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Research Article/Araştırma Makalesi

Modification of Natural Corn Starch Using Different Methods

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starch, modification, physical, ultrasonic, microwave

Abstract
Natural starch is one of the most abundant biopolymer can be found easily and extracted from many agricultural sources like corn, potato and rice. Natural starch can be used in various industries due to the low cost, biodegradability, to be green chemical, high efficiency in processes and renewability attributes. Food, cosmetics, pharmaceutical and paper industries are some of the areas which starch is being used. Besides these positive features, native starch has some limitations during process like low solubility in cold water, high viscosity, low gelatalization temperature, high tendency to retrogradation. To eliminate these disadvantages, modification is the best solution. Natural starch is being modified since many years with physical, chemical, enzymatic and genetic methods. In starch mills, in order to produce modified starches called cationic, many chemical reagents and high amount energy are being consumed. The aim of this study is, applying to corn starch environmental friendly pre-modification methods like ultrasonic(US) and microwave(MW) assisted modifications. Various conditions (different sequence of methods (US-MW, MW-US), treatment time and power) were applied, changes on granules morfology were characterized with SEM and FTIR analyses. It was aimed to reduce the energy consumption, long process time and amount of chemical reagents used in starch factories during the modification, and also extra analyses(XRD, viscosity, swelling power, brightness and solubility) will be carried out.

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1. Introduction

Starch is biodegredable, biopolymer which is easy to recover and energy reserved in plants as native form of storage of carbonhydrate. It has various application areas in industry due to the low cost and physicochemical properties (Yue, Yue J. Zuo et all, 2012; Shah, Umar et all, 2016). As environmental friendly, one of the renewable resource native starch is commonly used in cosmetics, paper and food industry. (Qing- Yu, Yang et all, 2019). Starch stored in semi-crystalline granules which composed of two main components: long linear chain amylose (20-30%) and mainly branched amylopectin (70-80 %) (Cai, Jinwen et all, 2014; Lima, Felipe, 2010). These components linked by two types of bonds: α-1,4 and α-1,6 glucosidic

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linkages (Sujka, Monika, 2017). Natural starches have limited features in processes. Consequently, starches mainly do not cover all demands of industry because of low gelatinization point, low solubility, tendency to retrogradation and instability thats why modification is essential to effect physicochemical properties of starch in possitive way (Hu, Aijun et all, 2013).

Modification treatments was applied in order to overcome negative physicochemical properties of starches and increase the usefullness of it via changing supramolecular structure (Kaur, Bhupier,2012; Zhu, Jie et all 2012). Native starch can be modified with varios methods like physical, enzymatic and chemical methods. Oxidation is one of the chemical modification method can be take place with different oxidants sodium peroxide, sodium perhypochlorite (Lukasiewicz, Marcin et all, 2011). Microwave irradiation and ultrasonic treatments are physical modification methods. Microwaves are electromagnetic waves in the frequency range of 300-300,000 MHz. Microwaves affect physicochemical properties of starch granules (Lewandowicz, G., et all 2000). Ultrasound is a frequency which is more than human hearing range (>15-20 kHz). Ultrasound is divided into three regions: power ultrasound between 16–100 kHz, high-frequency ultrasound between 100 kHz-1 MHz, and diagnostic ultrasound between 1–10 MHz. It directly attacks on amorphous region of starch granules. The final effect on starch granules, depends on many factors as processing time, power, starch and botanical source (Sujka, Monika and Jamroz, Jerzy, Jamroz, 2013). The aim of this work, pre- modify native corn starch with environmental friendly methods (ultasonic and microwave irradiation) to investigate effect on starch granules and physicochemical properties. It is also aimed to reduce the amount of chemical agent and energy consuming which are being used in starch mills to produce oxidized and cationised modified starches. In present study, modified starches were analysed with SEM and FT-IR spectrum. Furthermore XRD, FTIR, brightness, solubility and viscosity analyses will be carried out.

2. Materıals and Method

2.1. Materials

Corn starch was contributed from Pendik Nisasta with 11.11% moisture. NaOH and H2SO4 were purchased from Merck.

2.2. Preparation of ultrasonic treatment starch solution

Powder corn starch sample having 11.11% moisture was used at the experiments. Corn starch and distilled water were stirred at 600 rpm at room temperature to made a suspension. 30% by weight (w/w) starch suspension prepared.

2.3. Preparation of microwave irradiation starch solution

A powder form of corn starch was dried in 45 ^{0}C hot air oven and then get prepared for microwave treatment in petri dishes.

2.4. Ultrasonic and microwave modification

The prepared suspensions (30% w/w) were homogenized, pH setteled to 11 with 1 N NaOH using a magnetic stirrer at 600 rpm at room temperature and labelled. Ultrasonic modification was applied with sonication probe at 30 ^{0}C for 20, 30, 40

min. After ultrasonic treatment starch was filtered, solid phase separated and dried in hot drying oven at 45^{0}C for 24h. Dried powder starch was grinded and placed in petri dishes to prepare for microwave treatment. Ultrasonicated powder starch samples were exposed to microwave radiations for different power 90, 180, 360, 600 W and time periods 1, 2, 3 min. In last step, starch which was modified with ultrasonic treatment and microwave irradition methods were prepared for SEM, XRD and FT-IR analysis.

2.5. Characterization

The morphological properties of starch were observed using scanning electron microscope (SEM, Zeiss EVO LS10) with an accelerating voltage of 7 kV and a magnification of 10000X. After ultrasonic treatment, the samples were dried in an oven at 45 ^{0}C for 24 hours. The samples were coated with thin gold film before SEM analysis. The chemical structure changes in biopolymers were analysed by Fourier transform infrared (FT-IR) (IR Prestige 21, Shimadzu Corporation, Kyoto, Japan).

3. Results and Dıscussıon

3.1. Results of SEM Analysis

The SEM images of microwave and ultrasonic assisted modificated starches were given in Fig. 2. Starch samples were generally destroyed totally after ultrasonic assisted modification. Much flakes and smaller gel blocks were observed when the concentration and modification time were increased. On the contrary, microwave assisted modification did not gelatinize starch and caused limited corruption to the granular surface. The result of the surface morphology indicated that ultrasonic assisted modification caused more serious damage in a shorter time than microwave assisted modification at the same concentration and power (Li, Yang et all, 2019).

Fig 1. Native starch SEM observation (Zhu, Jie et all, 2012)

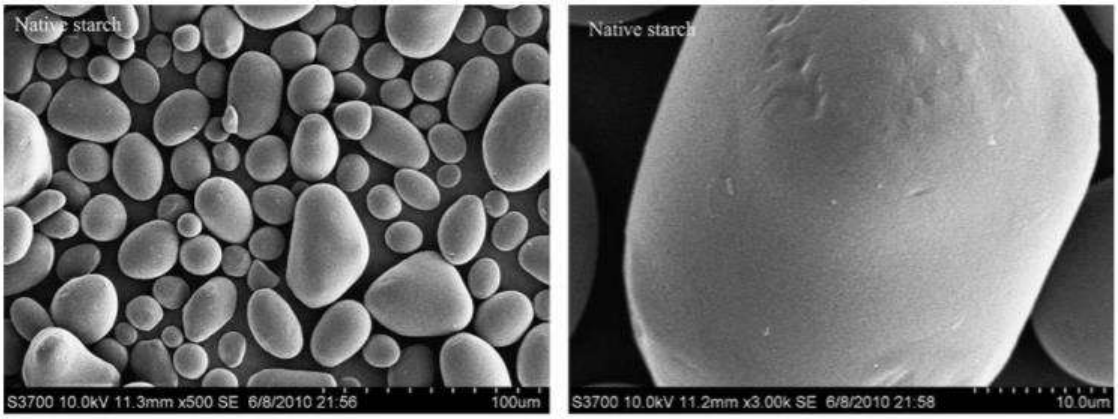
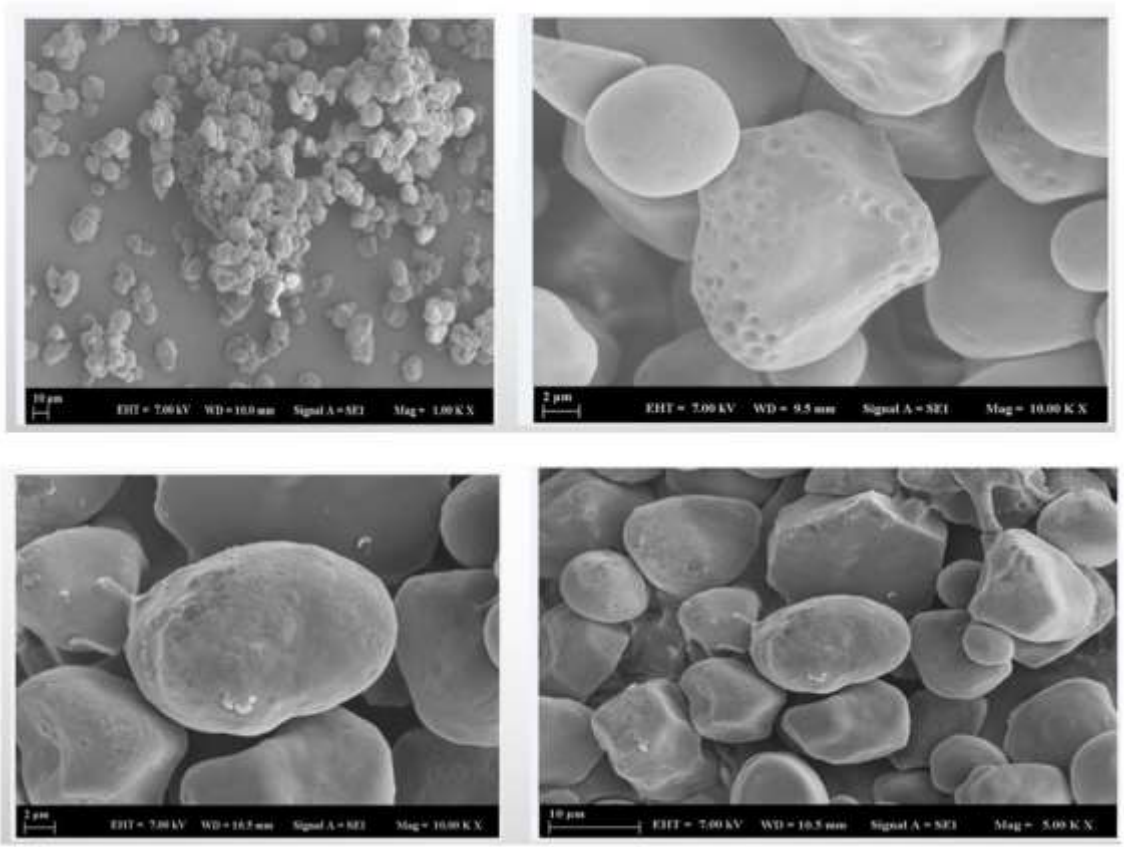


Fig 2. Modified starch SEM



3.2. Results of FT-IR analysis

Fig 3. Microwave (180W t=3 min)- US 40 dk modifided starch FT-IR image

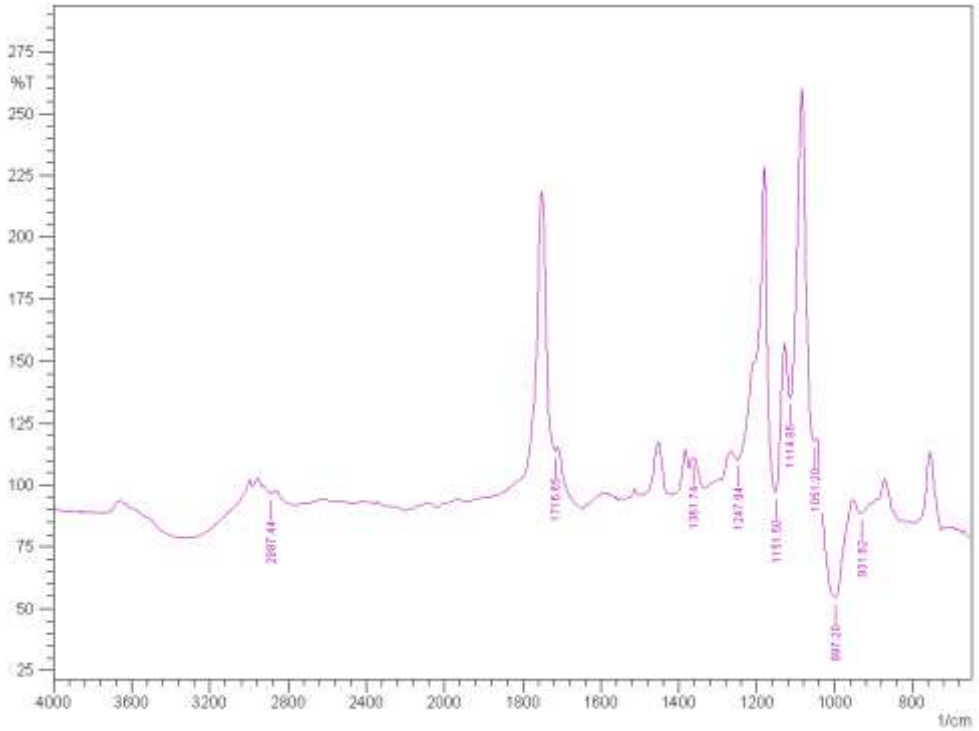
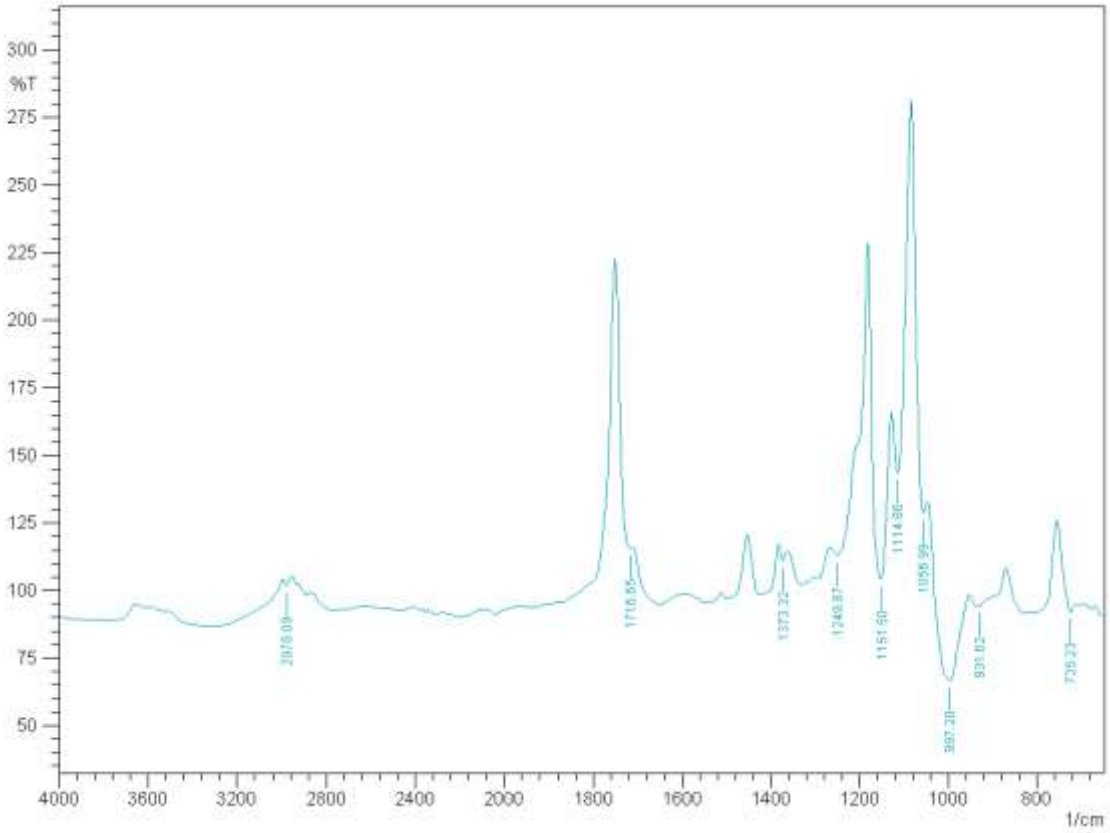


Fig 4. Ultrasonicated 40 min -microwave (180W t=3 min) modifided starch FT-IR spectrum



The FT-IR spectrum of microwave assisted modified starches was given in Fig.3. The band at 3240 cm^{-1}, represent hydrogen bonded O-H stretching vibration. The peaks at 2887.44 and 1716.65 cm^{-1} corresponds to C-H bond stretching and H-O-H bending vibration. The peak at 1361.74 and 1247.94 cm^{-1} represent O-C-H, C-C-H, C-C-H and C-O-H bending vibration. The peak at 1114.86 and 1051.20 cm^{-1} represent coupling of C-O, C-C and O-H bond stretching and asymmetric stretching of C-CC glycosidic bond. The band at 931.62 cm^{-1} represent the vibration of C-O-H (Shah, Umar et all, 2016). FT-IR spectroscopy of ultrasound assisted modified starches was given in Fig.4. The peak obtained at 2978.09 cm^{-1} represent O-H stretching vibration and C-H deformation vibration of glucose element respectively, the peak at 1716.65 cm^{-1} was found to have effect on the bending vibration of O-H in water and amorphous region of starch. (Cao, Meifang andGao Qunyu, 2020). There was not seen any difference depends on modification method order (MW-US or US-MW) at the same conditions.

4. Conclusion

As a result of both ultrasonicated and microwave irradiation modification, corn starch granules was affected by treatments in different dimensions. SEM images show ruptures, notches on surface which was caused by ultrasonic and microwave treatment. It might suggest to apply long ultrasonic frequency for larger scale application of starch.

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