

REVIEW

Thermoplastic starches: Properties, challenges, and prospects

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Thermoplastic starch (TPS) polymers were reviewed in this article. This review was categorized into the following studies: the role of starch as a thermoplastic polymer, transformation and melting mechanisms, plasticization and plasticizers, reactive extrusion (REX) and modifications, retrogradation, biodegradability, filler and blenders, and nano-particle incorporation in thermoplastic starch. This categorization allows us to understand the developments in this field in recent years and shows that the major challenges in the future are reducing sensitivity to moisture and retarding retrogradation of the thermoplastic matrix. Moreover, nano-particles such as clay can be used in TPS matrices to overcome these disadvantages.

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1 Introduction

Starch, a completely biodegradable polysaccharide that is biosynthesis by numerous plants, is one of the most abundant renewable resources known to man. In its granular form, starch is mostly composed of linear amylose and highly branched amylopectin. Thus, starch can be considered as a crystalline material. When mixed with a limited amount of water and subjected to heat and shear, starch undergoes spontaneous destructure. A homogeneous melt known as thermoplastic starch (TPS), which possesses thermoplastic characteristics, is formed [1].

TPS is compatible with the environment. TPS is a renewable material and can be incorporated into soil as an organic

fertilizer. The accumulation of plastic materials can contribute to environmental pollution to a particular extent. Although most traditional plastics are recalcitrant (inert to microbial attack), the pollution they produce is essentially visual. Thus, the development of biodegradable polymers that are derived from renewable natural resources has gained increasing interest [2]. At present, many basic and applied studies on starch as a cheap and abundant natural polymer are being conducted. The development and production of biodegradable TPS is considered important in reducing the total amount of synthetic plastic waste [3].

The term “de-structured starch” was apparently coined after the physically modified state of starch was obtained by the disruption of its granular state, which results in the loss of order and crystallinity. A brief literature review shows that in the 1970s, starch that contains low (10–30%) water contents was extruded at elevated temperatures to obtain a thermoplastic melt with no residual starch crystallinity [4].

TPS is a material that is obtained by the disruption (as amended) of the starch granule structure when it is processed with a low water content and with thermal and mechanical forces in the presence of plasticizers that do not easily evaporate during processing [5]. TPS has several attributes in addition to its biodegradability. TPS is a renewable and

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Abbreviations: **PBSA**, poly butylene succinate adipate; **PCL**, poly-ε-caprolactone; **PHB**, poly hydroxy butyrate; **PLA**, poly lactic acid; **REX**, reactive extrusion; **TPS**, thermoplastic starch

flexible material that can be easily used in different thermo-plastification processes with a standard equipment used in manufacturing synthetic polymers. These processes include injection molding, extrusion blow molding, injection compression molding, and extrusion [6–12].

Over the past 20 years, several studies have been directed toward the modification of starch in the production of thermoplastic materials [13–15].

However, the main disadvantages of TPS include their retrogradation and unsatisfactory mechanical properties, particularly in wet or dry environments [16, 17]. One problem with the use of bioplastics in TPS is the fragile nature caused by its relatively low T_g and the lack of relaxation of $\text{sub-}T_g$ because of the molecular chain of starch [18–20]. Moreover, the eventual migration of plasticizers into the environment increases the fragility of the material [21]. This fragility is a structural stability problem, which increases with time because of the decrease in free volume and retrogradation [22]. A wide variety of plasticizers, such as formamids, urea, acetamide, sugar, polyols amino acid, lipid, and phosphate sorbates, have been used to increase the flexibility of TPS [7, 20, 23–31]. Several studies argue that amide groups prevent retrogradation in starch gels longer than other additives, thereby increasing the stability of the gel [27, 32]. However, most nitrogen compounds found in the solid state and in the melt at high temperatures impart little flexibility [22]. Another problem in the development of TPS is the high amylose content that results in a decreased flexibility compared with TPS made from a material with a high amylopectin content [33–36]. Moreover, stored TPS made from native starch underwent structural changes, which exhibits greater stiffness or weakness depending on the plasticizer content [30].

The formulations vary between 50 and 90% of starch and between 10 and 50% of plasticizer additives. The development of TPS can be controlled based on mechanical and thermal conditions of the thermo-plasticization process [37]. In the present study, previous studies on TPSs were categorized in the following six fields:

- (i) Starch as a thermoplastic material.
- (ii) Melting and transformation mechanisms.
- (iii) Plasticization and plasticizers.
- (iv) Modifications and reactive extrusion (REX).
- (v) Biodegradation, retrogradation, and aging.
- (vi) Improvement of TPSs by mixing with other materials.

2 Starch as a thermoplastic material

Native starch is the term used to describe starch in the form in which it occurs in plants such as potatoes, wheat, cassava, rice, and maize. In plants, starch occurs in the form of granules. The granules vary in shape, size, and

relative proportions of amylose and amylopectin depending on the source of the starch. Starch is therefore described by its plant source as cornstarch, potato starch, tapioca starch, and so on [38].

Starch is composed of carbon, hydrogen, and oxygen in a ratio of 6:10:5 [$\text{C}_6\text{H}_{10}\text{O}_5$]. Thus, starch belongs to a class of carbohydrate organic compounds. Starch is considered as a glucose polymer with linkages between the glucose units that are formed during condensation. The glucose units are connected by an oxygen atom, which connects the carbon atom 1 of one glucose unit to the carbon atom 4 of the next glucose unit. Thus, a long chain of interconnected glucose units is formed. This linkage of one glucose unit to another through the C-1 oxygen atom is called the glycoside bond [38].

Starch granules show birefringence when observed in polarized light. Birefringence indicates a degree of molecular organization. X-ray scattering results have shown that granular starch has an overall crystallinity of about 20–45%. The amorphous regions are formed by amylose and residues around the branch points of amylopectin. The linear segments of amylopectin are present in the form of double helices that are crystallized into thin lamellar domains [39]. The starch granule is partially crystalline and insoluble in water at room temperature. Starch granules have different sizes and shapes depending on the biological source from which they originate. The form can be round, elliptical, oval, or polygonal lenticular [40]. The granules are smaller in rice and amaranth with diameters between 1 and 5 μm . The starch granules of potato and cassava have diameters between 15 and 100 μm [41]. Sago starch granules have a broad size range between 10 and 50 μm in diameter with an average granule diameter of 32 μm [42]. The average diameter of native cornstarch granules is 10 μm [43]. The surfaces of different starch granules generally vary depending on the botanical origin, and this variation remains an important research topic [44]. Starch is a major carbohydrate in food after glucose and other sugars. For several years, starch has become the subject of extensive research because of the range of possibilities it offers in food art. Starches are used in the food industry to produce bread, desserts, puddings, cake fillings, biscuits, sweets, sweet gum, chewing gum, and so on. Starches are also used on an industrial scale in stationery, stickers, glue, flocculants, hydrocolloids, gums, dextrin, and so on [45].

The use of starch as a film has been recorded in literature since the 1920s [46]. Since then, numerous research have been done on starch. However, starch has limited applications as a packaging material. The main advantages of starch as a material include its low cost, abundance, and availability from agricultural crops. Compared with synthetic polymeric materials, starch has the following two main disadvantages: (A) starch contains

hydroxyl groups that impart hydrophilic properties to it. Amylose dissolves in water and amylopectin swells in the presence of water. Thus, starch disintegrates in water and loses its properties when exposed to moisture [47]. (B) Starch in its native form is not thermoplastic. When it is heated, pyrolysis occurs before the crystalline melting point of starch is reached. Therefore, starch cannot be melt-processed via conventional plastic equipment [48].

Native starch hydrolysates or sheath were developed in different operational conditions because the production of raw materials at an industrial scale is still being assessed because of the different applications of starch. Starches from pea, wheat, maize, sorghum, barley, amaranth, potato, cassava, sweet potatoes, sago, and yams can be extracted via two methods (dry and wet). The production of starch has been generally changed in the case of cereals, which has starch content between 65 and 85% in roots and between 15 and 35% in tubers. Thus, TPS production is significantly influenced by the regional influence of starch. Plasticization studies have also been related to the extraction type, starch type, and its molecular organization, which demonstrate the impact of operational variables in thermoplastification processes [4, 49–53].

3 Melting and transformation mechanisms

Granular starch is partially crystalline in its native form. When dry starch granules are heated, thermal degradation occurs before the granular crystalline melting point is reached. As a result, starch cannot be melt-processed in its native form. The hydrogen bonds that hold starch molecules together have to be reduced to melt-process native starch. The reduction of starch hydrogen bonding can be achieved in the presence of a solvent such as water. When starch is heated in an aqueous medium, the phase transition state is transformed from an ordered to a disordered state. This process is called gelatinization [54, 55].

The properties of starch in water are the bases on which starch can be melt-processed. When starch is heated with a solvent at a critical temperature, the solvent interacts with the hydroxyl groups in starch, thereby reducing hydrogen bonding among the starch molecules. This phenomenon allows individual chains to move freely relative to each other, thereby allowing starch to be melt-processed. The critical temperature at which this phenomenon occurs is called the gelatinization temperature [56].

TPS is formed through the de-structuring of native starch granules by heating at relatively high temperatures, in high shear conditions, and with limited amounts of water [57]. Processing a native starch to form a material bioplastic is necessary to break and melt the original structure [30]. The stability, processing, and physical properties of TPSs depend on the nature of amorphous and crystalline

zones in the structure of the granules. The transformation of granular starch is influenced by process conditions such as temperature and plasticizer content. Water and glycerol are the most commonly used plasticizers. During different thermo-plasticization processes, the influence of water and glycerol in starch granules are of great importance because these plasticizers function as a lubricant that facilitates the mobility of polymer chains and slows the retrogradation of TPS products [30, 58–61].

Studies have elucidated the melting processes of starch. Studies have provided a theoretical description of models according to the melting of crystalline type (cereals), B (roots), and C (legumes) in native and hydrolyzed starches by using the first-order statistical thermodynamics (flow theory) [62, 63]. The interaction of native starch with non-aqueous plasticizers such as glucose, nitrogen compounds, poly-alcohols, fatty acids, and citric acid was also described. These plasticizers decrease the absorption of water in starch, which prevents the material from becoming fragile. In addition, the mechanical properties (elongation and strength) can be maintained at a relatively constant value between 25 and 30 days of storage [16, 26, 27, 63–79].

The present study also described the formation of crystalline structures, which are typically referred to as V_H , V_A , and E_H in the thermoplastic matrix. These structures are formed because of the presence of amylose in single helices. Moreover, the influence of recrystallization processes on the mechanical properties of TPS has been studied [30, 80–82]. The retrogradation of different processes is mainly due to the absorption of water within the thermoplastic matrix, which allows the realignment of polymer chains because of the presence of OH groups. Retrogradation affects the mechanical properties in which the tensile strength increases and the elongation decreases, which affects the quality of bio-plastics [83–86]. Residues of B-type crystal structures and the downstream of thermo-plasticization have been studied using X-ray because of their influence on the recrystallization process and their impact on the formation of V_H , V_A , and E_H structures [30, 61, 87]. In addition, these structures are influenced by the presence of water and plasticizers. A crystal structure with a low water content is formed, and V_A , V_H , and E_H crystal structures are results of the plasticizer–water mixture [30, 87].

The use of lubricants (vegetable oils) in the production of TPSs helps reduce thermal degradation of starch that is produced via de-polymerization and enhances the process conditions [88–90].

The specific heat capacity of starch–water–plasticizer as a function of temperature and composition was also investigated. The water content and temperature are directly related to the heat capacity of the system. However, the influence of glycerol content is related to the thermal property based on the type of starch used [91].

4 Plastification and plasticizers

This category consists of studies that involve the monitoring of separation of phases for carbohydrates (amylose/amylopectin) alone or mixed with plasticizers and of TPS obtained by extrusion molding or compression [63, 92–94]. In addition, the category also includes studies on the changes in mechanical and thermal properties as a function of composition and different storage conditions (relative humidity and storage time) [95]. A plasticizer is a material that is incorporated into a plastic material, and increases the flexibility and applicability of the plastic material. Plasticizer molecules penetrate starch granules, and destroy the inner hydrogen bonds of starch in high temperature, pressure, and shearing. These molecules eliminate starch–starch interactions because they are replaced by starch–plasticizer interactions. In the literature, other hydrophilic liquids that are used as plasticizers for TPS include glycerol, sorbitol, glycols, maltodextrin, and urea. Water is the most common solvent or plasticizer used in starch. The starch network can be easily deformed without rupture because plasticizer molecules are smaller and more mobile than the starch molecules [96]. Water and glycerol are the most common plasticizers used in the processing of TPS. The type of plasticizer used influences the T_g of TPS [36]. However, urea, various glycols (triethylene glycol, PEG, and glycerol), and mixtures of these have also been used as plasticizers for the gelatinization of cornstarch. At lower urea:glycol ratios (0.2:1), starch extrudates are brittle and shatter like glass despite the fact that T_g was lowered to 50°C. An increase in the urea:glycol ratio in the starch ribbon from 0.2:1 to 0.6:1 decreased the tensile strength from 19 to 7 MPa and caused a slight decrease in elongation. The mechanical properties of the ribbons remained stable with time at a relative humidity of 50%, which shows that T_g is below room temperature when the system is in thermodynamic equilibrium. Urea also disrupts starch hydrogen bonding, which does not allow retrogradation to occur. Starch ribbons containing high levels of urea were stiff because of the low mobility of urea compared with ribbons containing high levels of glycols. This result is due to the higher mobility or fluidity of glycols [67, 68, 71, 72, 97–103].

The melting and decomposition temperatures of starch decrease with increasing plasticizer content. The presence of 2% glycerol mono-stearate (GMS) in glycerol-plasticized wheat starch reduces the melt viscosity and improves water sensitivity. The melting and decomposition temperatures for cornstarch plasticized by glycerol decreased [85, 104–106].

During storage, the plasticizer content decreases because of the migration of the plasticizer from the matrix to the surface and the environment, thereby affecting

mechanical properties (tensile strength increases and elongation decreases). Similarly, thermal property changes cause an increase in both T_g and melting point [92, 107]. The permeability of the plasticizers to gases (O_2 , CO_2 , and water vapor) was studied according to the type of plasticizer used. The permeability increases with increasing plasticizer concentration, and the increase in permeability is greater in hydrophilic compounds than in hydrophobic ones [108–112].

During storage, aging was evident in different recrystallization processes of polymer chains and diffusion of plasticizers into the external TPS. This recrystallization (retrogradation) phenomenon depends on environmental conditions that affect the phase separation between the plasticizer and starch [113, 114]. Glycerol-containing starch plastics have been shown to recrystallize into various crystalline structures during storage, which results in mechanical property changes. The amylose content in TPS forms E_H -type crystallites that unstable and rearrange after several days into V_H -type crystallites. Amylose also forms B-type crystallites during storage similar to amylopectin [115]. The amount of single helical structures (E_H and V_H) is dependent on the amount of water used during processing rather than on the amount of the total plasticizer (glycerol and water). During aging, the amount of single helical structures does not increase. Therefore, retrogradation is caused by the recrystallization into double helical structures (B-type crystallinity). The formation of B-type crystallites is dependent on the plasticizer content. High glycerol-containing extruded materials absorb more water during storage, thereby increasing the rate of retrogradation [83].

5 Modifications and reactive extrusion

This category includes studies that are related to chemical and enzymatic changes during the extrusion process (single or twin screw), which is also known as REX, and studies related to the incorporation of fibers. During several decades of development, REX has been widely used in the modification of synthetic polymers to create various resins and thermoplastics. Later, extrusion also became important in food processing and starch modification for non-food applications. As previously reported, a co-rotating, fully intermeshing, twin-screw extruder was used as a reactor to prepare cationized, oxidized, and esterified starches and to convert starch to glycosides and starch graft copolymers. These applications have shown that REX is a feasible and efficient way to modify starches and produce better products. The high efficiency and accelerated rates at which modification reactions were carried out in the extruder compared with batch processes

is particularly noteworthy. However, research on starch modification that uses REX is just beginning, and fully understanding the mechanisms and controlling processing requires more time. A disadvantage for the process seen in the past is that the unused reagents remain in the extrudates because they cannot be removed in an economical manner [24].

Other studies have shown that starch can be modified by esterification, etherification, and oxidation before thermo-plasticization to achieve a high degree of substitution of hydrophilic-OH groups by hydrophobic groups. This substitution reduces the sensitivity of starch to water and improves the properties of mechanical and barrier materials made from TPS [116–118].

The mechanical properties of TPS that were reinforced with fibers of different origins and with a loading of up to 30% were investigated. The properties showed that the fiber reduced aging in the material, slowed the retrogradation process in the thermoplastic matrix, and improved the mechanical and barrier properties of the materials [119–130].

Numerous reactive chemistries are available to compatibilist starch and synthetic polymers. Although starch-based plastics have captured a major portion of the biodegradable plastic market, it is not the fastest growing one. A significant and faster growth is expected for products that are synthesized from 100% biodegradable polyesters like poly lactic acid (PLA) because many hurdles exist in using high amounts of starch (>25–30 wt%) even in reactive blends without compromising material properties. Thus, the application of starch-based blends is now limited to niche applications. Future research activities need to focus on reactive starch blends that contain significant amounts of starch or on modified starch that allows them to be used in a larger number of applications [131].

6 Biodegradation, retrogradation, and aging

The accumulation of plastic waste is a serious threat to the environment. Considering the attractive properties of plastics, they will continue to be used in large amounts by the industry and the general public. The strategy to be adopted in this situation is to develop plastic materials that can be easily degraded by the environment after use. Microorganisms are the natural allies of mankind in this struggle. Of all the methods proposed for handling plastic waste, the use of biodegradable plastic materials appears to be the most satisfactory solution. The recently developed thermoplastics with low starch contents belong to this category. They are based on materials that are already manufactured using well-established technology. These materials are assimilated into the environment over com-

paratively short periods of time. They possess properties that are almost as good as virgin plastic materials for such large volume applications like packaging [132].

One of the disadvantages of TPS is its brittleness caused by its relatively high T_g and lack of a sub- T_g main chain relaxation area. During storage, this brittleness increases because of retrogradation. Retrogradation is the change in mechanical properties of TPS caused by the recrystallization process. The recrystallization process is caused by the tendency of macromolecules to form hydrogen bonds during the expulsion of water and/or other solvents. This process can be divided into the recrystallization of amylose and the irreversible crystallization of amylopectin. Retrogradation is referred to as the long-term recrystallization of amylopectin because the reversible recrystallization of amylose is slower [21]. Above the T_g , further absorption of water increases the mobility of starch until the equilibrium moisture content is reached. During and after this period, retrogradation takes place and relaxation times increase because of the development of crystallinity [133].

This category of reported studies show a theoretical basis for the observation of aging presented in different TPSs and the change in MW using various methods such as the dynamic mechanical thermal analysis (DMTA) [134], XRD [135], DSC [136–139], AFM [140–142], SEM, high-resolution optical microscopy [143–145], gel permeation chromatography [146–150], NMR spectroscopy [76, 133, 151, 152], and Fourier-transform infrared spectroscopy [153, 154]. The mobility of water in these systems was monitored using thermo-plasticization studies of sorption and diffusion during storage [52, 113, 155]. In addition, studies were undertaken using biodegradation enzymes that rapidly degrade the TPS by using α -amylase. Amylose was partially resistant to attack by α -amylase because of the presence of residual starch in the material. The use of other types of enzymes that may accelerate the process of biodegradation requires further investigations [156, 157]. Furthermore, α -amylase was assessed during the biodegradation of mixtures of different biopolymers and TPS and during the biodegradation of TPS and plasticizers. The latter type of biodegradation is more rapid than that of TPSs and biopolymers [158–161].

7 Improvement of TPSs by mixing with other materials

This category includes research that used TPS in mixtures with other materials for medical applications and non-food items. Granular starch can be mixed with molten thermoplastics without gelatinizing the starch. In this case, the starch functions as filler for the polymer, which reduces the total material cost. The processing has to be done below

the thermal degradation temperature of starch because starch granules are not gelatinized or plasticized. Starch does not contribute to the mechanical properties of the mixture because starch retains its granular form. These properties decrease with increasing starch content. Many examples can be found in the literature for both biodegradable and non-biodegradable synthetic polymers [4]. This technique is only commercially viable if the saving in material cost is greater than the added processing cost. Unfortunately, an inverse relationship exists between starch content and material properties. Most of the time, material properties reach an unacceptably low level before significant cost saving can be achieved [162]. In polymer science, blending is done to improve unsatisfactory physical properties of the existing polymer. In starch plastics, associating TPS with other polymers was done because of moisture sensitivity and critical ageing. Only biopolymers are used to preserve the biodegradability of the final blend. When TPS is melt-mixed with any other thermoplastic, the mixture can be considered as a polymer blend. Starch forms compatible blends with polar polymers like polyesters because it is hydrophobic. Only biodegradable polyesters such as poly- ϵ -caprolactone (PCL), poly butylene succinate adipate (PBSA), poly hydroxy butyrate (PHB), and PLA are often used to retain biodegradability [148].

Blending starch with degradable synthetic aliphatic polyesters has become a major focus in developing biodegradable polymers. Wheat TPS was found to be not fully compatible with PCL at different ratios of TPS:PCL with TPS as the major phase of the blend (>50%). The addition of at least 10% of PCL significantly reduced water sensitivity and dimensional stability. The mechanical properties of the blend are dependent on the plasticizer level in the TPS. For low-plasticized TPS, the addition of PCL resulted in a decrease in the material's elastic modulus, but the impact strength was improved. For rubbery TPS, the addition of PCL increased the modulus, but the impact strength decreased [163, 164]. The application of starch–PCL blends is limited because this material has a melting point of 60°C and therefore softens at temperatures above 40°C [162].

The addition of PLA increases the resistance of TPS to water absorption and improves the mechanical properties of products that are used as buffers. These buffers expand the application of biodegradable products and replace synthetic ones [8, 147, 160, 165, 166]. The different retrogradation processes of TPS and chitosan blends decreased during storage because of the reorientation of amylose and amylopectin molecules within the thermoplastic matrix. In addition, the transfer of water vapor substantially decreased [167]. Another material is the ideal TPS and hydroxyapatite, which are biomaterials used in skeletal system implants in humans [168].

Other polyesters such as poly butylene succinate (PBS) or PBSA have been blended with starch to improve their mechanical properties. The rheology of PBSA–TPS blends was better than that of pure starch. The tensile strength of the blends was lower than that of pure polyester, but was independent of the amount of starch added. The addition of 5% starch significantly reduced the half-life of the material compared with that of pure polyester. The half-life declined with increasing starch content. A minimum starch content of 20% was recommended in PBSA blends [148]. PHB is fully compatible with potato TPS. Film formation started with a PHB:starch ratio of 0.3:0.7. The physical properties reached optimal values at a ratio of 0.7:0 [169].

TPS and nano-composites mixtures improve the mechanical properties and thermal barrier of materials [170–176]. A similar behavior was displayed and evaluated in TPS and clay matrices [98, 172, 173, 176–188]. This technology can be used to circumvent one of the main problems associated with starch-based plastics, namely, water resistance. This technology is a major step toward the development of starch-based plastics [98, 189].

8 Conclusions

TPSs can be considered as a new class of inexpensive, green polymers that can be returned to its natural state without any pollution after use. TPS materials are often based on a combination of starch, glycerol, and water. In this review, the behavior of starches when thermo-plasticized is considered, and several gaps are observed, which should be the focus of future studies to create new products in the service of humanity. The limitations on the use of TPS in various applications are its sensitivity to moisture and retrogradation processes. Therefore, more studies on starch (native and modified), plasticizers, and nanoparticles that focus on reducing water absorption and decreasing retrogradation of the material to avoid decreasing mechanical strength or stiffness during storage in the development of TPSs are required.

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9 References

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