agent at same time was explored. It was found that there was a critical point of water content (between



(a) De-bonded Area of Starch/AC Film (b) Lap Shear Strength Curve

Fig. 10. Lap shear strength curves of samples and photos of de-bonded area of Starch/AC after testing showing the failure mode (yellow arrow pointing to adhesive failure for untreated starch and blue arrow pointing to cohesive failure for treated starch and neat cured AESO coating) [Reproduced from Ref. [124] with permission].

16 and 18%) at which the expending ratio changed significantly since the cell structure changed from open to closed. When the water content is lower, the melting temperature Tm of starch-based materials is higher, and melting strength of the materials is lower that results in open cell structure. The water contained in the open cell will be evaporated mostly during the foaming process, which results in stable rigid foam structure. It is expected since lower melting strength cannot hold the bobble during foaming. Conversely, when the water content is higher, the melting temperature Tm is higher and melting strength will be also higher that can help bubble increase and results in closed cell structure. During foaming processing, the closed cell prevented moisture evaporation. The steam in the cell will condense as moisture when the temperature is cold down. The condensed moisture will soften the starch cell and create negative pressure in the cell, which resulted in foam shrinking.

From an application-oriented point of view, in order to decrease the cost of transportation of foam products, the fabrication was divided in two steps in the work [125,126]: 1) compounding the starch-based components to pellets for easy transportation and 2) foaming products near application place. This is because the foamed materials consist of more than 90% gas, so the transportation cost could be higher than the cost of the material itself. The compounded pellets can be easily transported to anywhere near the customer. Furthermore, the foaming can be simply carried by a small single screw extruder, which makes the manufacture much more flexible.

Fig. 11 shows the photos of various starch foams and their applications. It is seen that various foams from ball to sheet as well as many post-processed products have been developed.

5. Summary

Starch-based materials have showed greatly potentials, especially when more and more countries have passed the low or regulation of banning disposable plastics. Many products, such as films, capsules, sheets, foam etc have been developed and commercialized. Like all other materials, improving performance and decreasing cost are two on-going strategic. In principle, the properties of starch-based materials can be significantly improved by blending with synthetic oil-based polymers. However, these blends were not biodegradable, and thus the advantage of using a biodegradable polysaccharide was lost. The polymer blends and composites only from natural raw materials are discussed in this paper.

The starch based nano-composites have continuously attracted attentions, and have been successfully developed and commercialized. One of the challenges using nano-clay is to exfoliate it since the strong boundary between layers by iron. Another issue is to improve the hydrophilic surface of clay with hydrophobic surface of most conventional polymers, especially polyolefin. These two challenges can be simply solved in starch-based materials. Firstly, the hydrophilic water is a very efficient chemical to delaminate clay with the enhancement by ultrasonic. Secondly, starch itself is a hydrophilic polymer that can be well compatible with clay and water. Actually water is a plasticizer for starch-based materials.

Starch reinforced by cellulose is a typical example of natural polymer composites. These materials have the advantages of being renewable, biodegradable, abundantly available and inexpensive. Recently, the starch films reinforced by both cellulose and starch-

Fig. 11. Photos of starch foams: from foam ball to form sheet and post-processed products.

based crystals have been developed. There is good compatibility between starch matrix and the reinforcing fillers due to same chemical unit (glucose). Since all the components used belongs to food sources, the prepared films are biodegradable, safe for food packaging and can also be used to develop edible films and medicinal capsules. The new technique of self-reinforced composites has also been used for starch-based materials.

The well recognized weakness of starch-based materials is their moisture sensitivity. The hydrophilic nature of starch makes it susceptible to moisture uptake, resulting in inadequate performance, in particular water vapor permeability and tensile strength. To improve the moisture resistance and mechanical properties of starch-based materials, various blending and compositing techniques have been developed. However, the most efficient and easy way is coasting. Acrylated epoxidized soybean oil (AESO)-based coating was developed to reduce the moisture sensitivity and improve the gas permeability of starch-based film. Similar to starch, soybean oil also comes from renewable resource. In order to improve the surface adhesion between starch and AESO coating and further improve the moisture sensitivity, polyethylenimine (PEI) was used to improve the bonding between hydrophilic starch and hydrophobic coatings of AESO.

From an application-oriented point of view, in order to decrease the cost of transportation, the foaming system was prepared in two steps in this work: 1) compounding and 2) foaming. This is because the foamed materials consist of more than 90% gas, so the transportation cost could be higher than the cost of the material itself. It was found that there was a critical point of water content (between 16 and 18%) at which the expending ratio changed significantly since the cell structure changed from open to closed.

Based on above discussion, it is seen that both challenges and opportunities excite for starch-based materials. The future work will mainly continuously focus on improving performance and decreasing cost, in particular improving the well recognized weakness of starch-based materials: moisture sensitivity. The balance between chemical treatment for reducing moisture sensitivity and biodegradability shoul be seriously considered. Other applications of starch-based materials, such as in controlled releasing fertilizer, water treatment and new drug designing etc, have also attracted increasingly attention and showed great potential.

Declaration of Competing Interest

There is no conflict of interest.

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