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Review Article

A Brief Overview on Current and Potential Applications of Thermoplastic Starch

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Abstract

The production of plastics was a great idea until it started polluting our environment. To move towards a sustainable environment and prevent the disposal of plastic waste in the environment, the bioplastics have gained a lot of interest due to their high biodegradable ability. Bio-based polymers can be obtained from biomass. i.e., polysaccharides (starch and cellulose) and proteins (casein and gluten), or via renewable bio-based monomers (poly-lactic acid) or microorganisms, and they play a very significant role in protecting the environment because of the kind of properties they bring in the bio-plastics. This paper focuses on a starch-based bioplastics known as thermoplastic starch, their properties and their applications, in a large niche of market, as the best replacement to traditional plastics. It also draws light on the future prospects of TPS that can be accessed by modifying their properties and cost issues.

Keywords: Bioplastic; Biodegradable; Thermoplastic Starch; Starch-based

Abbreviations

TPS: Thermoplastic Starch; ROS: Reactive Oxygen Species; PEG: Polyethylene Glycol; PP: Polypropylene; PPG: Polypropylene Glycol; PE: Polyethylene; PS: Polystyrene; PVA: Polyvinyl Alcohol; PLA: Polylactic Acid

Introduction

Plastics are long chain polymers that have been widely used because of their characteristics. They have properties like being lightweight, durable, inexpensive; and thermally and electrically insulative [1]. In the early 20th century, plastics were considered a novel product and had very limited usage but now, they are present all around the market. As the usage of plastics increased, a surge in their production was also witnessed. The production of plastics was around 368 million metric tons worldwide in 2019 and it keeps increasing with the increasing demands (Figure 1) [2].

Figure 1: Growing trend of plastics in the world from the year 1950s to 2019.

The need for an alternate of plastics

As plastics entered all forms of market usage, its production and disposal rates also increased. As more and more plastic waste generated, their slow degradation rates became an issue. Now more and more of plastics are discarded off into water bodies and landfills each year (Figure 2).

(A)

(B)

Figure 2: Plastic waste accumulated in water bodies (A) and landfills (B).

The accumulation of plastic waste in water bodies is a matter of growing concern. Approximately 4% of fossil-fuel is exhausted annually to be used as raw materials for plastics [2]. The demand of fossil fuel, energy, and the associated carbon emissions by this industry will keep on increasing as the demand for plastics increases. For instance, in 2015, plastics production from different areas was around 407 million tones out of which 302 million tones ended up as waste [3] (Figure 3). So in order to reduce the generation of waste and pollution, the plastics was replaced by 'bio-plastics'. Bio-plastics are generally derived from renewable and biological resources, like vegetable oils, corn flour, fats and agricultural by-products. They have applications in large sectors of market like packaging, catering products, transportation and storage. Among all these applications, packaging constitutes the 65% of the complete bioplastic market in 2017 [4].

Figure 3: Plastic waste generation by Industrial sector in 2015.

Biodegradable plastic and Bioplastics

Biodegradable plastics can be biologically broken down into smaller components within a short time span. They are composed of traditional petroleum-based plastics which are combined with an additive that helps to makes them break down faster. This term is often used interchangeably with bio-plastics but the two are chemically quite different. Bioplastics are derived from renewable raw materials like corn flour, straw, woodchips, sawdust, etc. [5] (Figure 4 and Figure 5).

Figure 4: Chemical structure of Bioplastic (PLA: Polylactic Acid).

Figure 5: Chemical structure of Petroleum based biodegradable plastic.

Organic components based bioplastics

The most common bioplastics are based on:

- Starch
- Cellulose
- Protein
- Aliphatic Polyesters
- Organic Polyethylene.

Among all of these mentioned above, starch based bioplastics are most commonly used as it is an easily available, renewable and low-cost commodity that when processed into a thermoplastic has the potential to replace conventional petroleum plastics. The properties of starch based bio-plastics are mostly dependent on its amylase-amylopectin ratio as low-amylose starch can result in poor mechanical properties of the final product. Purely starch-based bioplastic turns out to be brittle, so plasticizers such as glycerol, glycol, or sorbitol are added to produce thermoplastic starch (TPS) [5,6] (Figure 6).

Figure 6: (a) TPS Rod (Source: 2013, Wiley Periodicals); (b) TPS Film.

Thermoplastic starch and its applications

Thermoplastic starch (TPS) is a biodegradable, renewable and flexible material that can be easily modified according to the needs. It is made by processing starch granules with low water content, plasticizers under various mechanical and thermal forces. These processing methods alter the internal bonds of starch granules, change its structure and forms TPS. Different thermo-plasticization processes that can be used for the synthesis of TPS are extrusion blow molding, injection molding, injection compression molding, and extrusion [7]. The qualities of TPS can be altered by varying the thermal and mechanical conditions of its plasticization process.

Thermoplastic starch polymers have a number of applications:

- Commonly used in film for shopping bags, overwrap, and mulch film.
- It is also suitable for coatings, cutlery, and other packaging.
- TPS can be used as a fuel source at the end of their life-cycles and double to income of factories producing them.
- Its disposed product can also be used as fertilizer.

Formulations needed in TPS formation

Plasticizers

Nafchi., *et al*. [8] states that plasticizer increases the flexibility of the material to which they are added. They enter the starch granules and replace its hydrogen bonds by starch–plasticizer bonds. In order for a plasticizer to be effective, it must be hydrophilic so it can be compatible with the starch. Also, its boiling point must be higher than the drying and processing conditions to avoid the evaporation of the plasticizer from the final product during processing. The most common plasticizers used in TPS production are glycerol and water. Other plasticizers include polyols like sorbitol, glycol, nitrogen based compounds (urea, amines) and citric acid [3,8].

Additives

Nanofillers are additives in solid form that are generally different from the base matrix in terms of their structure and composition. They include inorganic materials mostly but in some cases, it can also include organic materials. Most commonly known nanofillers include phyllosilicates, especially montmorillonite (MMT) [9]. Other kinds of nanofillers are carbonaceous nanofillers (like carbon nanotubes), polysaccharide nanofillers (like cellulose nano whiskers), metal oxides, metalloid oxides, and metal chalcogenides.

Lubricants

Lubricants are added to reduce the product's tendency to stick to the dye or clogging it. Some common lubricants include magnesium stearate, calcium stearate and fluoro-elastomers.

Composites

Composites are used to strengthen, limit property dependence on humidity or moisture, and control retro-gradation. They mostly include talc, clay or silica.

Stabilizers

These are additives which prevent premature biodegradation as stabilization against retro- gradation is important for future processing of the TPS [7].

Methodologies available for the preparation of TPS

There are various different plasticizers and additives that can be added with TPS to alter its properties according to the needs. Pacheco., *et al*. [10] has reviewed in his paper that although the preparation method is similar in all the cases, the reactions vary depending on the physical and chemical factors like water diffusion, crystallization, gelatinization, temperature, starch granules expansion, shear and melting.

As pure starch is brittle, TPS is mixed with different polymers to achieve various properties and potential [11]. Blending is when two or more polymers are mixed together and it results in improved properties in the final product. TPS is blended with many polymers along with different plasticizers to improve its properties and cost (Figure 8).

Most common TPS/polymer blends are as following:

- **TPS/Polyethylene Blends:** PE has unique properties like being chemically resistant to acid, base, or salt, low cost, electrical insulation, toughness and flexibility. These properties make it a suitable component for blending with TPS.
- **TPS/Polystyrene Blends**: They can be very brittle or very tough and they are mostly used in aircraft kit, containers, vending cups because of their low cost and ease of processing. They provide strength to TPS when mixed with it.
- **TPS/Polypropylene Blends**: PP has good electrical properties, insulating properties, resistance to various chemicals including like alcohols, acids, bases, esters, etc.
- **TPS/PVA Blends**: PVA has an OH group which is of small size that allows it to fit in the crystal lattice of different plastic blends. PVA is used in paper, textile treatments and wet-strength adhesives.
- **TPS/PLA Blends**: PLA is aliphatic polyester which is derived from sugar and corn. It is degraded to nontoxic compounds in landfills. It is also used in biomedical and pharmaceutical fields because of its properties like low molecular weight and low cost (Figure 7).

(A)

(B)

Figure 7: Schematic representation of starch thermal processing (A: Melt mixing and B: Thermo-compression).

Engineered modifications in TPS

Antimicrobial packaging

The current market demand of easy to prepare 'fresh' food products has been posing a great challenge for the food industry in terms of safety and quality. To overcome food-borne microbial outbreaks, companies are opting for anti-microbial packaging that can inhibit, control or retard the growth of microbes on food products [11].

Anti-microbial packaging can be done via various methods:

- Addition of sachets containing antimicrobial agents into food packages.
- Incorporation of antimicrobial agents directly into the polymers.
- Coating or immobilizing antimicrobials onto polymer surfaces.
- Using polymers that are originally antimicrobial.

Several recent studies have been working with cross linking silver nanoparticles to the surface of the TPS sheets to increase its antimicrobial properties. Also, the nanoparticles acted as a carrier for long-term and delayed release of antimicrobials into the product. The choice of added product is mainly dependent on its desired functions. A greater emphasis should be laid on safety features associated with the addition of antimicrobial agents in the packaging technology. Table 1 shows some common applications of biopolymers in antimicrobial food packaging (Figure 8).

Figure 8: Thermoplastic starch (TPS)/polylactic acid (PLA) blend.

Antioxidant packaging

Antioxidants are additives that play a major part in ensuring that our food products retain their taste and colour, and remain edible for a longer period of time, but their excess usage makes them toxic. Traditionally, synthetic antioxidants such as organophosphate, polyphenol, and thioester compounds were used in packaging materials, but their toxicity levels have posed great challenges to the industry [12]. The alternative approach that is being considered widely is the use of natural antioxidants, mainly tocopherol, plant extracts, and essential oils from herbs and spices [13].

There are two main modes of action for antioxidant packages:

- The release of antioxidants to the food, and
- The scavenging of undesirable compounds such as oxygen, ROS and metal ions from the food.

Oxygen and carbon dioxide absorbers

CO_2 is being used due to its antimicrobial effect and as a way to protect foods from oxidation. As explained in article by Kwon., *et al.* [14] that maintaining an optimal concentration of O_2 and CO_2 in the food package is necessary for its efficacy, because a CO_2 concentration above the tolerance limit can cause physiological injury to the product like its discoloration, off-flavor development and internal tissue breakdown. Gaseous absorbers can control aerobic microbial and bacteria growth in the packaged product.

Some common O_2 scavengers and CO_2 emitters are mentioned in the table 1.

O_2 Scavengers	CO_2 emitters
Iron	Sodium bicarbonate
Palladium	Citric acid
Gallic acid	Ferrous carbonate
Pyrogallol	Rosemary extract
Ascorbic acid	Green tea extract

Table 1: Common O_2 scavengers and CO_2 emitters.

Light barriers

Light absorber or light blocking agents are included into food packaging materials to reduce the photo-oxidation of the food, which is one of the leading causes of food degradation. Light sensitive compounds present in food ingredient are generally called 'photo-sensitizers' and often refer to pigments like chlorophylls, riboflavins, carotenoids, anthocyanins, and flavonoids. Aluminum or metal foil is considered as the best material for UV and visible light blocking. However, it has few drawbacks regarding its recyclability, high cost, and non-transparency. Currently, the use of UV is preferred because of its smart selection and application to different polymers as each of them are designed and developed for specific function [15]. Metal oxide particles are also used as light blockers because of their property to reflect, refract and scatter light rays (Figure 9).

Figure 9: Applications of Biopolymers in Antimicrobial Food Packaging.

Biomedical application of TPS

The properties of TPS can be altered to make them useful in different niches of application in the biological field. It can be chemically modified to achieve the required properties and usage (Figure 10). Some of the common chemical modifications in starch are its phosphorylation, carboxymethylation, hydroxypropylation, acetylation, and succinylation [16]. Carboxymethylation gives an extra hydrophilic character to starch, increasing its capability in water absorption and permeation.

Figure 10: Schematic representation of light absorption and scattering of metal oxide.

- Acetylation turns starch into a water-soluble and film-forming material that can be used in majority of pharmaceutical formulations.
- Hydroxypropylation provides starch with reduced porosity and high water absorption capacity.
- Succinylation provides starch with hydrophilic character increasing its solubility, improving the freeze-thaw stability, reducing the temperature of gelatinization and retrogradation and resistance to acids
- Phosphorylation of starch can result into variety of chemically modified products depending on the reaction conditions used.

Figure 11: Common Applications of Starch-based Bioplastics.

Currently, starch-based bioplastics have been widely used as;

- Substitute for soft gelatin capsules: As gelatin is animal based and there is a great interest for its vegan replacement in the consumer market. Also, the use of gelatin for hydrophilic lipid-based formulations causes the active formulation of the drug to crystallize due to the presence of high content of water in the matrix [17].
- Blend of starch and PEG-PPG-PEG copolymer is used to prepare bone wax, which helps in minimizing the bleed from a disrupted bone surface, by sealing the wound. [PEG= Polyethylene glycol, PPG= Polypropylene glycol]
- Starch hydrogels are prepared, which are 3-D networks, capable of absorbing water. They are used to keep the wound moisturized that aids in faster recovery time.
- The use of super-absorbent starches as a potential candidate for support of any drug release agent. They are produced by grafting acrylic acid or 2-hydroxy ethyl methacrylate to starch. This material is pH sensitive, so it can change its swelling degree according to the pH.
- Scaffolds are supporting materials used in tissue engineering applications to repair or restore damaged tissues and to support cell growth. Important parameters of scaffolds include their porosity, pore size, permeability, degradation post-usage and reabsorption efficiency [18]. Starch-based scaffolds are a great option as their structure and functions allow the user to control their pore size, pores morphology, porosity and scaffold's shape that will make them helpful in various applications.
- Starch-based biosorbable materials are now produced as a temporary replacement of the injured tissues so as to preserve their function. These are temporary implantable materials that must get degraded and reabsorbed by the body slowly once their requirement is over, providing ample time for the tissue to regenerate and heal the area. Starch is easily degraded by amylases, which can be found in the mouth of a human body. Based on this fact, a starch-based device was created for use in surgeries that can recover the stenosis of salivary ducts post-surgery. This device should be removed from the body if it's not degraded in the desired time. So, the great advantage of using starch is its resorbable feature, a simple and great alternative to that type of device.

- Some applications of TPS are in medical disease therapies like ophthalmology, orthopedics, cardiovascular diseases, wound closure, and nerve regeneration. These include formation of contact lenses, artificial orbital walls, internal adhesives, and balloon pumps for aorta, artificial valves, grafts, stents and many more.

Starch based-bioplastics have created a large sector in the biomedical, which can be further modified for more applications depending on their properties.

Discussion

The findings in this paper suggest that biopolymer can be the real alternate to plastics in all the niches of market. The growing need of a replacement of plastic materials has lead to growth in the research field for the substitutes that can be modified and altered according to customized needs of the consumers. Although developments have led to findings of various blends and additives for modifications of TPS, there is still a large gap to be covered regarding the commercialization barriers like cost of production and lack of awareness in public. As soon as these barriers are covered, the researches done for the better suitability of TPS in place of conventional plastic can actually b applied to use, leading to reduction in one great problem of world's sustainability goal.

Conclusion

The progressive usage of bio-plastics has been happening with success in terms of its applications in various fields, opening new horizons for its potential uses. These biopolymers met our environmental issues but they still have some limitations in the form of barriers and other mechanical properties related to costs. Hence, it requires further research in order to improve its quality, life and microbial safety. Starch based bio-plastics like TPS has paved the way for a cheaper and modified replacement to conventional plastics. However, the properties of TPS that have been withholding its entrance into the main market niche can be assessed and altered depending on the required modifications. The future developments of TPS can include different formulations and processing methods that can improve its sustainability and applicability together. Thus, TPS has great potential uses in the future and will achieve proper commercial utilization after required modifications.

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Volume 5 Issue 12 December 2021