

Review Article

Chemical Modifications of Starch: Microwave Effect

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This paper presents basic methods of starch chemical modification, the effect of microwave radiation on the modification process, and the physicochemical properties of starch. It has been shown that the modifications contribute to improvement of the material performance and likewise to significant improvement of its mechanical properties. As a result, more and more extensive use of starch is possible in various industries. In addition, methods of oxidized starch and starch esters preparation are discussed. Properties of microwave radiation and its impact on starch (with particular regard to modifications described in literature) are characterized.

1. Introduction

Starch is a commonly used biodegradable polymer which is increasingly used in many branches of industry because of its respective physicochemical properties [1]. It is naturally occurring in grains, fruits, and roots and tubers of plants and acts as their main storage material. It is obtained from potatoes, corn, wheat, and rice in separation process. Chemically, starch consists of two polysaccharides: linear amylose, wherein the units of α -D-glucopyranose are linked with α (1 \rightarrow 4)-glycosidic bonds (Figure 1), and branched amylopectin in which additional α (1 \rightarrow 6)-glycosidic bonds are present (Figure 2) [2, 3].

The starch may also contain proteins, lipids, water, and very small amounts of phosphorus, magnesium, and calcium compounds [4].

As a consequence of unfavorable properties of the native starch, like poor solubility and high hydrophilicity, it is being subjected to various modifications. The most common methods of providing significant improvement of the starch properties are chemical, physical, and enzymatic modifications. Figure 3 shows the basic methods of starch modification [5, 6].

2. Chemical Modifications of Starch

In general, the susceptibility of starch to modification is determined, primarily, by the fact that the material is biodegradable, by its macroscopic granular structure, and by the presence of certain functional groups. Moreover, depending on the location of the hydroxyl group and the bond type (α (1 \rightarrow 4)-glycosidic versus α (1 \rightarrow 6)-glycosidic), starch reveals different properties when chemical modification is concerned.

Hydroxyl group at carbon C6 is primary alcohol while at C2 and C3 carbons it is secondary alcohols. Starch is a triol when the glucose ring part $-\text{CHOH}-\text{CHOH}-$ is present in place of carbon atoms C2 and C3, and when there are glycosidic bonds present it is a hemiacetal [7].

It is the presence of the three hydroxyl groups in glucose that makes it susceptible to substitution reactions and enables the number of possible modifications of starch.

The grain size of the starch also affects its reactivity. The larger the grains are, the higher the modification susceptibility is. This is because in the case of larger grains the external factors have easier access to them [8].

The modification is the process of changing the typical properties of native starch by physical, chemical, or enzymatic

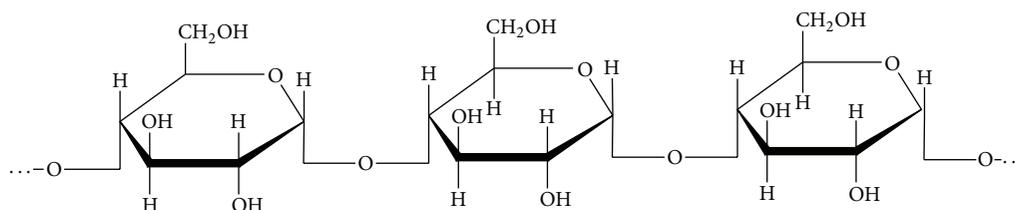


FIGURE 1: Amylose.

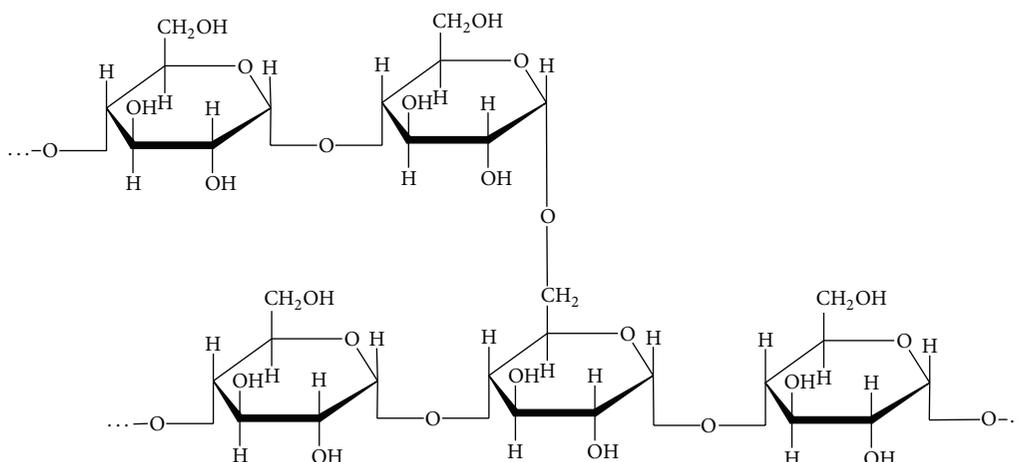


FIGURE 2: Amylopectin.

means. Although recently there is great interest in the physical modifications of starch (such as radiation as well as high and low temperature treatment), on industrial scale, chemical modifications are still the most commonly used. Among them are three basic reactions: oxidation, esterification, and etherification [9, 10].

2.1. Oxidation. Oxidation of starch is one of the most popular modification methods. The process involves oxidation of primary or secondary hydroxyl groups of the glucose units with formation of aldehyde or carboxyl groups.

Efficacy of oxidation depends on the type of oxidant used, the botanical origin of starch, and the process conditions. Moreover, the oxidation reaction may cause loosening of intermolecular bonds and/or partial depolymerization of the polymer chains [11].

The oxidized starch has better water solubility, lower viscosity, and retrogradation tendency in comparison to the native one [8].

The oxidation of starch can be carried out using oxidizing agents such as air or oxygen (in the presence of catalysts such as transition metal ions), inorganic peroxides (H_2O_2), organic peroxides ($NaClO$, $NaIO_4$), nitrogen compounds (HNO_3 , N_2O_4), and organic oxidants as well as metal compounds (CrO_3). A special case of oxidation is the combustion reaction resulting in a carbon monoxide and water [12].

The most important among starch oxidants are hydrogen peroxide, sodium hypochlorite, and sodium periodate [12]. Unfortunately, during processes involving these oxidants,

toxic substances are emitted into the environment making application of such oxidation limited. In fact, oxidized starches are very often used as food additives although their specific physicochemical properties provide additional variety of applications not solely for the food industry, like, for example, textile and paper industries [13].

2.1.1. Oxidation with H_2O_2 . Hydrogen peroxide appears to be a very promising oxidant of organic compounds, mainly, because of the peroxide's beneficial environment-friendly qualities like safety of use and production of nontoxic wastes (such as water). In fact, use of hydrogen peroxide is becoming more popular. The oxidant is characterized by very high content of active oxygen (47%) and very high oxidation potential (1.77 V), which makes it greatly effective and yet inexpensive oxidant. A limitation of the use of hydrogen peroxide is its low reactivity towards most organic functional groups and the fact that in the presence of the compounds with electrophilic character it behaves as a nucleophile, not exhibiting oxidizing properties [14].

As a result of the activation of hydrogen peroxide with catalysts such as metal ions, for example, Cu (II), Fe (II), Fe (III), Co (II), Ti (III), W (VI), or V (V), this unfavorable property can be eliminated. However, this type of oxidation cannot be applied while modifying starch for food, cosmetic, and pharmaceutical industries because obtained products may be contaminated by heavy metal ions which are strongly complexed by the oxidized starch [14, 15].

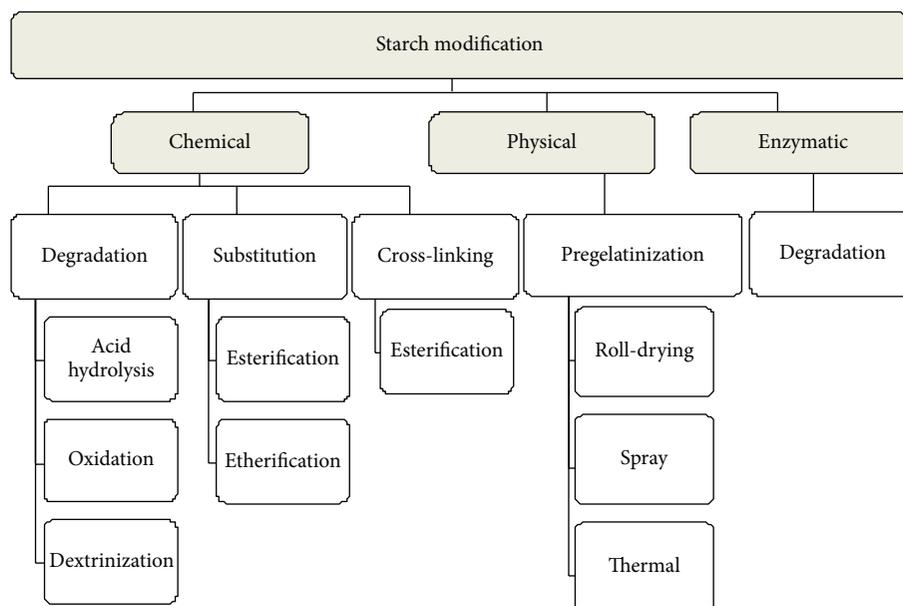


FIGURE 3: Methods for modification of starch.

Oxidation of starch with H_2O_2 mediated with metal catalysts follows radical or ionic mechanism. Radical mechanism dominates in reactions catalyzed with copper and iron compounds [16]. It is called Fenton's reaction. The process yields starch possessing aldehyde groups that can be oxidized "further" into carboxylic acids. It should be also clear that the depolymerization of the polysaccharide chains occurs during the oxidation of starch with H_2O_2 . Furthermore, starch loses its crystallinity, its hydrophobicity increases as a result of depreciation of the hydrogen bonds, and thermoplastic properties are improved [16].

2.1.2. Oxidation with $NaClO$. The process of starch oxidation in the presence of sodium hypochlorite ($NaClO$) occurs in a gelatinized polymer solution. Primary hydroxyl groups are oxidized into either aldehyde or carboxyl groups. The oxidation, depending on the process conditions, converts only 1 per 35–50 glucose units and a partial depolymerization of the polysaccharide main chains was observed. Depending on the concentration of the oxidant, the botanical origin of starch, and the pH, various degrees of starch oxidation are obtained. Transformation of larger number of groups can be obtained by using high concentration of the oxidant and carrying the reaction out at a lower pH. Botanical origin of the starch, or more specifically the protein content in the starting material, also affects the modification of hydroxyl groups. This is caused by the fact that initially proteins are oxidized followed by starch reaction. The starch oxidized by $NaClO$ is characterized by higher resistance to amylase activity and better stability at higher temperature and is capable of complexing calcium ions while exhibiting the polyelectrolyte properties. Starch oxidized with sodium hypochlorite is referred to as E 1404 and is the only one approved as a food additive. The E 1404 was used as a stabilizer in cake fillings and during ketchup manufacturing

and as gelation agent and thickener for creams, puddings, sauces, and jellies.

Additionally, such oxidized starch was used in the paper industry to increase paper's resistance to tearing [8, 17].

2.1.3. Oxidation with $NaIO_4$. Starch oxidation with sodium periodate causes C2 and C3 carbons bond cleavage and aldehyde group formation. As a result of this process, dialdehyde starches are formed (Figure 4) which are widely used in many industries. The dialdehyde starches are used in the paper industry and food industry and as the raw materials for the production of biodegradable plastics. The oxidation of dialdehyde starch leads to production of a dicarboxylic starch [18, 19].

To obtain more favorable properties of the products (lower viscosity and better water solubility), oxidation is carried out after prior gelatinization. In the process of gelatinization, both intramolecular and intermolecular hydrogen bonds are cleaved, so chemical reactions proceed easier as a consequence of easier penetration of the gelatinized starch [20].

2.2. Esterification. On the other hand, starch is modified to improve its hydrophobicity *via* esterification. Hydrophobization of the starch improves its thermoplastic character. Obviously, starch esterification involves hydroxyl groups which are converted into hydrophobic ester groups. The susceptibility of starch to esterifying agents allows the synthesis of a number of starch esters, which are used in both food and nonfood applications. Numerous syntheses of starch esters are caused by the fact that starch has two or three hydroxyl groups per glucose unit which can be converted into ester groups. Esterification takes place under the influence of organic and inorganic acids and their derivatives such as acid anhydrides, oxychlorides, and chlorides. Starches yielding high degree

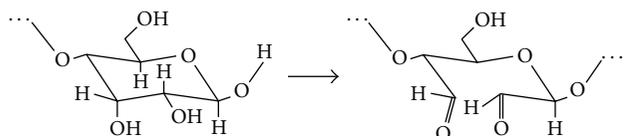


FIGURE 4: Formation of dialdehyde starch.

of substitution (DS) are obtained under stringent reaction conditions [21].

2.2.1. Starch Acetates. Starch acetates are obtained mainly by esterification of starch with acetic acid or acetic anhydride. Mark and Mehlretter proposed a method of native starch acetylation with acetic anhydride carried out in the presence of an activator which was a sodium hydroxide solution [22] while Kakusche and Rappthel applied acetic acid as an activator a few years later [23].

Recently, Volkert and Lehmann applied potassium carbonate as the activator in the reaction of starch acetylation with acetic anhydride and obtained the starch esters with the highest degree of substitution [24]. Starch acetates are commonly used in the food industry as an ingredient in salad dressings (E1420), mayonnaise (E1422), and the ice creams production (E1414).

2.2.2. Starch Phosphates. Among the modified starches, starch esters of phosphoric acid were widely used due to their very attractive properties such as the ability to swell in cold water and tend to form viscous dispersions. There are monostarch phosphates and distarch phosphates [25]. Monostarch phosphates are obtained after treatment with sodium or potassium phosphates (V). In comparison to native starch, the phosphates have the ability to swell in cold water and they reveal high water binding capacity.

Salts of starch phosphate esters containing magnesium, calcium, or aluminum ions are used in the pharmaceutical industry, whereas phosphate esters without metal ions are used in the food industry and they act as a thickener in the desserts (E1410).

The phenomenon of swelling and the values of swelling power are widely described in the literature [26–31]. Table 1 shows the values of swelling power of the different types of starch [28].

Distarch phosphates are formed by the action of phosphorus oxychloride or sodium trimetaphosphate on starch. The degree of cross-linking of the starch diphosphate influences its ability to swell. Grains with high degree of swelling manifest greater resistance to high temperature and mechanical impact. At a low degree of cross-linking, material has high swelling ability but with increasing degree of cross-linking; swellability in water decreases, until complete loss of this ability [32].

In parallel with the increase of cross-linking, temperature of gelatinization and viscosity of gruel are also growing. However, at high degrees of cross-linking, this viscosity decreases, which involves loss of swellability in water. Distarch phosphates also exhibit stability during freezing and thawing; they

TABLE 1: The values of swelling power [28].

Starch source	Swelling power (g/g) [°C]
Normal wheat	18.3–26.6 (100)
Normal potato	1159 (95)
Normal corn	22 (95)
Normal rice	23–30 (95)
Starch (phosphorus content (0.17%))	5.1 (50)
Starch (phosphorus content (0.36%))	3.7 (50)

are resistant to elevated temperatures and do not have the retrogradation tendency. The distarch phosphates are mainly used in the food industry including manufacture of potato dough products (E1442) [33].

3. Microwave-Assisted Modification of Starch

Microwave radiation is the electromagnetic radiation in range from 3000 MHz to 30 GHz (Figure 5) and is one of the physical methods used to improve the functional properties of starch. It is a very good source of energy and allows fast transfer of the energy into interior of the material where the energy is converted into heat, along with significant reduction of processing time when compared to conventional processes. Microwave field also has influence on the properties of the finished product [35].

Recently, microwave radiation is commonly used in various processing methods such as toasting, heating, thawing, and sterilization in industrial applications as well as at home. Therefore, research is conducted also on the effect of microwave radiation on the physicochemical properties of starch [36].

3.1. Properties of Microwave Radiation. Microwave radiation has many advantages of which the most important are fast process, selectivity of heating, and volumetric heating and what is most significant is that microwave heating is environmentally friendly. In addition, microwave heating helps reducing operating costs, because the energy produced by microwaves is focused on material which significantly improves the performance of implemented processes [37].

Confirmation of microwave radiation advantage over conventional methods of synthesis is provided in works of Xing et al., who conducted synthesis of starch maleate in bulk. For this purpose, they used a household microwave oven for reaction of dried corn starch with maleic anhydride. After 5 minutes of exposure to the microwave, they achieved a degree of substitution equal to 10%, which corresponds to 98% conversion [38].

Also Bogdał et al. conducted research on the effect of microwave heating on the reaction of salicylaldehyde with chloroacetic acid ethyl ester in the presence of potassium carbonate and tetrabutylammonium bromide as catalysts. This reaction was carried out in duplicate at the same temperature but first with conventional heating (oil bath) while the second one was microwave-assisted. The reaction

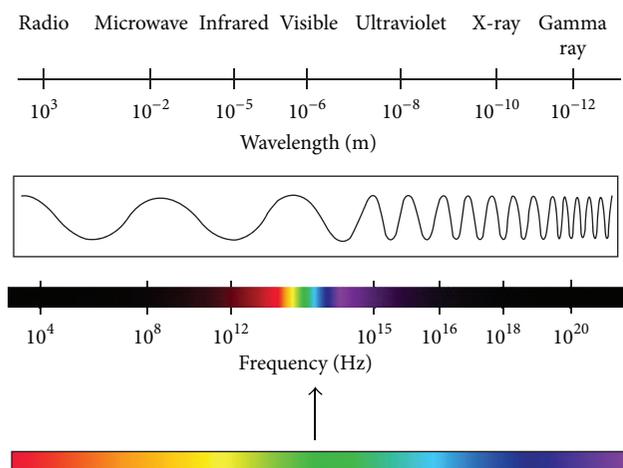


FIGURE 5: The electromagnetic spectrum.

yield was significantly higher when microwave radiation was applied, in particular, at lower temperatures [39].

Despite the beneficial properties of microwave field, this kind of irradiation has some limitations. This may be due to the problem of optimization of process parameters and financial outlays necessary to be incurred when purchasing specialized equipment. Applying microwaves is still being limited by insufficient knowledge of the dielectric properties of heated materials.

In case of materials in which the dielectric constant increases with the temperature, microwave heating may cause uneven heating and can lead to the thermal instability (degradation) of the material.

Achieving the proper and uniform temperature during microwave heating can be difficult and requires continuous monitoring of the process. Factors influencing the behavior of starch in microwave field are those dependent on starch, which are its type, water content, density, dielectric properties, the penetration depth, and factors associated with the microwave treatment process, which are frequency, power, and time of exposure [40, 41].

3.2. The Impact of Microwave Radiation on Starch. Already in the 90s of the 20th century, Muzimbaranda and Tomasik as well as Lewandowicz et al. were investigating the impact of microwave irradiation on starch [42, 43].

Frequencies used in industrial microwave ovens are equal to 915 MHz and in household microwave ovens 2450 MHz. The main effect of microwave interaction with the material is dielectric heating.

Strong heating of water contained in the material occurs which is caused by the rapid reorientation of the dipoles and the plucking of hydrogen bonds. Eventually, this results in the formation of structural changes [44–46].

When using the microwave frequencies (2450 MHz), the dielectric constant value and the dielectric loss value depend on water and salt content in the material.

The dielectric constant is characterizing the microwave penetration into the starch, and the dielectric loss factor indicates the ability of starch to store the energy. The penetration depth of microwave radiation is regulated by the microwave frequency and the dielectric properties of the material [46].

Motwani et al. studied the dielectric properties of corn starch slurries of 10–50% w/w; starch concentration was measured in the frequency range from 15 MHz to 3 GHz and at temperature between 40°C and 90°C. As a result of the reduction in the polarisability of water molecules, the dielectric constant decreased with increasing starch concentration. The dielectric constant of starch slurries decreased with increasing temperature throughout the frequency range (15 MHz–3 GHz). It increased with the temperature in the frequency range of 15–450 MHz and decreased with the temperature in the higher frequency range of 450 MHz–3 GHz [47].

The dielectric properties are very important factors in microwave processing of granular starch and are strongly dependent on type of starch, moisture content, microwave frequency, and temperature [41].

Originally, it was thought that nonmodified starches belonging to the dry ingredients of the food are electrically neutral, so most of the work on the interaction of microwave field on starches relied on systems containing large amount of water [42]. Even small doses of microwave radiation in systems of this type resulted in the gelatinization of the starch slurry, with no change in the solubility of the starch. Higher microwave energy induced degenerative changes, and in the case of microwave radiation effect on acidified gruel, total depolymerization of starch to glucose occurred [48].

3.3. Effect of Microwave Heating on the Physicochemical Properties and the Structure of the Starch. During microwave heating, the temperature increase is affected by the microwave power and the type and moisture of the starch; therefore, the relationship of temperature increase over time is nonlinear. Water content in the material has significant effect on the heating process. Research has shown that the starch samples with low moisture undergo transformation differently than samples with high moisture. In the case of starches with low humidity (in the range of 1–5%), rapid rise in temperature occurs, whereas at higher moisture in the range of 7–15% increase in temperature is less pronounced. When moisture of starch is above 20%, there is a plateau period present, which is longer with the increase of moisture. These correlations are inconsistent with the idea that dehydrated foods are electrically neutral and that the microwave heating is affected only by the water content. Slower rate of temperature rise in the samples with higher moisture content is due to the fact that water has high specific heat capacity, which makes it a very good cooling-heating medium [41].

Microwave processing is able to change the gelatinization mechanism and affects the rheological properties of the starch. Gelatinization is one of the most important functional properties of starch and has a particular meaning in the processing. Microwave effect on the starch in general leads

to an increase of gelation temperature and decrease of the process enthalpy, which occurs under the influence of structural changes of the starch macromolecules [43].

Microwave heating can bring the significant changes in the rheological properties of starch, especially, reducing its viscosity.

In their studies, Lewandowicz et al. observed a significant decrease in viscosity when wheat and corn starch with 30% of moisture was treated by using microwave power of 0.5 W/g [49].

By studying the swelling ability of waxy corn starch under the action of microwave radiation, it turned out that they were nearly unchanged. This is because the waxy corn starch is made of almost only amylopectin which, opposite to amylose, is resistant to heating [43].

The study is also a source of knowledge on the impact of microwave heating on the structure and properties of starch. In the case of air-dry potato and corn starches, microwave radiation induces changes in properties such as solubility and reduction ability at the level similar to those caused by conventional heating at 130–200°C [43, 50].

Determination of the microwaves impact on starch structure, and more accurately grain structure and crystalline form, was possible using a scanning electron microscope (SEM), X-ray crystallography (XRD), near infrared (NIR), and Fourier transform infrared spectroscopy (FTIR). Starch, depending on the water content, its botanical origin, and the parameters of the microwave reactor used, is characterized by differences in the morphology of the grains. By comparison of the structure of native starch and starch treated with microwaves, changes in the appearance of starch granules can be observed [51].

The SEM micrographs of the native and microwave treated starch are presented in Figure 6. Microwave treating changed the structure of starch granules. Native starch granules have a regular elliptical shape and smooth surface. After 5 seconds of exposure to the microwave at 40°C, small defects and cracks on the surface of some of the granules are visible. After 10 seconds of heating in microwave oven at 55°C, flaws or fractures on the starch granules are visible but the time and temperature do not cause the loss of the grain structure integrity. Further microwave radiation for 15 seconds at 80°C resulted in the formation of surface cracks or deformation of the granules, whereas the action of microwave for 20 seconds at 95°C resulted in serious deformation, cracks, and destruction of most of the starch granules [34, 52].

Changes in the starch crystal structure can be caused by damage due to the temperature rise or as a result of the crystalline structure reorganization due to the loss of water. Differences in the crystallinity degree of starch can be observed by the XRD technique [49].

Microwave irradiation decreases the degree of crystallinity of wheat starch while in case of waxy corn starch the crystallinity remains virtually unchanged. Susceptibility of different starch molecules to microwave radiation depends not only on its crystal structure but also on amylose content [49].

4. Microwave-Assisted Modifications

So far, in the literature regarding the starch microwave modifications such processes are described as oxidation, hydrolysis, esterification, and etherification [53–56].

4.1. Microwave-Assisted Oxidation. Currently, works on the use of microwave radiation in order to improve the oxidation of starch are ongoing [57–59].

The literature describes application of hydrogen peroxide in the oxidation of primary alcohols to carboxylic acids and secondary alcohols to ketones [60]. Yet still oxidation of starch using microwaves and H₂O₂ as an activator is poorly described [61–63].

Łukasiewicz et al. [63] showed that starch interacts with microwaves strongly and has completely different properties than conventionally heated one.

Oxidation of starch paste caused significant changes in its rheological behavior in relation to initial material. Modified starch pastes have 10–100 times lower viscosity. No yield stress was observed and there were no differences in the consistency coefficient.

Although microwave irradiation causes higher degradation of starch, the resulting products were characterized by a high degree of oxidation (high content of –CHO and –COOH groups) and wide spectrum of possibilities of application [63].

4.2. Microwave-Assisted Esterification. It has become increasingly popular to apply microwave field in the esterification of different types of starch. The first method of starch esters synthesis using a microwave field was the reaction of tapioca starch with succinic anhydride and the succinates obtained in this reaction had higher viscosity and higher water absorption capacity as compared to native starch. Esterification of corn starch with maleic anhydride and acetic acid and its anhydride was also carried out as well as esterification of tapioca starch with citric acid [43, 64].

Biswas et al. utilized microwave heating in the reaction of starch with acetic anhydride. The reaction was catalyzed by iodine and within 2 minutes at 100°C with catalyst concentration of 0.16–2.5 mol%, starch acetates with a degree of substitution equal to 3 were obtained [65].

Rajan et al. attempted to esterify the starch using enzymes, where the convection heating method was compared with the microwave field heating. In esterification reaction of starch with palmitic acid or hydrolyzed coconut oil they used a lipase obtained from *Candida rugosa* as biocatalyst. This experiment was carried out by heating for 4 h at 70°C and by exposure to microwave radiation with power of 80 W at incubation period of 135 seconds. Based on this experiment, it was demonstrated that the use of microwave field allows obtaining products with better thermal stability, minimal sensitivity to water absorption, and significantly improved mechanical properties [66].

The use of microwave radiation in the reaction of starch with amides was presented by Siemion et al. The reactions of starch with urea and biuret [67], thiourea [68], semicarbazide hydrochloride [69], and thiosemicarbazide were described [70].

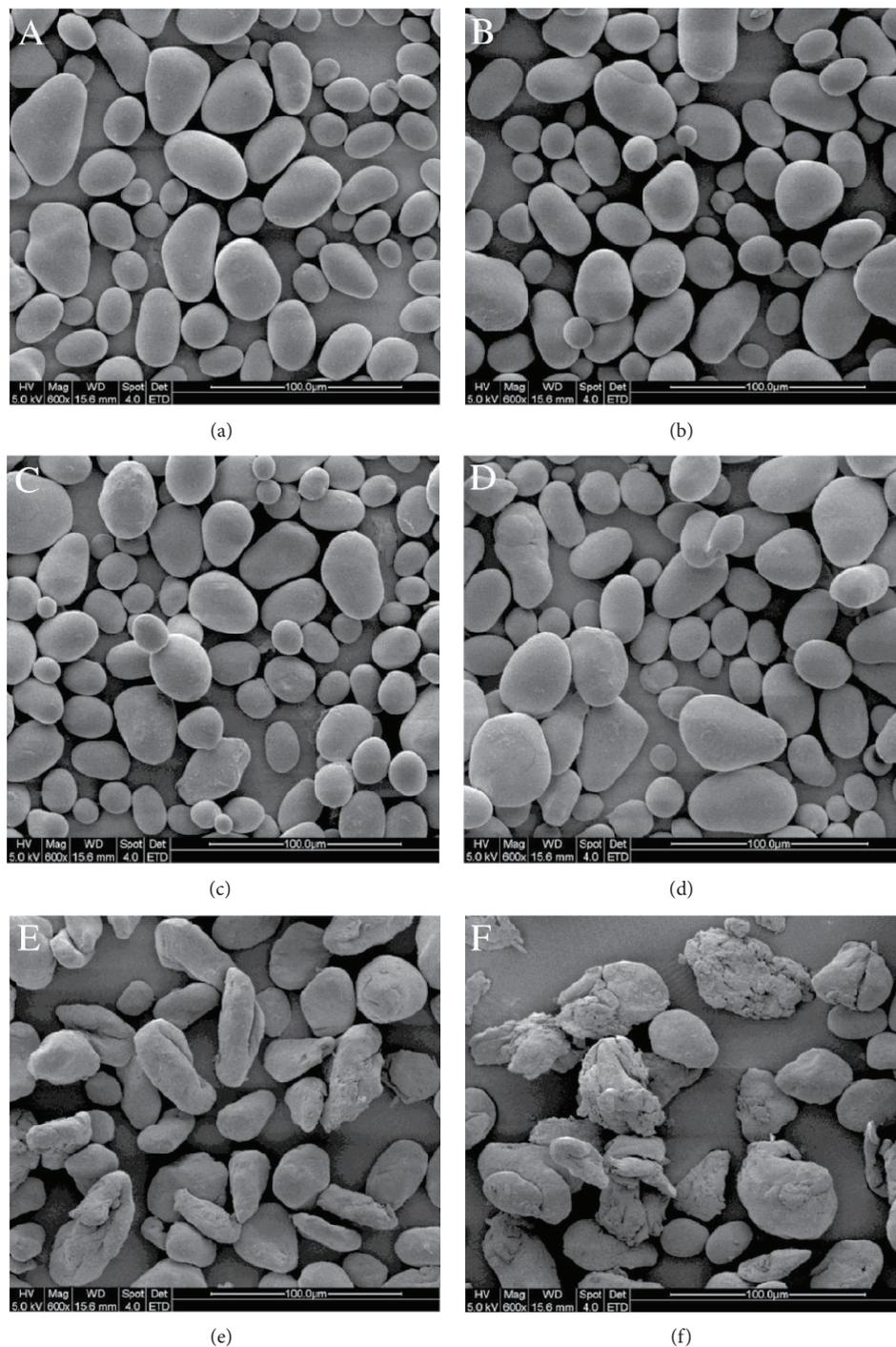


FIGURE 6: SEM micrographs of (a), (b) native starch and (c), (d), (e), and (f) microwave treated for 5, 10, 15, and 20 seconds, respectively [34].

Reaction of starch with urea was performed in a microwave oven during 10–15 min and without any catalyst at 900 W. The convection heating was carried out at the same time. The samples were heated for 1 h at temperatures 158°C and 180°C, respectively. The reaction scheme of starch with urea is shown in Figure 7. The *D*-glucose unit (1) acting as a nucleophile attacks urea molecule (2). Intermediate compound (3) could react through dehydration and

β -transelimination to unsaturated *D*-glucose unit (4) and recovery of urea. An alternative possibility of decomposition of (3) would involve the elimination of water and ammonia molecules and formation of the cyano group at the C2 atom (5) [67].

The reaction of starch with thiourea consisted in the fact that air-dried potato starch was blended with thiourea and heated in the microwave oven at 900 W. Figure 8 shows

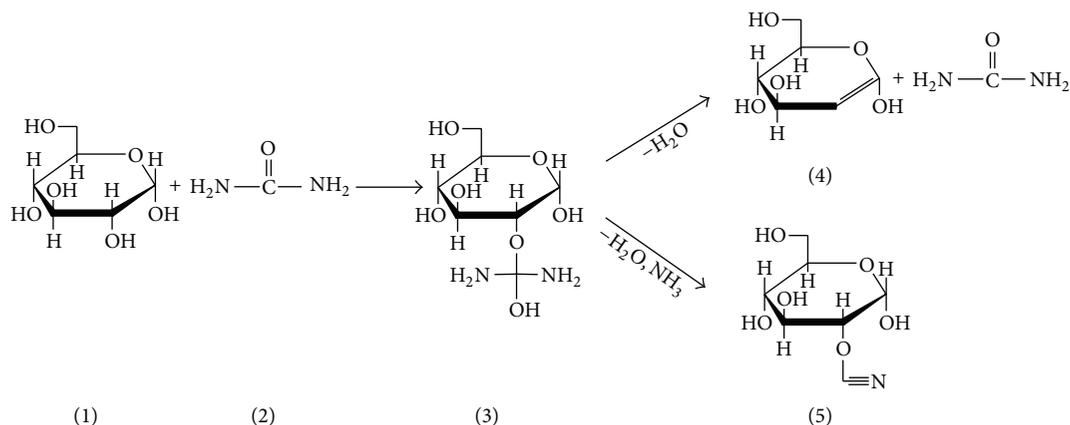


FIGURE 7: Proposed scheme for reaction of starch with urea.

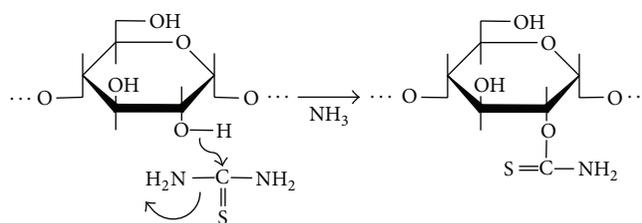


FIGURE 8: Proposed scheme for reaction of starch with thiourea.

reaction of starch with thiourea. As a result of one of the hydroxyl groups of the glucose units attack on the thiocarbonyl carbon atom, ammonia is evolved. As before, at the same time, convection heating was carried out [68].

The reaction mixture of starch and semicarbazide hydrochloride was heated, conventionally and in the microwaves field. Both heating methods provided approximately the same products. The convectional heating was more critical for the macrostructure of starch than microwave heating [69].

Potato starch was reacted with thiosemicarbazide with use of conventional and microwave heating respectively. The microwave heating resulted in a higher degree of conversion of the reaction mixture than in case of convectional heating and the product of the microwave-assisted reaction was more stable thermally [70].

The above results indicate that the microwave-assisted reactions of starch are much faster comparing to conventionally heated processes.

Summary

Modification is the process of changing the properties characteristic for native starch with the use of physical, chemical, or enzymatic methods. Both oxidized starches and starch esters, as compared with native starch, display better water solubility, lower viscosity, and a retrogradation tendency as well as improved overall mechanical properties.

Microwave heating has number of advantages compared with conventional heating. The reaction mixture can be heated uniformly and the power and heating energy towards

the reactants can be adjusted in relation to the specific solvent. Microwave activation often leads to improved yield and selectivity of the reaction. Microwave processing is able to change the physicochemical properties of starch. It affects the mechanism of gelation and rheological properties of starch and also causes a change in the structure of grains and crystalline form of the molecule. Among chemical modifications, microwave radiation is used in the reactions of oxidation and esterification of starch. In both of these reactions, it allows accelerating the reaction and significantly improving its yield.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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