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Physical and chemical modification of starches - A review**Zia-ud-Din, Hanguo Xiong*, Peng Fei**

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ABSTRACT

The development of green material in the last decade has been increased which tends to reduce the impact of human on the environment. Starch as an agro-sourced polymer has become much popular recently due to its characteristics such as wide availability, low cost and total compostability without toxic residues. Starch is the most abundant organic compound found in nature after cellulose. Starches are inherently unsuitable for most applications and, therefore, must be modified physically and/or chemically to enhance their positive attributes and/or to minimize their defects. Modification of starches is generally carried out by using physical methods that are simple and inexpensive due to the absence of chemical agents. On the other hand, chemical modification involves the exploitation of hydroxyl group present in the starches that brings about the desired results for the utilization of starches for specific applications. All these techniques have the tendency to produce starches with altered physicochemical properties and modified structural attributes for various food and non-food applications. This paper reviews

the recent knowledge and developments using physical modification methods, some chemical modification methods and a combination of both to produce a novel molecule with substantial applications, in food industry along with future perspectives.

Key words: Physical, Chemical, Starch modification, Physicochemical properties, Structural attributes

Abbreviations

ANN, annealing;

DS, degree of substitution;

ECH, epichlorohydrin;

GCWS, granular cold water soluble;

HHP, high hydrostatic pressure;

HMT, heat moisture treatment;

PEF, pulse electric field;

PGS, pre-gelatinized starch;

POCl₃, phosphoryl chloride;

SDS, slowly digestible starch;

STMP, sodium trimetaphosphate;

STPP, sodium tripolyphosphate

1. Introduction

Starch is one of the most abundant biopolymers and serves as energy reserve in many plants including cereals, tubers, roots, fruits and seeds. Starch molecules are the polymers of anhydrous glucose units which are typically accumulated in the unique and independent granules. Depending on the origin of starch, the granules can vary in shape, size, structure and chemical composition (Smith, 2001). Starch granules are generally found in roots, seeds and tubers, as well as in leaves, stems, fruits and even pollen. Grain seeds, for example, maize kernels, contain up to 75% of starch. The granule grows by apposition as the biosynthesis of the starch granules is initiated in the hilum part of the seed. The granules occur in all shapes and sizes (spheres, polygon, ellipsoids, platelets and irregular tubules). Depending on their botanical origin, they have the diameters ranging from 0.1 to 200 μm (Gallant, Bouchet, Buleon, & Perez, 1992; Hoover, 2001; Jane et al., 1994; Srichuwong et al., 2005; Tester & Karkalas, 2004).

From starch granules, two components of starch polysaccharides can be extracted: Amylose which is a pre-dominant α -(1-4) linked glucan and a more complex α -(1-4) linked branched glucan called amylopectin. Amylose has the tendency to retrograde and produce strong films and tough gels. On the other hand, amylopectin is more stable and produces weak films and soft gels when dispersed in water. The formation of entanglements is possible between amylose and amylopectin along with the presence of minor components such as proteins and lipids and all these can affect the physicochemical properties of starches to different extent depending upon the botanical source of the starch (Perez & Bertoft, 2010). The level of crystallinity in the native starches is being determined by the short branches of amylopectin within the granule. The starch

polysaccharides are arranged into concentric rings inside the granule that radiate out from the central hilum to the surface of the granule (French, 1984).

The amorphous part of the starch granule is preferentially degraded by acid hydrolysis, α -amylase can solubilize both crystalline and amorphous regions (Colonna et al., 1988; Gerard et al., 2001). However, the process involved in the hydrolysis of crystalline region and especially the disruption of double helices from crystallite and their disentanglement are not well known (Andre, Buleon, Haser, & tran, 1999). Starch is believed to affect the viscosity, adhesion, texture, binding, gel formation, film formation and moisture retention. It is mainly used in bakery products, snacks, batters and coatings, meat products, sauces and gravies and dairy confectionery (Davies, 1995). Non-food applications of starch enlist textiles, alcohol-based fuels and adhesives and pharmaceuticals. Whereas the new applications include biodegradable packaging materials, low-calorie substitutes, thermoplastic materials with improved thermal and mechanical properties and thin films (Biliaderis, 1998).

Starch does not have physical and chemical properties suitable for certain type of processing in its native form due to their poor shear and thermal stability and high degree of retrogradation (Jayakody & Hoover, 2008). Furthermore, native starches can easily undergo syneresis besides the gelling tendency of the pastes (Bemiller, 1997). Therefore, the applications of starch in various industries like food, paper and textile can be increased by adopting various techniques of modification. In order to promote and enhance specific functional properties, starches are frequently modified by physical, chemical and enzymatic processes. The physical modification of starch is accomplished by moisture, heat, shear, or radiation and this modification has been gaining wider acceptance because of the absence of chemical reagents in the modified starch.

Acquiring of desired functional properties is possible by using various methods of modification, which have specific applications in various industries. Chemical modification is extensively implemented, but there is also a mounting significance in the physical modification of starch, especially in food applications. The most important advantage of modification is that the starch is considered to be a natural material and a highly safe ingredient (Bemiller, 1997). Modification of starch is an ongoing process which can design a huge market for many new functional and value added properties resulting from these modifications (Kaur, Ariffin, Bhat & Karim, 2012).

Starches have been modified by adopting various methods of modification over the last few decades in order to acquire the desired industrial applications. Basically, there are four basic broad kinds of starch modifications; physical, chemical, enzymatic and genetic. A number of review articles (BeMiller, 1997; Jobling, 2004; Tharanathan, 2005) on the subject of starch modification are available. However, there has been an intense interest among the researchers in the last decade to develop novel methods for starch modification. This article is designed to be a critical overview for the science community on how to employ different modification methods to obtain a modified starch with well-designed composition and morphology.

2. Physical modification of starch

Physical modification of starch can be safely used in food products and can be achieved through alcoholic-alkaline, micronization and drum drying (Yan & Zhengbiao, 2010; Majzoobi et al., 2011; Ren et al., 2010). New methods are being evolved and one of the most common methods of physical modification of starch is pre-gelatinized starch (PGS) which has found wide applications in food industry. This type of physical modification is produced by drum drier, extruder and spray drier and generally regarded as instant starches (Karapantsios, 2006;

Majzoobi et al., 2011). Heating of starches in aqueous alcohol, high pressure and high temperature and alcoholic-alkaline treatment can be used to prepare granular cold water soluble (GCWS) starches. As compared to the traditional pre-gelatinized starches, GCWS starches exhibit smoother texture, greater viscosity and more processing tolerance (Yan & Zhengbiao, 2010). Vacuum ball grinding machine is generally used for preparation of micronized starches and during this process the granules are broken into small irregular granules by means of forces between the granules and the grinding balls (Ren et al., 2010).

Native starches are used for food processing but their commercial applications are limited because of their physical properties and colloidal sols (Laovachirasuwan et al., 2010). Due to instability under various kinds of pressure, shear and temperature, most of the native starches could not able to find their wider commercial type of applications. These starches lack the specific functional properties due to inertness, insolubility and highly resistant to enzymatic hydrolysis. To make the native starches suitable for industrial applications, these starches are modified in various ways to acquire the desired features such as heat tolerance, texture, adhesion and solubility (Anderson et al., 2002; Khunae, Tran, & Sirivongpaisal, 2007; Watcharatwinkul, Uttapap, & Rungsardthong, 2010; Viera & Sarmiento, 2008; Jiranuntakul et al., 2001; Fechner, Waterwig, Kiesow, & Heilman et al., 2005). Many different methods are available now a days to modify the starch polymer (Piacquadio, Stefano, & Sciancalepore, 2000; Shin et al., 2005; Varavinit et al., 2007; Cham & Suwannaporn, 2010; Lin, Wang, & Chang, 2008). The molecular integrity plays a vital role in the classification of starches in a way whether the molecular integrity is preserved or destroyed after the process of modification. High moisture treatment (HMT) and annealing (ANN) are the processes in which the starch integrity is preserved and

these are regarded as hydrothermal processes. Whereas, the molecular integrity and the granular order is lost completely in the pre-gelatinization processes that comprises of drum drying, spray drying and extrusion (Ashogbon & Akintayo, 2014). Some of the new physical methods used for starch modification that have been developed over the past few years are listed in the Table 1.

2.1 Pre-gelatinized starch (PGS)

Pre-gelatinized starches also called as instant starches are pre-cooked and dried with the help of a drum that enable the products to form moderate stable type of suspension that disperse in cold water (Hodge & Osman, 1976). These types of products are extensively used in the textile industry, as a thickening agent in food industry and as an adhesive in foundry core binders (Colonna, Buleo, & Mercier, 1987). Drum drying is a widely accepted technique at industrial level. The process of drum drying enables the product to gain various textures and porous structures which ultimately affect its functional properties as displayed by the intensity of treatment used (Bonazzi et al., 1996). The control of drum drying equipment is laborious due to the affinity of dried sheet to moisture exchange as the online moisture measurement requires very short time to respond (Vlachos & Karapantsios, 2000). The rheological behavior of the pre-gelatinized starch treated with double drum dryer tends to form weak paste as reconstitution with water takes place. Therefore, the possible effects of the time (residence) of the material must be given great importance inside the gelatinization pool. The swollen starch granules played a vital role considering the rheology of the pastes (Anastasiades et al., 2002).

Spray drying is the most commonly used technique in food industry as a microencapsulation method for ingredient (Gharsallaoui et al., 2007). Since a long time ago, spray drying technique has been used by many scientists and researchers to prepare the pre-gelatinized starch without losing the granular integrity. It is a rapid technique which readily converts the liquid solution droplets into amorphous and semi-amorphous particles (Pitchon et al., 1981; Ruben, 1992). The dried spherical particles dried by spray drying through atomizing starch solution are commonly used to modify the starches physically. The drying kinetics involving single drop of inconsistent sizes played a vital role towards the understanding of spray drying operations related with food (Adhikari et al., 2003) especially in the context of morphology. The starch granules treated with spray drying often show hollow structure in the middle of granule and presenting a regular shape (Yan & Zhengbiao, 2010). This technique has the ability to produce spherical particles for improving the fluidity of solid. Fruit and vegetable powder have been produced using spray drying (Abu-Jdayil et al., 2004). Spray dried sweet potato powders have the characteristics to be added to various food system to provide a variety of functional benefits.

Conventional extrusion cooking process involves the use of high temperature which brings about physical modification in starchy and proteinacious kinds of food. The starchy and proteinacious food tends to swell at exposing to extrusion cooking owing to its pressure, high temperature and shear forces (Liu et al., 2011). During the process of extrusion cooking, the starch is compressed with the help of high pressure and forces that resulted into molecular changes and ultimately changing starch from granular and semi-crystalline material into a highly viscous, plastic material (Brummer et al., 2002). The retrogradation behavior after improved

extrusion cooking technology for the rice starches showed that extrusion cooking technology is an appropriate and potential method for the preparation of rice starch products with low percentage and rate of retrogradation in food industry. Another advantage associated with extrusion cooking is the absence of effluents and chemical reagents which may overcome the pollution and further analysis and hydrolysis of starch can bring about desired results such as microencapsulation (Zhang et al., 2014).

2.2 Hydrothermal modification

Annealing (ANN) and high moisture treatment (HMT) are the two most widely accepted hydrothermal treatments used to modify the starches without losing the integrity of the granules. The distinguished feature of these methods is that both processes occur below the gelatinization temperature of granules which ultimately help in preserving the granular structure. Moreover, the starch granules must remain in the mobile rubbery state during these hydrothermal modification processes. Detectable changes can be seen in the physico-chemical properties of starches during these processes within instantaneous time. Both processes bring about modification in the structure and properties of starches to different extents (Jayakody & Hoover, 2008). These modification methods require certain temperature and moisture levels to accomplish in the starch granules during certain period of time. HMT refers to the treatment of starch when low moisture levels are used whereas ANN is used for the treatment of starches having low or intermediate moisture levels.

2.2.1 Annealing (ANN)

The process of annealing is an effective method used for the reorganization of the molecular chains. This process has the advantage to increase the crystallinity of materials and weakens the

structural relaxation. Furthermore, the process of annealing provides theoretical evidence for the improvement of material by developing the thermal stability and mechanical properties of material (Shanshan et al., 2015). Based on the changes in structural and functional properties, it was proposed that annealing treatment helped in the enhancement of long range interaction of amylopectin molecules by re-arranging the molecules of amylose. Annealing process reduces the solubilization of α -glucan during swelling below 100°C which means that amylose must be more restricted from leaching out of the granule. This strengthens the view that there is molecular reorientation in the starch granule which makes the amorphous region more glassy with an elevated T_g (Morrison et al., 1993; Hoover & Vasanthan, 1994). This enhanced interaction of amylopectin ultimately resulted into homogeneity of crystal structure and stability of annealed starches thus, protecting the integrity of granules by increasing the gelatinization temperature and narrowing the temperature range of thermal transition. Furthermore, the increased interaction of amylopectin clusters lead to the decreased paste viscosity by inhibiting the swelling of normal starch granules (Shujun et al., 2014).

The main objective of the annealing process is to approach the glass transition temperature (T_g) in the presence of solvents such as water or glycerol which results into an increased molecular mobility and preventing the initiation of gelatinization process at the same time. In fact, the amorphous region of the starch granules is the most susceptible area to the initial water absorption and plasticization. Before the absorption of water, this region is more static and glassy and it is the hydration due to which the mobility of amorphous region increases (Weigh, Keto, Donald & Gidley et al., 2000). This situation results into vibrational movements of chains in both amorphous and crystalline regions (Tester & Debon, 2000). As the process of annealing

continues, the weaker and imperfect crystallites gradually reduce in number whereas the remaining crystallites become more perfect due to the process of re-crystallization and fusion (Jayakody & Hoover, 2008). The process of annealing has important industrial implications. The annealing process proved helpful in imparting different novel processing characteristics. Annealed starches result in higher gelatinization temperatures where many inexpensive chemical processes can be employed, thus justifying this process in terms of energy and time (Tester & Debon, 2000).

2.2.2 Heat Moisture Treatment (HMT)

Heat moisture treatment (HMT) refers to the hydrothermal technique involving the agitation of starch granules at low moisture levels but at high temperatures (80-140 °C) and low gelatinization temperatures (Jacobs & Delcour, 1998; Hoover, 2010). Changes that are induced by HMT in the starch product often resulted into properties such as starches with intact granular forms. HMT brings about changes for instances, decreases starch solubility, swelling power, amylose leaching and peak viscosity but increase in the pasting temperature is noted for starches treated with HMT (Chung, Liu, & Hoover, 2009; Gunaratne & Corke, 2007; Pinto, Vanier, Klein, Zavareze, Elias & Gutkoski et al., 2012; Sui et al., 2011). The degree to which these changes in the physicochemical characteristics of starches occur is mainly the function of modification in the semi-crystalline structure of starch granules (Ambigaipalan et al., 2014; Gunaratne & Hoover, 2002). Hoover and Manuel (1996) established that the process of HMT brought about changes in the both crystalline and amorphous regions to different extent. The prominent changes were proposed to occur in the amorphous region of the starch granules

through chain reactions in different botanical starches such as cereal, tuber and legumes (Hoover & Vasanthan, 1994; Jacobs & Delcour, 1998; Vermeulen et al., 2006).

Due to the diversity of the reaction conditions, it is very difficult to define the properties of HMT treated starches in a consistent way. These diverse reaction conditions include moisture content, temperature, botanical source, heat source, cooling process and length of treatment. Among these conditions, moisture and temperature are the most extensively studied HMT parameters (Vermeulen et al., 2006; Ambigaipalan et al., 2014). However, the moisture contents and heating length both affected the properties of maize starches to a greater extent (Zhongquan et al., 2015). HMT treated starches find applications on industrial level where these are used in the preparation of infant foods. Moreover, potato starches are also processed through HMT to improve its baking qualities and freeze-thaw stability in food industry (Collado & Corke, 1999).

2.3 Non-thermal physical modification of starches

Most of the food is preserved by exposing the product to high temperatures for a short period of time. These treatments resulted in the loss of essential nutrients, vitamins and flavors. In order to overcome these disadvantages, non-thermal technology is used to kill the pathogenic and spoilage causing organisms. Non-thermal treatments can be used to preserve color, texture, taste, nutrients and other components of food as compared to the traditional thermal processes (Li et al., 2008; Marselles-Fontanet & Martin-Bellose, 2007; Sampedro et al., 2007; Torregrosa et al., 2006). Different kinds of non-thermal treatments have different effects on the physicochemical properties of starches. Some of the non-thermal processes are using ultrasound effect, high hydrostatic pressure and microwave treatment of starches.

Ultrasonication can be used as a green technology to modify the structure, properties and composition of starches from different botanical sources. Depending on the conditions of experiment, ultrasonication either degrades or has a little effect on starch chains on the molecular level. The physicochemical properties of starch can be affected by the structural changes. Ultrasonication has been showed to increase the water solubility, decreases the gelatinization/ pasting viscosity/ swelling parameters/ retrogradation which shows that this process depends on factors like frequency, intensity, water and temperature of the starch-water system, duration of ultrasonication, type and structure of starch and composition of gas in the atmosphere. Ultrasonication induced cracks and pores in the granular structure of starch which further provide assistance in the modification of starch by augmenting the efficiency of the reactions. The process of ultrasonication has been employed by food and non-food industries and has achieved various benefits such as enhanced product yield and purity, shortened processing time, environment friendliness, production cost and reduced energy consumption (Zhu, 2015). This technique is very important in the following areas of food processing; deforming, extrusion, separation, viscosity alteration, crystallization, extraction, emulsification and homogenization (Iida et al., 2008).

In food industry, high hydrostatic pressure (HHP) involves treatment of food material using pressure from (100-1000 MPa) at room temperature to acquire the modification and sterilization of food material. This treatment destroys the non-covalent bonds which resulted into serious structural damages such as protein naturalization and starch gelatinization (Hu et al., 2011). Moreover, the important application of this technology is the achievement of starch gelatinization at room temperature. Starch gels treated with HHP has lower swelling index and

lower susceptibility to amylolytic enzymes as compared to the starch gels that are heat gelatinized (Blaszcak et al., 2005; Vallons & Arendt, 2009). The HHP gelatinized non-waxy and waxy rice starches has higher slow digestibility than the heat gelatinized ones during retrogradation while the slowly digestible starch (SDS) percentage was not positively co-related with enthalpy change of starch retrogradation. The higher SDS percentage was mainly attributed to the intact starch granules which were retained by using HHP treatment (Tian et al., 2014). Wheat starch suspensions were homogenized at increasing pressure up to 100 MPa to approximate the electrical and structural characteristics of wheat starch. Qiu et al. (2014) reported that the starch granules began to lose their native pattern at 60 and 80 MPa, moreover, many starch granules disintegrated into gel-like structures and their mean particle diameter increased significantly when homogenized at 100 MPa. A positive application of pressurized starch could be to use it as a fat substitute, these might stimulate fat droplets as these are considered micro-particles of well defined size distribution (Stute et al., 1996).

Pulse electric field (PEF) technology is a non-thermal food preservation method which involves preservation of food by killing and inactivating the pathogenic micro-organisms and enzymes resulted into minimum loss of original taste, color, nutrients, texture and heat liable functional components of food (Knorr & Angersbach, 1998). The technology of PEF treats the pumpable liquid material with high intensity electric pulses (over 10 kV cm^{-1}) at short duration (less than $40 \text{ }\mu\text{s}$) in a processing chamber. PEF technology has been widely used for modifying larger molecules and enhancing chemical reactions apart from non-thermal pasteurization. The advantages of PEF treatment include continuous processing nature, uniform treatment intensity, low processing temperature and short treatment time. The PEF treatment can lead to an intra-

granular molecular re-arrangement of potato starch granules which resulted into changes related different physicochemical properties of treated starch inducing some new characteristics and functions (Han et al., 2009).

3. Chemical modification

Chemical modification is carried out by introducing a functional group into the polymer molecule of the starch granule in its native form that brings about distinctive changes in the physicochemical properties of starch molecule. This type of modification produces reflective modification in the gelatinization, proximate composition, pasting characteristics and retrogradation of native starch granules. Such modification helps in the stabilization of intra and inter-molecular bonds at different positions and locations. Factors such as starch source, reaction conditions, degree of substitution, type and distribution of substituting agent along the molecule of starch affect the functional and chemical properties of the modified starches. Chemical modification of starches is generally accomplished through derivatization such as acetylation, cationization, acid hydrolysis, oxidation and cross linking. However, these techniques are limited due to issues such as consumers' safety and environment. There has been an increasing trend to combine different kinds of chemical techniques to create new kinds of modification. Similarly, different chemical modification methods have been combined with physical modification methods such as radiation, extrusion and microwave to produce a starch with specific functional properties. Some of the recent chemical modification methods are summarized in Table 3.

3.1 Acetylated (Ac) starch

Acetylation of starch is a common chemical modification method during which part of the hydroxyl groups of glucose molecule is replaced by acetyl group resulted into modified molecular structure of the starch. These starches are produced by using acetic anhydride and an alkaline catalyst such as sodium hydroxide (Bello-Perez et al., 2010). Acetylated starches performed different functions depending upon the degree of substitution (DS). These starches having a low DS of about (0.01-0.2) may act as adhesion, thickening, texturizing, film forming, stabilizing and binding agent and also find numerous applications in food industry in baked goods, sauces, frozen foods, canned pie fillings, baby foods, snack foods and salad dressings. Acetylated starches with intermediate DS (0.2-1.5) and high DS (1.5-3.0) have been reported for high solubility in acetone and chloroform and thus, can be used as thermoplastic material (Luo & Shi, 2012). Acetylation of starches is performed to bring about desired changes in physical, functional and chemical properties of starches (Xu et al., 2004) and has been used by many researchers (Bello-Perez et al., 2010; Diop et al., 2011; Garg and Jana, 2011; Huang et al., 2007; Mbougoueng, Tenin, Scher, & Tchiegang, 2012). Different factors play vital role in the inducement of changes caused by acetylation such as the source, ratio of amylose and amylopectin, the molecular structure of starch and the degree of substitution. The reaction efficiency and the number of acetyl groups induced in the starch molecule during the process of acetylation depend upon the reaction time, presence of catalyst, botanical origin, reagent concentration and structural characteristics of starch granules (Huang et al., 2007; Huber & BeMiller, 2000).

Acetylated starches with DS above 0.22 exhibited changes in the morphology of the starch granules. As compared to the native starch, acetylated starches are more resistant against

shearing and heating (Mello El Halal et al., 2015). The crystallinity of starch in context of breakdown, peak and final viscosities, swelling power, its pasting temperature and solubility is reduced by the process of acetylation. The decrease in the pasting temperature facilitates in getting the products having characteristics such as sensitivity to high temperatures and products having more stability during the process of cooking (Colussi et al., 2014). A significant amount of resistant to amyloglucosidase activity and small changes in the rheological properties are noted for the acetylation of retrograded starch as compared to the chemically unmodified starch. Additionally, the process of acetylation for the retrograded starch and its cross linking with adipic acid (compared to the chemically unmodified starch) resulted in an increased resistant against the amyloglucosidase action (30.56g/100g) (Zieba et al., 2014).

Acetylation of starches leads to structural reorganization owing to steric hindrance resulting in repulsion between starch molecules, thus facilitating an increase in water percolation within amorphous regions of granules and a consequent increase in swelling capacity (Lawal, 2004). Additionally, acetylation retards the development of an ordered structure following gelatinization which ultimately helps in retarding retrogradation, resulting in more fluid paste and better long term clarity (Lawal, 2004).

Introduction of acetyl groups in starch molecule resulted in structural changes as reflected by thermal properties of starches. Using the technique of differential scanning calorimetry (DSC), many researchers concluded that at lower temperatures, the acetylated starches go through phase transition as compared to their native counterparts, moreover, the heat of phase transition (enthalpy) is lower for acetylated starches although it is recorded on high pasting temperatures (Afolabi et al., 2012; Bello-Perez et al., 2010). Thermogravimetric studies (TGA) also reveal

high heat resistance for acetylated starches as compared to the native starches (Emeje et al., 2012; Garg & Jana, 2011; Luo & Zhou, 2012; Mina et al., 2011; Singh et al., 2011; Xia et al., 2011; Zhang et al., 2009; Zhang et al., 2012).

Currently, research has been carried out for exploring acetylated starches as loose substance (Fornal et al., 2012), surface active substance by enzymatic hydrolysis (Konowal et al., 2012), use of acetylated starch for production of films with barrier properties (Lopez, Zaritzky, Grossmann & Garcia, 2013; Zamudio-Flores et al., 2010), encapsulating properties (Murua-Pagola et al., 2009; Robert et al., 2012), biodegradable material (Mina et al., 2011), or reinforcing agents for bio-nanocomposites (Valodkar & Thakore, 2011).

3.2 Cationic starch

Cationic starches are vital industrial derivatives produced by introducing a positive ionic charge with the help of functional groups such as ammonium, imino, amino, sulfonium or phosphonium.

The hydroxyl group of the native starches is commonly replaced by an ionic charge by utilizing 2,3-epoxypropyltrimethylammonium chloride (ETA) as a cationic monomer under wet, dry or intermediate process. The wet method is the most commonly used process among the three. During the wet cationization of starches, the reaction is proceed in the forward direction by mixing starch with water to form a homogeneous suspension with a concentration of 40 % and adjusting the pH within 11-12 with the help of addition of chemical cationising agent. A starch will be cationized completely by maintaining all these reaction conditions and a temperature of 40-45 °C in 12-16 hours (Heinze, Haack, & Rensing, 2004). In dry cationization process (absence of liquid phase), the reagent is sprayed onto dry starch during the process of extrusion

whereas the same process is repeated and the mixtures are thermally treated during the semi dry processing. The main advantage of these processes is that these two methods are environment friendly but there is a likelihood of the by-product that may be produced along with the desired product and it may also be costly to separate both from each other (Radosta, Vorwery, Ebert, Begli et al., 2004). More dense starch would be resulted by following the dry cationization process compared to the wet cationization method. However, high amount of higher molar masses are obtained for wet cationic starch compared to the dry method (Santacruz, 2014).

Cationic starches find its application on large scale in the paper industry where these can play their role as an additive, surface size and coating binder agents. Cationic starches having ammonium groups on quaternary position are commonly used for commercial applications (Xie, Liu & Cui, 2005). Cationic starches are believed to have a potent activity against the microbes consequently used in the antimicrobial products formulations. Keeping in the view its antimicrobial activity, cationic starches have been able to draw the attention of the researchers for both academic and industrial point of view. The use of such polymeric materials with antimicrobial activity can act as matrix holding the antimicrobial agent or the polymer by itself can possess the antimicrobial activity (Munoz-Bonilla & Fernandez-Garcia, 2012). It has been shown in the previous studies that the starch derivatives with quaternary ammonium group can act as an antimicrobial agent but these are bacteriostatic rather than bactericides (Bendoraitiene et al., 2013).

Generally, the process of cationization brings about considerable changes in the granular structure and physicochemical properties of the starch especially in those having high degree of substitution. Higher peak viscosities, changes in setbacks and lower pasting temperatures were

also noted in the RVA of different types of starches exposed to cationization (Siau et al., 2004). Furthermore, lower transition temperature and smaller ΔH are noted for cationic starches in a comparative study with the native starches using the technique of DSC (Radosta, Vorwery, Ebert, Begli et al., 2004). Cationic starches has found numerous applications as flocculants for water treatment (Krentz, Lohmann, Schwarz, Bratskaya et al., 2006) as an additive in cosmetics products and textile (Heinze, Haack & Rensing, 2004) and these kind of starches (cationic starches) can be used for the dynamic coating for protein analysis in CE (Sakai-kato, Kato, Nakajima, Toyo'oka et al., 2006).

3.3 Cross-linked starch

Cross linking is a chemical modification method during which the native starches are chemically modified using different cross linking agents like sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin (ECH) and phosphoryl chloride (POCl_3). This technique is believed to play an important role in improving the functional properties, the freeze thaw and the cold storage stabilities of the starch molecule (Chung et al., 2004; BeMiller, 2011). STMP, STPP, POCl_3 and a mixture of adipic acid and acetic anhydride can be used as cross-linking agents for food use. Among these reagents, the STMP, which is one of the most important food additives with low toxicity, is an efficient cross-linking agent (Gui-Jie, Peng, Xiang-Sheng, Xing, & Tong, 2006). One type of cross linked starch is distarch phosphate which is produced under alkaline conditions by reacting starch granules with STMP or POCl_3 (Wurzberg, 1986). The process of cross linking is believed to add intra- and inter-molecular bond at various location in the starch molecule that resulted in the stability of the granule (Acquarone & Rao, 2003; Singh et al., 2007) by utilizing the chemical reagents that form ether

or ester linkages between hydroxyl groups in the molecule of starch (Rutenberg & Solarek, 1984). It is reported that both amylopectin and amylose in starch granules can be cross linked. The amylose molecules, however, has less of the tendency to be cross-linked (Jane, Xu, Radosavljevic, & Seib, 1992). Likewise other chemical modification methods, cross linking of starches is also affected by many factors like source of the starch, the reagent composition and concentration, pH, extent of substitution, temperature and reaction time (Chung, et al., 2004). The molecular structure of starch granules is different by using different types of cross linking agents, therefore, the functional properties of treated starch are determined by the type of cross linking agent used (Sekar & Hanna, 2006).

The solubility of the cross linked starches was decreased with an enhancement in the degree of cross linking when measured as a function of temperature (Koo et al., 2010). Similar reports were presented by Kaur et al. (2006) for potato starches using different concentration of cross linking agents such as EPI and POCl_3 . The decreased solubility can be explained by the fact that the degree of cross linking results in the compactness of granular structure in the starch molecules which ultimately cause less disintegration of starch granules during the process of gelatinization (Jyothi, Moorthy & Rajasekharan, 2006). Starches cross liked with STMP/STPP lead to a considerable decrease in paste clarity (Koo et al., 2010). This substantial decrease in paste clarity can be attributed to the change in the structure of starch granules caused by cross linking (Morikawa & Nishinari, 2000a). Moreover, no difference in crystallinity pattern has been found when modified corn starch is compared to the native starch. This can be reflected to the fact that the process of cross-linking mainly takes place in the amorphous region of starch granules showing no alteration in the crystalline patterns of the starches (Koo et al., 2010).

Cross linked starches show more thermal stability as evident by decrease in the weight loss compared to their native counterpart (Wongsagonup et al., 2014). These attributes make cross linked starches more suitable for various industrial applications as exhibited by their stronger granular structure. The most interesting phenomenon is that the cross linked starches decompose promptly but the amount of residues are larger after the decomposition process as compared to the untreated starches. The thermal decomposition of cross linked starches is facilitated by the large number of phosphate group in the amorphous region as evident by the XRD spectra of cross linked sago starch showing more amorphous region with reduced diffraction intensity that might be resulted due to the replacement of some hydroxyl groups with phosphate groups during the process of cross linking (Singh & Nath, 2012).

Starch paste from cross-linked starch is highly viscous, heavy bodied, shorter textured and less likely to breakdown during severe agitation, cooking and exposure to low pH conditions. These starches are thus suitable for thickening and stabilizing the food system, e.g. soups, gravies, sauces, baby foods, fruit fillings, pudding and deep fried foods (Rutenberg & Solarek, 1984; Singh, Kaur, & McCarthy, 2007).

3.4 Other chemical modification methods

Modification of starches using mineral acids such as HCl or H₂SO₄ is a common type of modification method and these starches has a vast potential of applications. Depending on the desired viscosity or degree of conversion, the concentrated starch slurry is treated at temperature below the gelatinization temperature for a specific period of time (Thirathumthavorn & Charoenrein, 2005). Starches treated with acid manifest numerous properties such as increased solubility and alkali number, decreased tendency to retrograde, decreased swelling power,

increased ΔH and broadened temperature of gelatinization and loss in pasting viscosities (Beninca, Colman, Lacerda, Carvalho, Bannach et al., 2013; Osunsami et al., 1989; Sanguanpong et al., 2003; Atichokudomchai et al., 2001; Atichokudomchai et al., 2002). The mineral acid attacks both the amylose and amylopectin region of the starch but during the early stages of the process, the amorphous region is more vulnerable to its attack and later on the acid slowly shifts its activity towards the crystalline region of the starch granule (Wang & Wang, 2001). Keeping in the view these facts, the surface morphological attributes of acid thinned (6% HCl) starches are studied under scanning electron microscope (SEM). These starches have eroded their surfaces by acid suggesting that the process of erosion took place on the surface of starch granule (Atichokudomchai et al., 2000). It was observed that the surface is pre-dominantly occupied by amylopectin and phosphate containing domains with increasing the concentration of an acid (Wuttisela et al., 2009). Using the technique of atomic force microscopy (AFM), it was revealed that the roughness in the surface of starch granule can be minimized by treating the starches with acid hydrolysis (Beninca, Colman, Lacerda, Carvalho, Bannach et al., 2013).

Starch oxidation is an alternative method for improving starch properties that is widely used in industry. Oxidized starch is prepared commercially by reacting starch with a specific amount of oxidant under controlled pH and temperature. Oxidants such as potassium permanganate, sodium hypochlorite, hydrogen peroxide, peracetic acid, nitrogen dioxide and chromic acid have been employed to oxidize starches. Sodium hypochlorite is the most commonly commercial oxidant used for this technique (Sandhu et al., 2008; Wang & Wang, 2003). The oxidizing agent penetrates deeply into the amorphous regions and has minimal effect on the crystalline regions. These oxidizing agents formed carboxyl group on the starch molecule that resulted into low

retrogradation and syneresis of oxidized starch paste, whereas carbonyls play a negligible role in the prevention of retrogradation of starches (Kuakpetoon & Wang, 2006). These starches have attracted many researchers and these have numerous applications in food and non-food sectors. The reaction conditions and the type of oxidizing agent determine the functional properties of the final product (Lawal et al., 2005). The process of oxidation brings about changes that can be related with lower gelatinization temperature and ΔH of the starch consequently retarding the retrogradation of starch molecule as evident by the analysis of light transmittance (Sangseethong et al., 2009). During the process of oxidation of starches, the hydroxyl group of the starch molecule is first oxidized to carbonyl group and then to carboxyl group, so the level of oxidation in the treated starch is primarily determined by the number of carbonyl and carboxyl groups which believe to take place at C-2, C-3 and C-6 position on D-glucopyranosyl unit (Sanchev-Rivera et al., 2005; Guerra-Della Valle et al., 2009).

Starches are usually treated with propylene oxide in alkaline medium to prepare the hydroxypropylated starches (Schmitz et al., 2006). Improved freezing-thawing stability, water binding capacity, light transmittance, swelling power and improved solubility were noted for hydroxypropylated starches whereas phenomena like enzyme susceptibility, syneresis of paste and retrogradation can be hindered by exposing starches to propylene oxide (Schmitz et al., 2006; Jyothi, Moorthy, & Rajasekharan, 2007).

3.5 Dual modification

In order to further improve the functional properties and utilization of starches in various kinds of applications, chemical dual and other types of dual modification methods have been introduced in different kinds of starches. Dual modification of starches involves the combination

of either chemical and physical modification methods or chemical and enzymatic modification method. But the most commonly used is the dual chemical modification method that is widely used to modify the starches which involves a combination of two chemical modification methods such as acetylation/oxidation, cross linking/acetylation or cross linking/hydroxypropylation (Carmona-Garcia et al., 2009; Huang et al., 2007; Raina et al., 2006; Lui & Corke, 1999; Adebowale, Afolabi, & Olu-Owolabi, 2006; Zamudio-Flores et al., 2010). Chemically dual modified starches find large number of applications in food industry as binder, thickeners and emulsifiers whereas in non-food industry these can be utilized as heavy metal absorbents. It has been observed that the chemical and physical properties of the native plantain starch have been successfully improved by exposing the native starch to dual chemical modification process (oxidation/acetylation) (Zamudio-Flores et al., 2010). The swelling power is the most prominent factor in determining the outcome (Wattanachant et al., 2002) of the final product during the process of dual modification (hydroxypropylation and cross linking).

4. Conclusions and future outlook

The challenges involved in the modification of starches are the mitigation of the inherent shortcomings in the native starches such as loss of viscosity, easily to retrograde, insolubility and loss of ordered structure that ultimately provides the feasibility basis for wide applications of starches. The physical and dual modification has been the most promising methods of modification with large number of innovated techniques. Physical modification of starches can be divided into three categories (a) PGSs; (b) hydrothermally treated starches; and (c) non-thermally treated starches.

The most important application of PGSs starches is in puddings, pie fillings and baby foods as a thickening agent because of their ability to hydrate instantly and swell in water at ambient temperature. These can be obtained by heating the slurry above the gelatinization temperature and subsequently drying by drum, extrusion or spray drying. Hydrothermally treated starches involve the techniques of annealing and high moisture treatment that ultimately brings about changes in the physicochemical characteristics keeping the granular structure intact. Techniques such as HHP, UHP, microwave and PEF treatment can be included in the category of non-thermal treatment of starches and the functional and physicochemical characteristics of the treated starch depend upon the forces or pressure applied to the type of starch.

Progress in understanding the high value of chemically modified starches has encouraged the starch industry to produce modified starches using different modification reagents and starch sources. Some factors such as starch composition, concentration, type of reagent and reaction conditions may affect the reactivity of starch during chemical modifications like acetylation, hydroxypropylation and cross linking. The heterogeneity of granule population within a single starch source may also affect the extent of modification. The changes observed in the physicochemical, morphological, thermal and rheological properties of starches after modification may provide a crucial basis for understanding the efficiency of the starch modification process at industrial level. Products are also being looked for forming new items for consumption with conventional and non-conventional properties using the method of dual modification of starches.

For better understanding the process of modification of starches, research should be done and focused on the following given points:

- a) It has been appeared that the same test and analysis has been repeated for the problems and issues that had been resolved long ago. So, more through study and investigation should be done to avoid the repetition of the same procedures.
- b) New combination of techniques is required in order to obtain starches with more diversified and promising applications with variations in structure, composition and properties. Novel techniques such as ultrasound and microwave treatment can be adopted to obtain starches that would be environment friendly, the concept that recently coined as “green technology”.
- c) Starch modification is being carried out since long ago in 1800. Though the efforts are large in chemical modification resulting in novel nutritional properties of resulting starches, but the health of the consumer and environment should also be taken into account.

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Table 1 Recent methods of physical modification of starches

Physical modification	References
Deep freezing	Szymonska et al. (2000)
Multiple deep freezing and thawing	Szymonska et al. (2003)
Osmotic pressure treatment	Pukkahuta et al. (2007)
Superheated starch	Steeneken and Woortman (2009)
Instantaneous controlled pressure	Zarguili et al. (2006)
Iterated syneresis	Lewandowicz and Soral-Smietana (2004)
Corona electrical discharges	Nemtanu and Minea (2006)
Thermally inhibited treatment (dry heating)	Chiu et al. (1998); Lim et al. (2002)
Pulse electric fields treatment	Han et al. (2009)
Micronization in vacuum ball mill	Che et al. (2007)
Mechanical activation- with stirring ball mill	Huang et al. (2007)
Drop (DIC) process	Maache-Rezzoug et al. (2009)

Table 2 Annealing and gelatinization parameters for tuber and cereal starches

Starch Source	ANN parameters				Gelatinization parameters					References
	Tem p (°C)	Steps	Time (h)	W:S ^{a)}	S:W ^{b)}	T ₀ ^{c)} (°C)	T _p ^{c)} (°C)	T _c ^{c)} (°C)	ΔH (J/g)	
Potato (native)	-	-	-	-	-	59. 1	61. 9	66. 8	18.3	Vermeylen et al. (2006)
Potato (annealed)	50	Singl e	72	10:01	-	61. 1	63. 1	70. 7	18	Kohyama & Sasaki (2006)
Cassava (native)	-	-	-	-	-	65. 4	71. 5	81. 5	8.8	Atichokundomch ai et al. (2002)
Cassava (annealed)	51	Singl e	72	3.01	-	70. 7	74	81. 3	9.4	Atichokundomch ai et al. (2002)
Normal maize (native)	-	-	-	-	1:05	56. 9	67. 7	76. 5	17.6	Qi et al. (2005)
Normal maize (annealed)	55	Singl e	168	Exces s	1:05	72. 1	76. 4	82. 3	16.9	Qi et al. (2005)

Waxy maize (annealed)	55	Singl e	168	Exces s	1:05	73. 3	77. 3	83. 1	17.3	Qi et al. (2005)
Waxy rice (native)	-	-	-	-	1:03	76. 2	81. 2	87. 1	19.2	Shi (2008)
Waxy rice (annealed)	70	Singl e	48	3:01	1:03	86. 9	90	93. 7	19.6	Shi (2008)

-, data not reported. a) Water: starch b) Starch: water

c) Onset (T_o), mid-point (T_p) and conclusion (T_c) temperatures of gelatinization.

ΔH Enthalpy of gelatinization

Table 3 Some common methods of chemical modification of starches

Chemical modification	References
Cationization	Han and Sosulski (1998)
Oxidation	Tran et al. (2007), Sangseethong et al. (2009,2010), Amorim et al. (2011), Klein et al. (2014), Beninca, Colman, Lacerda, Carvalho, Demiate et al. (2013)
Acid hydrolysis	Osunsami et al. (1989), Sanguanpong et al. (2003), Akubor (2007), Rolland-Sabate et al. (2012)
Alkaline	Raja (1992)
Cross-linking	Nabeshima and Grossmann (2001), Jyothi, Moorthy and Rajasekharan (2006), Tran et al. (2007), Varavinit et al. (2007).
Hydroxypropylation	Schmitz et al. (2006), Jyothi, Moorthy, and Rajasekharan (2007), Takahashi, Maningat, and Seib (1989)
Acetylation	Moorthy (1985), Tran et al. (2007), Osundahunsi and Mueller (2011), Mbougung, Tenin, Scher and Tchiegang (2012)
Acid hydrolysis in alcohol	Ferrini et al. (2008), Cavallini and Franco (2010)

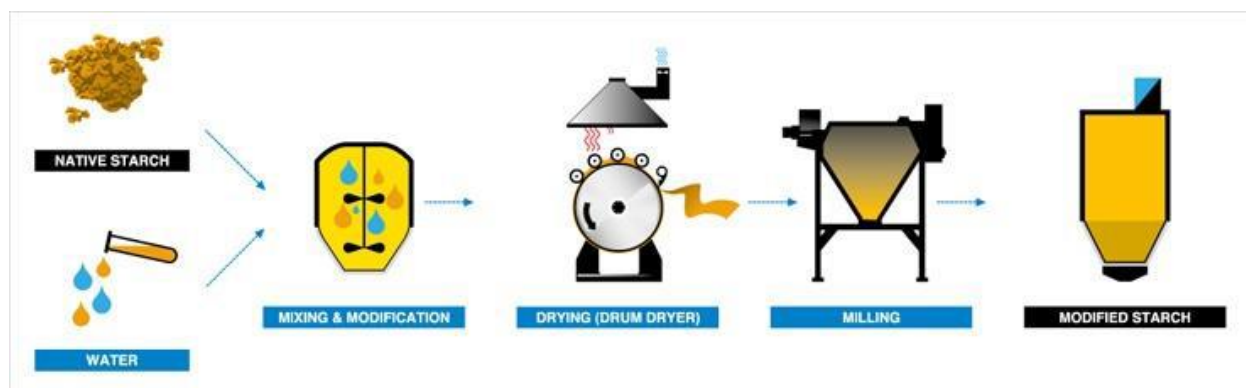


Fig.1 Drum drying technique for modification of starch

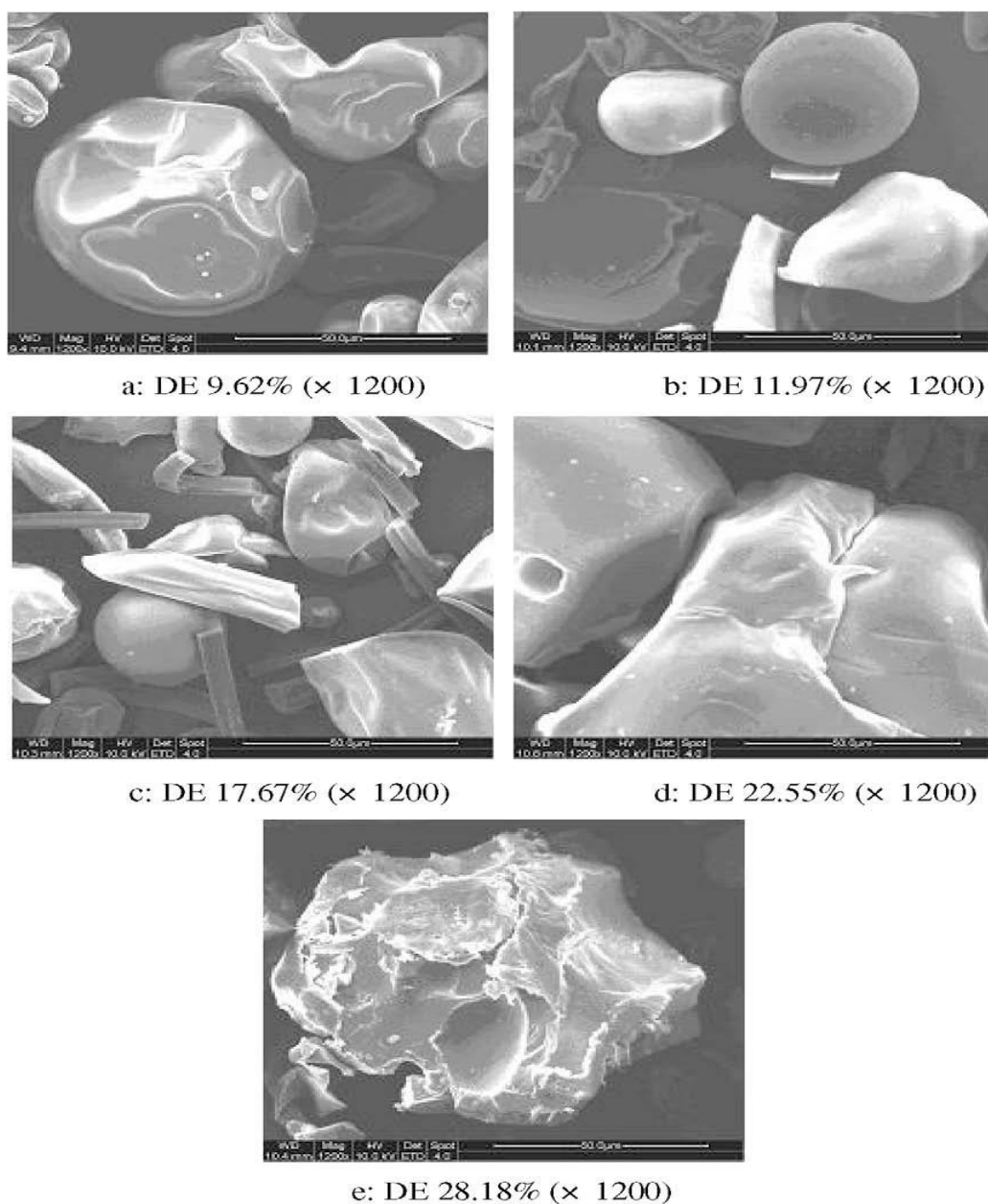
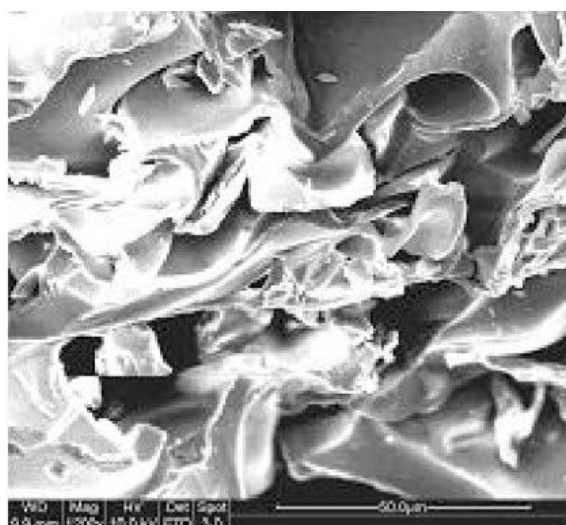
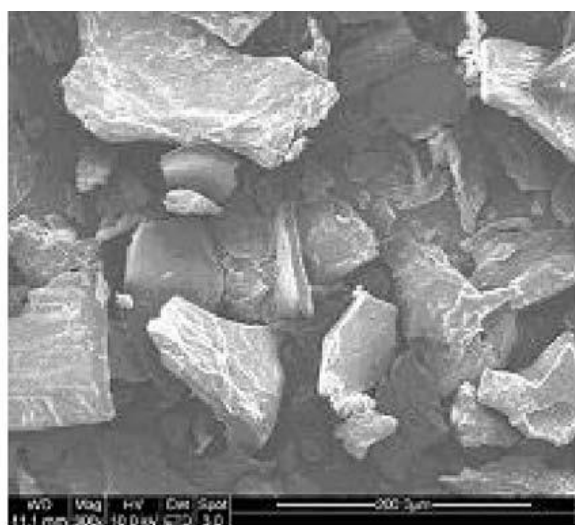
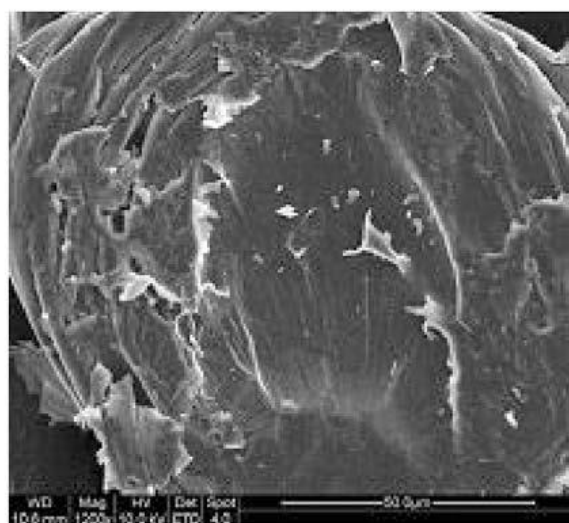


Fig. 2 SEM micrographs of maltodextrin granule from spray-drying

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a: pregelatinized corn starch ($\times 300$) b: pregelatinized corn starch ($\times 1200$)



c pregelatinized potato starch ($\times 1200$)

Fig. 3 SEM micrographs of pregelatinized starch granule from extrusion

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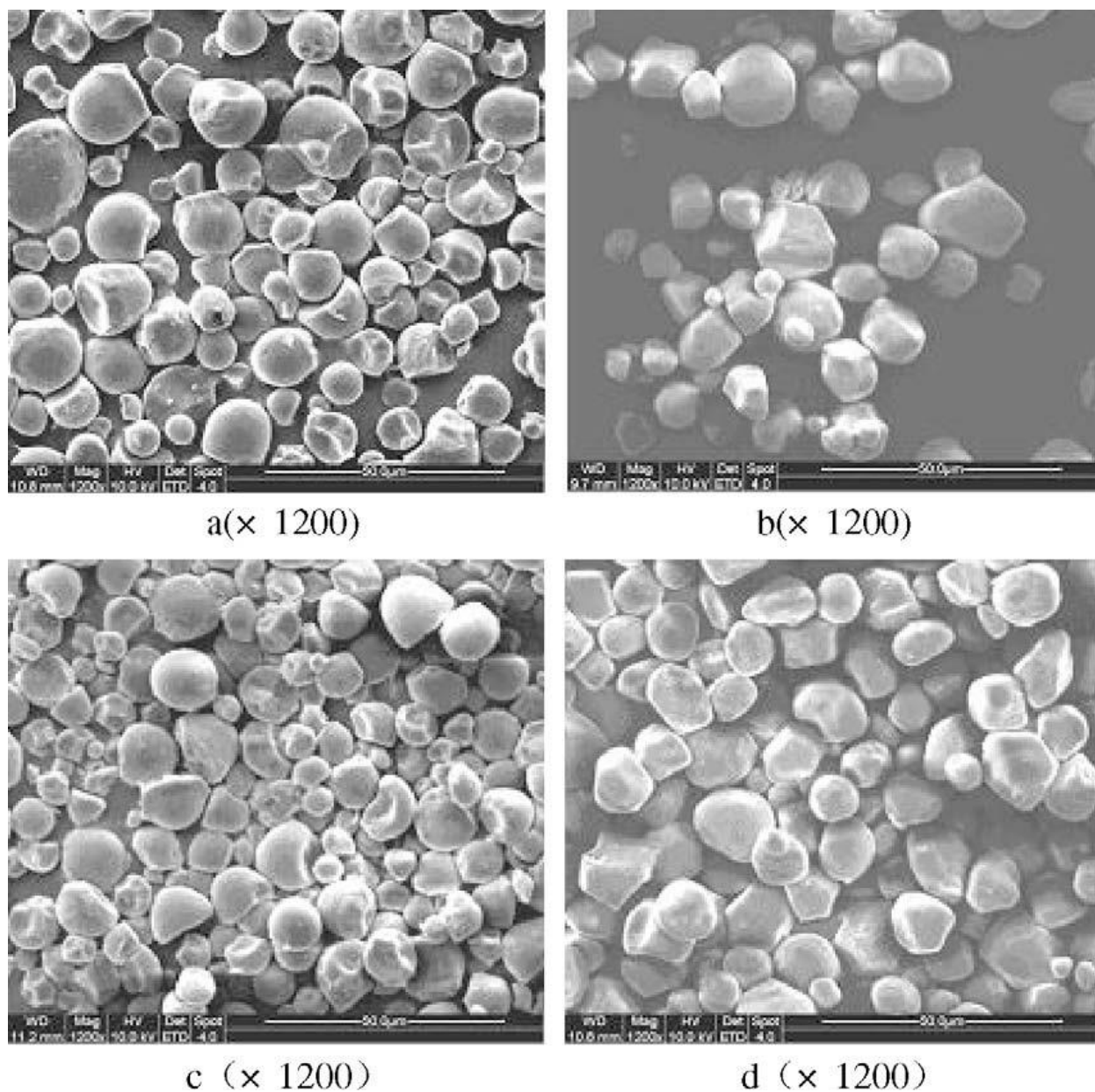


Fig. 4 SEM micrographs of low DS chemical modified starch granule (a: corn starch acetate; b: phosphorylated starch; c: oxidized starch; d: cationic starch)

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