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Physical and/or Chemical Modifications of Starch by Thermoplastic Extrusion

Maria Teresa Pedrosa Silva Clerici
Federal University of Alfenas-UNIFAL-MG
Brazil

1. Introduction

Starch makes up the nutritive reserves of many plants. Starch biosynthesis is a complex process, which may be summarized as during the growing season, the green leaves collect energy from the sun, this energy is transported as a sugar solution to the starch storage cells, and the sugar is converted into starch in the form of tiny granules occupying most of the cell interior. The conversion of sugar into starch takes place through enzymes (Corn Production Source, 2011; Tester et al., 2006).

Starch granules are composed of two types of alpha-glucans, amylose and amylopectin, which represent approximately 98–99% of the dry weight. The ratio of the two polysaccharides varies according to the botanical origin of the starch and classifies starch as the 'waxy' starches contain less than 15% amylose, 'normal' 20–35% and 'high' amylose starches greater than about 40% (Tester et al., 2006; Wurzburg, 1989).

Amylopectin is a much larger molecule than amylose with a molecular weight and a heavily branched structure built from about 95% (α 1- 4) and 5% (α 1- 6) linkages. Amylopectin unit chains are relatively short compared to amylose molecules with a broad distribution profile. They are typically, 18–25 units long on average (Tester et al., 2006; Wurzburg, 1989).

Nutritionally, starch is consumed as an energy source, and it is the most abundant energy source in the human diet as it is present at high amounts in cereals, roots and tubers, which products range from breads, cookies, pastes to consumption as snacks, porridges, or as processed cooked grains (white rice, corn grain) or whole grains (whole grain of rice, wheat, popcorn, etc.).

It may be technologically considered as a nutrient of great versatility, with numerous applications in the food industries and others such as in cosmetics, pharmaceutical, paints, children toys, glues and adhesives, and nowadays as a biopolymer for the production of packagings.

This versatility is related to some characteristics of starch such as being of low cost and easy to undergo physical and chemical modifications which allow changes to the physical-chemical and rheological properties of starches.

The main starch modifications obtained with the use of the thermoplastic extrusion process will be addressed in this chapter.

2. Starch

The different kinds of starch with commercial importance are corn, wheat, potato and cassava starch:

- Corn, *Zea Mays*, is grown in most countries throughout the world. It requires, however, warmer climates than those found in the temperate zones to grow to maturity. It is classified into several kinds, with different uses (Table 1), and it has the largest production.
- Wheat starch granules are divided in two groups by size, B-starch (15 - 20 % and 2 - 15μ) and the larger A-starch (80 - 85 %, 20 - 35μ in diameter) granules. B-starch is contaminated with pentosans, fibers, lipids and protein to an extent requiring special treatment in the factory.
- Cassava is the term usually applied to the roots, and tapioca is the name given to starch and other processed products. There are many varieties of cassava, but they fall into two main categories, namely bitter and sweet cassava (*Manihot palmata* and *Manihot aipi*), depending on their content of cyanohydrins. For industrial purposes bitter varieties are most frequently used because of their higher starch content. Sweet cassava is preferred for food because of its taste and dough forming ability.
- Potato starch: 75% of the potato crop is grown for industrial processing and Danes produce per capita more starch than any other nation (Corn Production Source, 2011).

Corn	Scientific name	Use	Characteristics
Dent	*Zea mays Indentata*	Food, animal feed, and industrial products	Hard and soft starch Become indented at maturity
Flint	*Zea mays indurata*	Food, animal feed, and cornstarch manufacturing	Hard, horny, rounded, or short and flat kernels soft and starchy endosperm completely enclosed by a hard outer layer
Waxy	*Zea mays*	Special starches for cornstarch manufacturing	A waxy appearance (only branched-chain starch)
Sweet	*Zea saccharata* or *Zea rugosa*	Green corn is eaten fresh, canned, or frozen	High percentage of sugar
Popcorn	*Zea mays everta*	Popcorn	They are popped on exposure to dry heat
Indian	*Zea mays*	Food and animal feed	White, red, purple, brown, or multicoloured kernels
Flour	*Zea mays amylacea*	Tortillas, chips, and baked goods	Soft corn

* Corn Production Source (2011).

Table 1. Kinds of corn*

These four types of starches are industrially produced and present great applicability in the food industry. Other starch sources, such as other cereals, tubers and fruits are produced at smaller amounts, limiting their wide utilization, and some are produced with research purposes for viability of new starch sources (Govindasamy, 1996, 1997; Alves et al., 1999).

Starch must be gelatinized in the human diet in order to be digested by the amylolytic enzymes of the human digestive system. The classic model of obtaining gelatinized starches, where starch granules are slowly heated in a medium with little agitation and much water, which promotes imbibition, swelling and polymer release (Leach, 1965) for a prolonged time, such as in the obtaining of cooked rice, corn flour porridges, was replaced by other methods, such as extrusion, spray-drier and drum dryer, which promote fast starch gelatinization and followed by drying may obtain flours and/or pregelatinized starches of long-term stability and quick preparation.

Pregelatinized starches or flours are paste-forming products in the presence of cold water or (partially or totally) soluble products in cold water (Colonna et al.,1984) and present the following characteristics: they disperse more easily and absorb more water than their untreated matches, they form gel at room temperature and are less prone to deposit (Powell, 1965).

The use of gelatinized starch in food products affects their characteristics and qualities, such as bread volume and crumb (Williams & Lesselleur, 1970); elasticity and softness of pastas (pasta), digestibility and palatability, tolerance in the properties of beating and cake mixtures, ice creams, doughnuts, growth of sugar crystals in food products (Powell, 1965); texture, volume, shelf-live and stability during thawing of cakes and breads (Michael & Brown, 1968).

In the food industry, pregelatinized starches are used to achieve thickening or water retention without employing heat, for example, puddings, instant lactic mixtures and breakfast foods; to prepare ready-to-use bread mixtures, where the increased absorption and retention of water improves the quality of the product, to work as an agglutinant in the meat industry; and, as a filling for fruit pies, as they make the use of heat dispensable and increase flavor retention. They also have a non-food use, such as in the industries of textiles and in drugs, paper, metallurgy, etc (Powell, 1965).

Pregelatinized flours may be obtained on an industrial basis through extrusion or drum-drying and through the use of atomizers (spray-drier).

The use of atomizers is economically limited as starch pastes are highly viscous and require drying at a low content of solids (Chiang & Johnson, 1977).

Drum-dryers are simple and commonly used, but they present the disadvantage of high-cost products due to low efficiency, low production, difficult operation, constant need for drum maintenance and adjustment (Greenwood, 1976).

The extrusion process presents the advantages of versatility, high productivity and low cost (Smith, quoted by Harper, 1979) and more strict control of the desired gelatinization degree, where small modifications in the equipment and/or in the raw material may lead to different final results (El-Dash, 1982). According to Lorenz & Jansen (1980), the low cost of gelatinization through extrusion is due to the fact that it efficiently converts electrical energy into thermal energy and also the manpower and space per kilogram of cooked product required are lower than any other cooking method.

The market of fast preparation products has grown and many varieties of pregelatinized flours are available in the market nowadays. The main trends in the use of thermoplastic extrusion process applied to starchy ingredients will be approached in this chapter.

3. Thermoplastic extrusion process

El-Dash (1982) defined the process of thermoplastic extrusion as being a continuous process in which mechanical friction is combined with thermal heating in order to continuously mix, plasticize and gelatinize the starch, denature protein materials, restructuring them for the obtaining of products with new textures and shapes.

Single-screw cooking extruders were developed in the 1940's to make puffed snacks from cereal flours or grits. An expanding demand for precooked cereals and starches required machines with larger capacity, so extruders with a nominal capacity of 5 ton per hour were developed in the 1960's, with numerous news applications: snacks, infant feeding, pet foods, etc. In the 1970's products containing more than one component were developed, such as egg rolls and ravioli for coextrusion. Then, the use of two extruders in series, the first for cooking and the second one for forming and structuring, resulted in several products. At the end of the 1970's, the use of twin-screw extruders for food processing that expanded the range of application began (Mercier & Feillet, 1975; Linko et al., 1981; Harper, 1979). Finally, the extruders are meant for specific markets, as it will be seen for extruders intended for the productions of biodegradable packagings (Flores et al., 2010; Mandrogón et al., 2009).

Food extruders are generally available with segmented screws and barrel section, facilitating total control over the configuration of the machine to get a combination of various process parameters. Extrusion cooking is a high-pressure operation that provides sudden expansion of the processed products. The physical characteristics of the extrudate reflect the effectiveness of the process and suitability of ingredients (Patil et al., 2005).

Beneficial effects include destruction of antinutritional factors, gelatinization of starch, protein denaturation/texturization, increased soluble dietary fibre and reduction of lipid oxidation. But Maillard reactions between protein and sugars can reduce the nutritional value of the protein, depending on the raw material types, their composition and process conditions. Heat-labile vitamins may be lost to varying extents (Singh et al., 2007, Patil et al., 2005).

Some of the use applications of the extrusion process to physically and/or chemically modify starch both in the areas of food and biopolymers will be presented below.

3.1 Ready-to-eat cereals and snacks

They are produced with cereal flour and starch ingredients, the extruded products are highly expanded and have several shapes and textures.

Ready-to-eat cereals are manufactured from mixtures of cereal flour and starch combined with small amounts of malt, fat, sugars, emulsifiers and salt. The extrusion process requires moisture of 20% and temperature >150ºC, after the extrusion, they are dried and toasted.

Much research has been made to obtain ready-to-eat cereals, as the control of the extrusion process is rather complex, due to the large number of variables affecting it (Ostergard & Bjorck, 1989, Stojceska et al., 2009).

Some early works, such as that of Lawton et al. (1972) considered extrusion temperature and initial moisture in the raw material as the variables with greater effect on starch gelatinization, and the maximum degree of gelatinization and shear occur when these variables act with opposite end values and when both values are high or low, low degrees of gelatinization occur. Other works showed that the extrusion process destroys the organized crystalline structure of the starch granule, with different degrees of intensity which depend on the ratio of amylose to amylopectin and on the independent variables used such as humidity and shear (Charbonnieri et al., 1973). Thus, starch may be gelatinized, which is what occurs at the extruder with humidity lower than 20% (Linko et al.,1981), dextrinized, which happens in more severe conditions and with low humidity content (Gomez & Aguillera, 1983, 1984). The process may also lead to starch liquefaction and partial hydrolysis of starch molecules (Faubion et al., 1982).

The production of snacks through extrusion represents a great achievement for the Food Technology area as it efficiently converts crude cereal flours into products with different shapes, flavors and long shelf-life.

At first, snacks were obtained from whole grains combined with moisture content, cooking temperature and drying, considered the first generation (Huber & Rokey, 1990).

The second generation snacks presented more expansion ability, and were obtained with flours refined from cereals and cereal and tuber starches. These snacks have a large volume and require appropriate packagings to avoid humidity, light and heat, and they must protect the product against mechanical shocks, in order to avoid breaking during transport and storage. These facts boosted the development of third generation snacks (Huber & Rokey, 1990).

Third generation snacks are not expanded through the extrusion process, for this reason they are known as pellets or half-products, for they will be expanded through a process of deep-frying or hot air, or with the use of microwaves, during consumption. Although they have an additional process for expansion, these products present great advantages in transport and storage (Huber & Rokey, 1990).

With the worldwide tendency of weight gain by the population, studies showed that gelatinized starch, if excessively consumed, contributes to an increased number of diseases, such as obesity, diabetes and increased blood triglycerides, which may lead to serious heart diseases (Jenkins et al., 1980).

A ranking for starch has been made:

- Rapidly digestible starch (RDS): amount of glucose release after 20 min.
- Slowly digestible starch (SDS): amount of glucose released between 20 and 120 min of *in vitro* digestion.
- Resistant starch (RS): total starch minus amount of glucose released within 120 min of *in vitro* digestion (Singh et al., 2010).

Studies evaluating the digestibility of starches in snacks showed that they presented RDS type starch (Singh et al., 2007; Goni et al., 1997). Thus, the tendency is to promote the return of the use of the whole grain, addition of fibers and ingredients leading to increased SDS and RS in snacks, in addition to ingredients beneficial to health, such as antioxidants, and omega oils. That is, the new generation of snacks must include benefits to the consumer's health, in addition to being nutritious.

3.1.1 Oils

Abu-Hardan et al. (2011) investigated the addition of three commercial vegetable oils (1 to 8%) to extruded wheat starch, namely: palm oil, soybean oil and sunflower oil. The effects of the addition of the oils on the sectional expansion of extrudates was complex in which a significant increase up to a 5% oil concentration was reached and further increase of oil quantities resulted in a drastic reduction and no significant differences between oils were noticed. However, the crystallinity indexes indicated no interference from the three oils in the complex formation. These authors suggested that the endogenous lipids naturally present in wheat starch were sufficient to complex the starch.

3.1.2 Protein

Limón-Valenzuela et al. (2010) obtained a functional third-generation snack food with good expansion characteristics using a microwave oven, and this snack has health benefits due to the addition of milk protein concentrate (0-10%) and quality protein maize (20%) in a blend of corn starch (80%). These authors used a laboratory single-extruder with a 3:1 compression ratio, feed moisture (20-30%), a rectangular die, and a central composite non-routable model with two variables

According to the increased demand for new healthy snacks as an alternative for fried starch-based snacks with low nutrient density, Cho & Rizvi (2010) showed the potential of supercritical fluid extrusion (SCFX) technology for healthy snack food production containing high whey protein concentration. SCFX chips had uniform cellular microstructure that cannot be obtained using conventional steam-based extrusion.

Lobato et al. (2011) developed a functional puffed product for extrusion containing 250 g/kg corn starch, 375 g/kg soy flour, and 375 g/kg oat bran extruded under the process conditions of 250 g/kg moisture; 45 g/kg inulin and 130ºC). The puffed product had 212.6 g/kg fiber, 281.0 g/kg protein, and a caloric value of 319.1 kcal/100 g and it was well accepted by the panelists in the sensory evaluation, mainly in terms of texture.

3.1.3 Fibers and resistant starch

Céspedes et al. (2010) obtained extruded orange pulp using a Brabender laboratory single-screw extruder (20:1 Céspedes 2010) and observed that it could also be added to high-fiber foods as a low-calorie bulk ingredient to reduce the calorie level, since it showed potential hypoglycemic effects.

Souza & Lionel (2010) verified that the mixture of cassava starch and dried orange pulp extruded under different conditions (0 to 20% of fibers in the mixture), (14.6 to 21.4% moisture), and (60.8 to 129°C temperature of extrusion), could aim at the use in high-fiber instant products.

Bello-Pérez et al. (2006) extruded starches isolated from unripe banana (*Manguifera indica* L.) and mango (*Musa paradisiaca* L.) fruits to obtain a product with high content of resistant starch (RS) and verified that RS formation in the extruder for banana starch was affected positively by temperature and inversely by moisture. Moisture did not significantly affect RS formation in mango starch.

Two types of products were produced: pure whole meal products and breakfast cereals made from whole meal/maize blends were processed by pilot-plant extrusion and the enzyme-resistant starch (RS) content and hydrolysis index (HI) were not correlated to the extrusion temperature, but with whole meal products (Chaunier et al., 2007).

Yanniotis et al. (2007) verified the effect of pectin alone or in combination with wheat fiber on the physical and structural properties of extruded cornstarch, under specific moisture content, barrel temperature and screw speed conditions were studied using a laboratory single-screw extruder. These authors observed that fibers reduced the size of the cells and increased their number and pectin increased porosity and reduced expansion ratio and hardness of the snacks.

Stojceska et al. (2009) investigated the use of brewer's spent grain and red cabbage barley and red cabbage in wheat flour and corn starch extruded in co-rotating twin-screw extruder, under the conditions studied, the results were promising towards the increase of total dietary fibre and the level of total antioxidant capacity and total phenolic compounds of the snacks.

3.1.4 Antioxidant activity

The blends of various formulations of durum wheat flour (8-20%), partially defatted hazelnut flour (PDHF) (5-15%), fruit waste blend (3-7%) and rice grits were extruded using single-screw extruder and when higher, PDHF and fruit waste content caused an increase in the total phenolic content and antioxidant activity of the extruded samples, whereas percentage starch gelatinization and digestibility values decreased (Yaĝci & Göĝûş, 2009).

Limsangouan et al. (2010) demonstrated the effect of extrusion processing on the functional properties of extruded snack foods developed from cereal and legumes, and the by-products from herbs and vegetables, and the extrusion process slightly decreased the antioxidant capacity and phenolic content.

Table 2 shows new starches that are been used in thermoplastic extrusion researches.

3.2 Chemical modification of starches

Starch may be modified through physical or chemical methods and its use relates to improved quality and decreased cost of the products.

According to Light (1990), modified starch is used in foods, for 3 main reasons:

- to provide functional features in food applications which native starches may not normally provide. For example: pudding mixture,
- it is readily available, and
- provides economical advantages in many applications where more expensive additives are used. For example: gums.

Some researchers used simultaneously a chemical reagent and the extrusion process to obtain modified starch for various purposes, such as production of expanded extruded products (Lai et al., 1989); starch phosphate production (Chang & Lii, 1992); alcohol production (Chang, 1989), extruded rice flour (Clerici & El-Dash, 2006) and acidic extruded rice flour (Clerici et al., 2009) for production gluten-free bread, and lactic beverage production (Lee et al., 1992) . The simultaneous use of these modifications poses advantages such as saving reagent, and absence of effluent formation, low reaction time, processing at lower moisture content, and the elimination of drying the starch dispersion.

Starch or flour	Process	Application	Reference
Sago +Alfa-amylase	Single screw extruder	Hydrolylisis or dextrinization	Govindasamy (1997)
Sago	Co-rotating twin-screw extruder	Limited degradation	Govindasamy (1996)
Yam (*Dioscorea alata*)	Single screw extruder	Decrease of retrogradation tendency, high cold thickening capacity, high gel strength	Alves et al. (1999)
Foxtail millet grains	Flaked, extrusion cooked and roller-dried products	Ready-to-eat , popped millet	Ushakumari et al. (2004)
Unripe banana (*Manguifera indica L.)*	Single-screw equipment	No effect in the resistant starch formation	Bello-Pérez et al. (2006)
Mango (*Musa paradisiaca L.*)	Single-screw equipment	No effect in the resistant starch formation	Bello-Pérez et al. (2006)
Amaranth flour *Amaranthus cruentus* L	Single-screw equipment	Potential for use in instant meal products	Menegassi et al. (2011)

Table 2. News source extruded starches

3.2.1 Starch phosphates

Native starches usually contain small amounts of phosphorus (0.1%). In tubers and roots, phosphorus is covalently bound to starch (Hodge et al., 1948), while in cereal starches, it occurs mainly as a phospholipid contaminant (Lim et al., 1994).

Starch phosphates are esters derived from phosphoric acid. When only a hydroxyl is involved in the starch phosphate binding, the product is a monoester. The other starch phosphate class is the *cross-linked* type which contains mono-, di- and triester starch phosphate (Hamilton & Paschall, 1967). Approximately 60%-70% of total phosphorus of starch monophosphate is located at C-6 while the rest is located at C-3 of anhydroglucose units (Tobata & Hizukuri, *apud* Wurzburg, 1986). Most phosphate groups (88%) are on chain β of amylopectin (Wurzburg, 1986)

Cross-linked starch is obtained by introducing an agent capable of reacting with the hydroxyl groups of two different molecules within the granule. These synthetic bridges reinforce the natural hydrogen bonds, delaying the speed of granule swelling and reducing the rupture of the swollen granule (Wurzburg, 1986). Its main use is as filling in fruit pies and canned goods.

Chang & Lii (1992) compared the conventional process to that of extrusion for phosphatation of cassava and corn starches and they verified that, in order to prepare starch phosphate with a similar degree of substitution, the extrusion process requires less reagent than the conventional method, and the latter requires an excessive amount of reagents and causes water pollution, increasing the cost of production.

Salay & Ciacco (1990) also found that it is possible to obtain starch phosphate with a low degree of substitution (DS) value through the extrusion process and observed that the extrusion temperature of 200°C, concentration ≥ 1.4 g/100 mL of sodium tripolyphasphate and pH 8.5 were the conditions that resulted in a higher value of DS.

Nabeshima & Grossmann (2001) obtained cassava cross-linked starch with different DS and degree of gelatinization for use in food by using cassava starch with sodium trimetaphosphate (STMP) processed on a Cerealtec single-screw extruder at different extrusion temperatures and concentrations of STMP and NaOH.

Seker et al. (2003, 2004, 2005a, 2005b) mixed starch with sodium hydroxide and sodium trimetaphosphate, the mixture was then extruded in both single- and twin-screw extruders and it was verified that the mixing elements did not change the amount of phosphorus incorporated into the starch in both processes. They developed works showing the phosphatation process through starch extrusion and its changes in rheological properties.

3.2.2 Acid-modified starch

Acid-modified starch suffers hydrolysis of some glucosidic bonds, which occurs first in the amorphous regions of the starch containing branch points and α-D bonds (1→6), reducing the molecular size and diminishing the viscosity of the paste. Depending on the treatment intensity, there is formation of dextrins (Wurzburg,1986). Kerr, quoted by Wurzburg (1986) showed that during acid modification, the amount of starch amylose increases, indicating that acid preferably hydrolyses amylopectin.

Acid-modified starches are normally made out of a starch paste (about 36% to 40% of solids) heated at a temperature below the starch gelatinization temperature (about 40°-60°C) and the addition of mineral acid, agitation for a varied period (about one to several hours). When viscosity or degree of conversion desired is reached, the acid is neutralized and the starch is retrieved through filtration or centrifugation, washing and drying. The type of mineral acid, its concentration, temperature, starch concentration and reaction time influence starch properties (Wurzburg, 1986).

Acid-modified starches differ from granular starch in lower viscosity of the paste (under cold and hot conditions) and other properties. However, they have the same physical form, insolubility in cold water and similar birefringence (Shildneck & Smith, 1967).

The literature indicates, most of the times, starch modification through mineral acid. However, Mehltretter (1967) used organic acids to modify starch and found that some carboxylic acids such as formylic acid react with starch at room temperature and in the presence of water; whereas other acids, such as acetic acid and citric acid do not react in an aqueous medium and require heating to force the reaction.

3.3 Biodegradable polymers

Due to increasing environmental awareness and the environmental legislations, scientists around the world have made strong efforts to develop methods using natural polymers as an alternative to the petroleum synthetic polymers for industrial and consumer applications. (Liu et al., 2009).

Biodegradable polymers represent a promising solution to the environmental problem of plastic waste disposal. Among the candidate polymers, starch, a low-cost natural polymer, can be processed as a thermoplastic (Rosa et al., 2008).

Starch is being researched both for the production of biodegradable packagings with the use of extrusion blow molding machine, where bags are made even for the formation of edible films to coat industrialized foods or fruits.

The shelf-life of foods is governed by their numerous interactions with their surroundings and can be extended by using protective films. The deterioration of packaged foodstuffs largely depends on the transfers that may occur between the internal environment of the packaged food and the external environment. Edible films can be used to reduce water vapor, oxygen, lipid, and flavor migration between components of multicomponent food products, and between food and the surroundings. Many proteins and polysaccharides have good film-forming properties and can be used in the preparation of edible films (Torres, 1994).

For packagings, which will be used for food transporting, such as bags and boxes, plasticized starches that are commonly called thermoplastic starches (TPS) are used (Stepto, 2003).

TPS can be processed through traditional processing conditions (extrusion, blow molding and injection molding increase the properties of the blends and the content of TPS in TPS/PE blends (Rodriguez-Gonzalez et al., 2003).

Carvalho et al. (2005) used carboxylic acids to decrease the viscosity of TPS by controlling the macromolecules of starch. After melt processing in the presence of glycerol, water and carboxylic acids, both the molar masses and viscosity of TPS are decreased. In their previous work (Yu, Wang & Ma, 2005) citric acid (CA) is also used as an additive to modify TPS during melt processing. CA can effectively restrain starch re-crystallization, except for increasing the fluidity of TPS. But the mechanical properties of TPS are decreased, especially the tensile strength (below 4 MPa).

Chaudhary et al. (2008) obtained thermoplastic resin with a mixture of different concentrations of unmodified starches with 0%, 28%, 50% and 80% amylose; 80% amylose hydroxypropylated starch using extrusion process with several variations of screw speed, die pressure, motor torque, mean residence time and specific mechanical energy.

Pea starch-based composites reinforced with citric acid-modified pea starch (CAPS) and citric acid-modified rice starch (CARS), respectively, were prepared through screw extrusion to obtain biodegradable polysaccharide (CA-modified granular starch/TPS) composites to be used with a potential replacement for edible films, food packaging, biodegradable packaging, etc. The CARS/TPS composites exhibited better storage modulus, tensile strength, elongation at break and water vapor barrier than CAPS/TPS composites because of the smaller size of granular CARS (Ma et al., 2009).

Flores et al. (2010) used a mixture of experimental design to study the physical and microbiological properties of tapioca starch-based glycerol edible films with the addition of xanthan gum (XG) and potassium sorbate (PS) and obtained through extrusion technology. The results showed that PS presence decreased the ultimate tensile strength and elastic modulus and increased strain at break. XG produced a reinforcing effect on the films and also enhanced solubility in water and decreased moisture content.

Guan & Hanna (2006) have extruded biodegradable composite foams based on starch acetate and poly (tetraethylene adipate-co-terephthalate) (EBC). It was reported that low EBC contents in the blends favored the miscibility of the two polymers, as characterized by an increase of the glass transition temperature of starch acetate, a decrease in the melting point temperature of starch and EBC in a differential scanning calorimetry (SEM) analysis and the formation of a homogeneous morphology observed with SEM. Large amounts of EBC decreased the miscibility of these two polymers.

Multifunctional epoxy-based copolymers can be used as chain-extender (CE) to increase the molecular weight and create branching in polylactides (PLA). Li & Huneault (2011) studied the effect of a multifunctional epoxy-acrylic-styrene copolymer on the properties of PLA/Thermoplastic Starch (PLA/TPS) blends that were prepared by twin-screw extrusion. The plasticizers were mixed together in the first half of the extruder to complete starch gelatinization. Water was removed by devolatilization at midex-truder and the PLA matrix was mixed with the water-free TPS in the latter portion of the compounding process. The standard blends comprised 27% TPS in the PLA matrix. The TPS phase itself comprised 36% plasticizer in the form of glycerol or sorbitol. The blends were injection molded into standard test bars and their tensile properties were measured. It was found that the combination of interfacial modification and chain-extension strategies led to greatly improved ductility. The viscosity of the PLA/TPS blends was also dramatically increased by adding a small amount of epoxy-based chain extender. This is of great interest for polymer processing techniques (such as foaming or film blowing) that require high melt strength.

Nabar et al. (2006) produced the cylindrical starch foam shapes on a small scale (~11-12 kg/hr) Werner Pfleiderer ZSK-30 twin-screw extrusion (TSE) process using water, which functions as a plasticizer as well as a blowing agent. The properties of the starch foams depend on the type of starch used (hydroxypropylated high amylose corn starch, 70% amylose), the amount of water and additives (poly(hydroxyamino ether)) (PHAE) used, and extrusion conditions such as temperature and the screw configuration.

Table 3 summarizes some other works with biopolymers using starch as base.

Starch+ Polymers or another composite	Process	Authors
Potato starch + polypropylene	Corotating twin-screw extruder	Roy et al. (2011)
Tapioca starch+ glycerol	Twin screw extrusion at 150°C	Yunos & Rahman (2011)
Starch + polylactides (PLA)/ Thermoplastic starch (TPS)	Twin-screw extrusion	Li & Huneault (2011)

Starch+ Polymers or another composite	Process	Authors
TPS + PLA	Co-rotating twin-screw extruder	Świerz-Motysia et al. (2011)
Thermoplastic acorn starch(TPAS)/ Polycaprolactone (PCL) + different plasticizers:ethylene glycol, glycerol, monoethanolamine, iminobisetnanol and triethanolamine	Hot-melt extrusion	Li et al. (2011)
TPS + poly (butylene adipate-co-terephthalate – PBAT) + organically modified nano-clays	Melt intercalation technique	Mitrus & Mościcki (2011)
Starch+ chitosan + oregano essential oil	Single screw extruder	Pelissari et al. (2011)
Cassava starch+ glycerol + vegetable fibres	Single screw extruder	Debiagi et al. (2010)
(hydroxypropylated high amylose corn starch + amylase+ water and additives (poly-hydroxyamino ether- PHAE)	Twin-screw extrusion and cylindrical starch foam shapes	Nabar et al. (2006)
High amylose potato starch and normal potato starch+ glycerol	Buss co-kneading extruder	Thuwall et al. (2006)
TPS /natural rubber/montmorillonite type clay nanocomposites	Twin-screw extrusion	Mondragón et al. (2009)
Corn starch+ low density polyethylene (LDPE)	Singlestep twinscrew extrusion or by a twostep process involving compounding (pelleting) of the ingredients before film formation	Pushpadass et al.(2010)
Cassava TPS + PBAT+ surfactant Tween 80	Extrusion	Brandelero et al. (2010)
TPS–silica (sio2) PVOH composite films + tetraethyl orthosilicate (TEOS)	Extrusion	Frosta et al. (2011)
High amylose hydroxypropylated starch + films nanosilicate additives+ montmorillonite	Extrusion	Dean et al. (2011)
Wheat flour+ glycerol	Extrusion followed by compression molding	Sreekumar (2010)
Tapioca starch–glycerol+ xanthan gum (XG) + potassium sorbate (PS)	Extrusion technology	Flores et al. (2010)
TPS+ glycerol	One-step combined twin-screw/single screw extrusion	Rodriguez-Gonzalez et al. (2003)
TPS + glycerol	Extrusion	Rosa et al. (2008)

Table 3. Biodegradable polimers obtained with thermoplastic extrusion

4. Conclusion

The thermoplastic extrusion process is capable of causing changes in starch, making it present a large variety of applications both in the food industry and in other industries; and, as a matter of fact, the use of starches in packagings has increased due to the easy process in modifying and promoting interactions between starch and other polymers.

5. References

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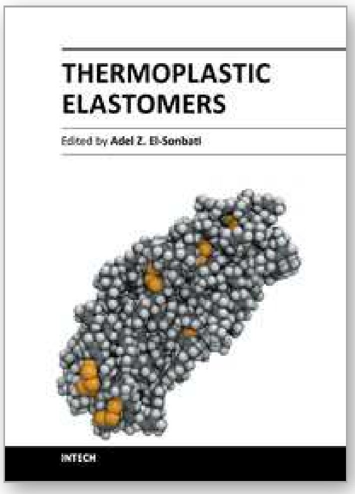

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Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

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InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821