KİÜ FEN, MÜHENDİSLİK VE TEKNOLOJİ DERGİSİ
KİÜ JOURNAL OF SCIENCE, ENGINEERING AND TECHNOLOGY

Isıl, Asidik ve Enzimlerle Bozunmuş Adana Menşeli Mısır Nişastası Granüllerinin Alan Emisyon Tabancası – Taramalı Elektron Mikroskobu (AET-TEM) Kullanılarak Mikroyapı ve Bileşim Tasarımı Modellemesi

Yakup ERMURAT[1,2]

Öz

Doğal veya işlenmiş nişastalar; beslenme, ilaç, kumaş, kağıt, deterjan ve biyobozunur plastik endüstrilerinde yeni algılanabilir ürün yaklaşımlarının geliştirilmesini vaat etmektedir. Bu çalışmada Adana menşeli mısır nişastası granülleri ısıl, asidik ve amilaz enzim bozunma işlemlerine tabi tutularak mikroyapı analizi ve kompozisyon tasarım modellemesi amacıyla Alan Emisyon Tabancası-Taramalı Elektron Mikroskobu (AET-TEM) kullanılarak incelendi. Nişastanın bileşenleri ve mikroyapısal tasviri daha da açıklığa kavuşturuldu ve nişastanın üretimi ve kullanımına yönelik faydalı bilgiler sağlandı. Amilopektin polimer tabakalarının nişasta nanoparçacıklarının form yüzeyindeki genişlemeleri ve parçalanmaları öncelikle şaşırtıcı bir doğrulukla gösterilmiştir. Bozunmuş nişasta granüllerinin nanoparçacık şekil yüzeyi ve element analizi yapıldı. Bozunma basamakları üzerine amilopektin polimer katmanlarının bozunma aşamaları özellikle fevkalade bir hassasiyetle sunuldu. Glikoz molekülündeki karbon ve oksijen elementlerinin deneysel uyum oranları benzeşiklenmesi sırasıyla 0,99 ve 0,29 olarak belirlendi.

Anahtar Kelimeler: Isıl Asidik ve Enzimatik Bozunma, Adana Menşeli Mısır Nişastası Granülleri, Mikroyapı ve Bileşim Tasarımı Modellemesi, Yapısal ve bileşim analizleri, Alan Emisyon Tabancası – Taramalı Elektron Mikroskobu (AET-TEM)

Microstructure and Composition Design Modeling of Thermal, Acidic and Enzyme Degraded Adana Origin Maize Starch Granules Using Field Emission Gun-Scanning Electron Microscope (FEG-SEM)

Abstract

Native or modified starches are utilized in nutrition, medicine, fabric, paper, detergent and biodegradable plastic industries promising the development of new perceptible product approaches. In this study, Adana origin maize starch granules were treated with thermal, acidic and amylase enzyme degradation processes and examined using the Field Emission Gun-Scanning Electron Microscope (FEG-SEM) for the microstructure analysis and composition design modeling. The nanoparticle shape surface and elemental analysis of the degraded starch granules were determined. The components and microstructural depictions of starch were further clarified, providing useful knowledge for the production and use of starch. The amylopectin polymer layers' expansions and breakdown on the starch nanoparticle's form surface were primarily demonstrated with startling accuracy. The destructions of the amylopectin polymer layers upon the degradation steps were particularly presented in extraordinary precision. The experimental deviation ratios modeling of carbon and oxygen elements in glucose molecule were determined as 0.99 and 0.29 respectively.

Keywords: Thermal Acidic and Enzymatic Degradation, Adana Origin Corn Starch Granules, Microstructure and Composition Design Modeling, Structural and compositional analysis, Field Emission Gun-Scanning Electron Microscope (FEG-SEM).

[1]Bolu Abant İzzet Baysal University, Engineering Faculty
[2]Kahramanmaraş İstiklal University, Engineering Architecture and Design Faculty, Department of Basic Sciences, Kahramanmaraş, Türkiye, yakupermurat@ibu.edu.tr https://orcid.org/0000-0002-0159-5283

*Sorumlu Yazar/Corresponding Author **Geliş/Received:** 08.02.2024 **Kabul/Accepted:** 04.04.2024

1. Introduction

Native or modified starches are broadly investigated biopolymer materials that are used in advantageous discoveries leading considerable manufacturing inventions. Varieties of starches depending on the origin and process are consumed in nutrition, medicine, fabric, paper, detergent and biodegradable plastic industries. The global starch demand is supplied by various plants as corn, cassava, wheat, and potato plants (Hill & Dronzek 1973; Jane, 1995, BeMiller, 2009; Vilpoux & Silveira 2023).

Starch biopolymer materials are purely composed of glucose (dextrose or sucrose) molecules as shown in Figure 1 (PubChem 2023), making of linear amylose and branched amylopectin biochain layer microstructures which are 1 to 100 μm sized spherical, oval or ellipsoidal shaped starch granular nanoparticles as displayed in Figure 2 (Pfister et al., 2020).

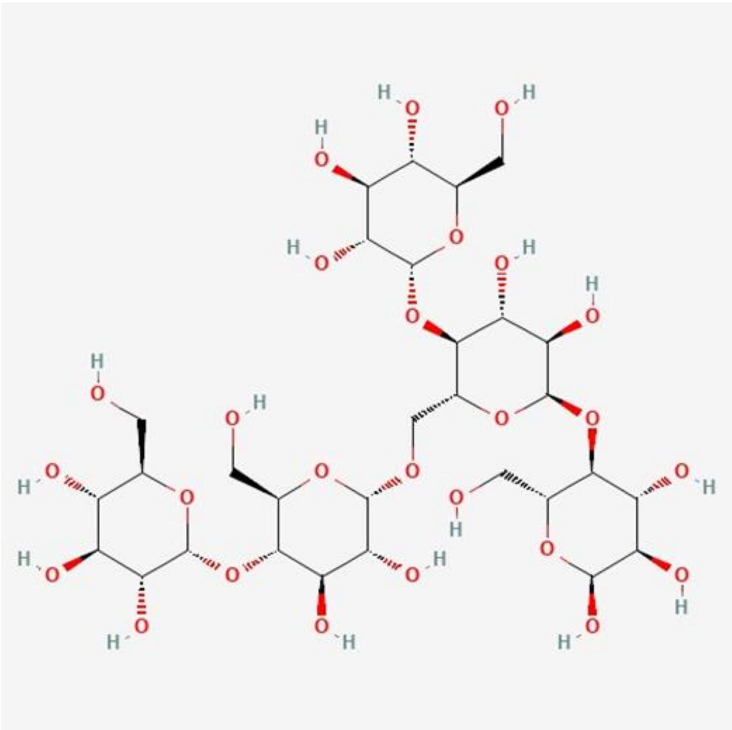

Figure 1. Amylose and amylopectin comprised purely glucose (or sucrose) molecules (PubChem 2023)

Figure 2 shows an illustration quoted from the study conducted by Pfister et al. which offers progressive diagram techniques to demonstrate molecular configuration of starch granules (Pfister et al., 2020; Vilpoux & Silveira 2023, PubChem, 2023).

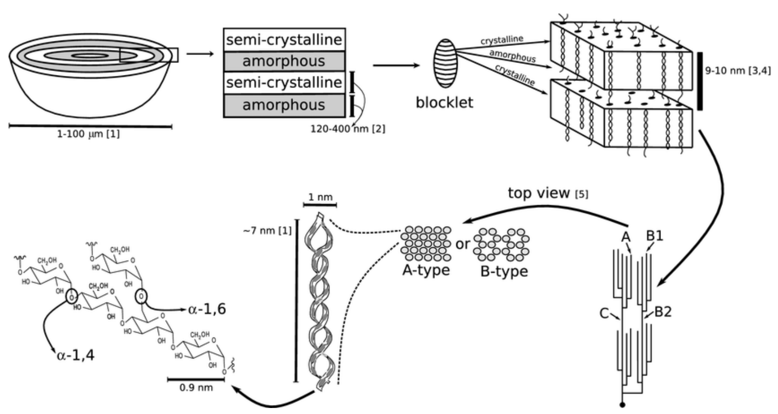

Figure 2. Configuration of glucose polymer amylose and amylopectin simulations of starch [3]

Glucose with $C_6H_{12}O_6$ molecular formula holds approximated mass percentages of carbon, oxygen and hydrogen as 42%C, 51%O and 7%H theoretically.

The structure of starch granules is susceptible to breakdown under thermal, chemical and biochemical operations to make starch more useful for food and non-food industries. The value of native starch polymer properties can be improved through physical and chemical modifications to expand textural characteristics to provide functional performances as flexibility, solubility and adhesion properties for industrial uses. Starch biopolymers can be degraded under high temperature conditions, and hydrolyzed in acidic or enzymatic breakdown applications. Potential use of interest in this case, the heat degraded starch is named as modified starch in which amylose and amylopectin molecules are degraded resulting more useful decomposed structure. Glucose bonds in starch polymers are hydrolysed to obtain complete yield to dextrose molecules by acid or enzyme hydrolysis process which are used for the productions of sweets as dextrose, maltose and fructose syrups or syrup mixtures such as high fructose corn syrup blends, commonly used as nutrition supplements for drinks, meals or serum productions (Bachler et al., 1970; Liu et al., 2016; Robyt, 2008).

The starch a polymeric material made of α-glucose chain structure is used as one of the most preferred biodegradable plastic materials contains ecologically pleasant constituents (Jane 1995). The starch polymers can be converted into biodegradable plastics by application of derivatization and degradation reactions. Chemical modification processes are used to fix functional groups into the starch polymer molecules to produce biodegradable plastic materials by derivatization; etherification, esterification and crosslinking or degradation; hydrolysis and oxidation reactions (Chen et al., 2018; Castillo et al., 2019). The most studied in the field of biodegradable plastics, etherification reaction mechanism was first developed by Williamson in 1850, comprises a nucleophilic substitution to the hydroxyl groups of starch biopolimers (Olawoye et al., 2023).

It is greatly practiced study to investigate microstructure and composition of starch biopolimers to be benefited more efficiently and productively in relation to its applications in the industry (Nikuni, 1978; BeMiller, 2009). Morphology of untreated native or treated modified starch varieties systematically and extensively examined for the structure and constituent exploration by electron microscopy. The microstructural electron microscopy images of the native or modified starch granules in the size and shapes were scrutinized in several numerous preceding studies (Fannon et al., 1992; Li et al., 2010; Chakraborty, 2020; Govindaraju et al., 2020).

Corn is cultivated and harvested as both the primary and secondary crops in productive Adana province of Çukurova region where high amount of corn starch is produced (Say & Erdogan 2011; Rolbiecki et al., 2022).

The aim of this study is accomplishing the microstructure and composition design modeling of thermal, acidic and enzyme degraded Adana origin maize starch granules using Field Emission Gun-Scanning Electron Microscope (FEG-SEM).

2. Materials and Methods

Adana origin corn starch samples were heat roasted at 340 °C using pyrolysis process, hydrochloric acid acidified and applied to amylase enzyme conversion at 35 °C temperature and pH 3.0. The thermal, acidic and enzyme processed starch samples were dried at room temperature, than used for microstructural imaging by Field Emission Scanning Electron Microscopy (FEG-SEM) in facility of University of Düzce.

3. Results and Discussions

The thermal, acidic and the enzyme modifications of starch were accomplished in this study which offers native starch to have more opportunities of utilization in food and non-food products manufacturing. Native Adana origin starch granules were examined using the Field Emission Gun-Scanning Electron Microscope (FEG-SEM) after modification by heat, acid and enzyme application for the microstructure analysis and composition design modeling. Figure 3 represents the microstructural image of heat, acid and enzyme degraded starch granule which was provided in the sizes of 1 mm and 100 μm. The degradation of the amylopectin polymer layers upon the degradation steps were particularly presented in astonishing exactness for revealing molecular structure of starch granule in this observed figure.

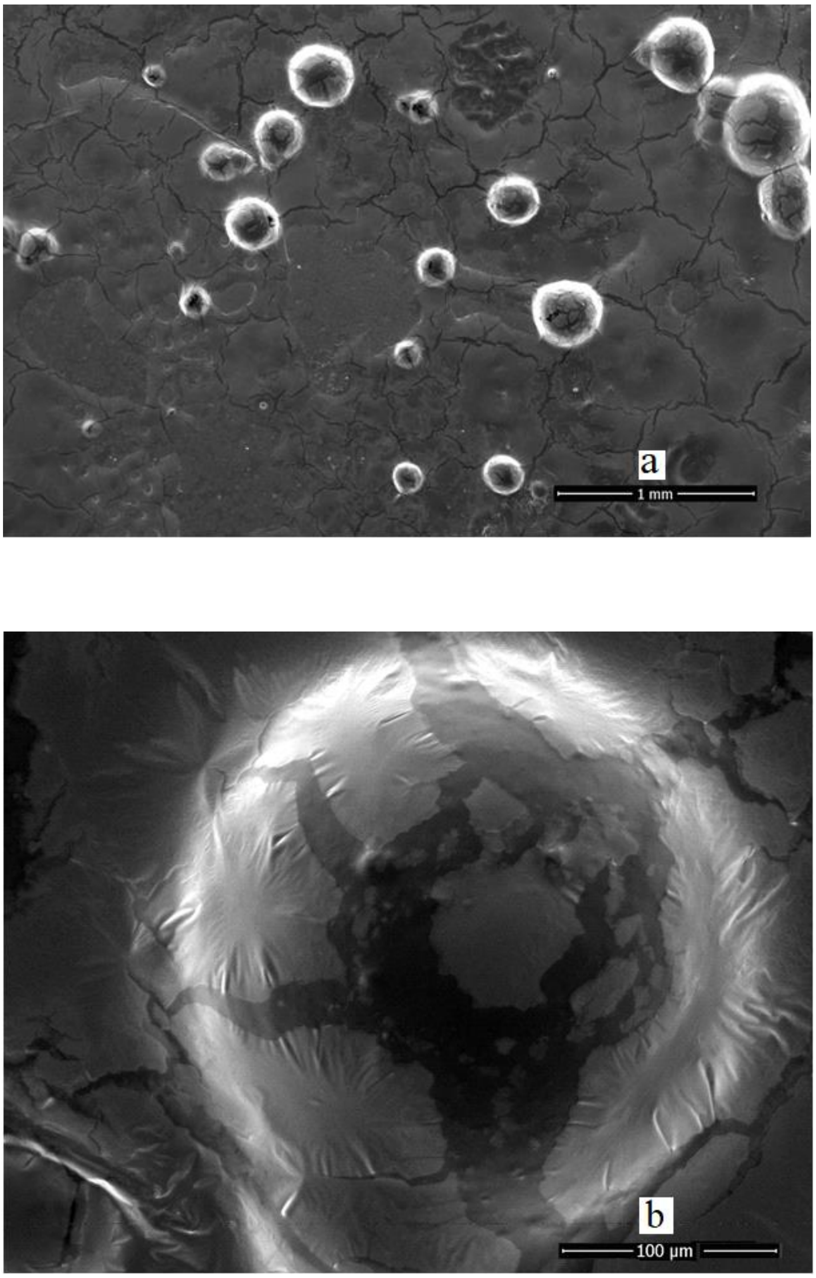

Figure 3 (a-b). The SEM images of the treated starch granule

Modified Adana origin maize starch granule was presented blustered spherical starch surface microstructure image as shown in Figure 3 (a-b) to reveal molecular structure of degraded starch granule as investigated in the previous studies. The polymeric material of starch, made of α-glucose chain structure constituent was biodegraded, and the destruction of the amylopectin polymer layers upon the degradation steps were particularly presented in astonishing precision similar to simulated and described in Figures 1 and 2 (PubChem, 2023). Above all, this starch microstructural image observation was significantly elucidated beneficial information offering for the starch manufacturing and utilizing than the formerly starch structural visualization surveys found in the numerous related literature (Hill, 1973; Nikuni, 1978; Bertoft, 2017; Shi et al., 2019). In a very earlier classical starch structural investigation, Hall and Sayre compared various starch granules using both scanning electron and ordinary light microscopy techniques that established the concomitant microscopy study of starch granules (Hall & Sayre 1973), though this study dealt with single starch sample but more advanced microscopy technique. Surface scratches on the spherical starch granule in this study present more detail than that of Fannon et al. who observed starch granule surface pores (Fannon et al., 1992). Astounding accuracy was observed in Figure 3 (a-b) which was proved exactness of the layers of the decomposed spherical starch granule than that of Chakraborty et al. who studied molecular structure of starch granules using advanced microscopy techniques to divulge microstructure of the granules (Chakraborty, 2020), and Govindaraju et al. who surveyed structure and morphological properties of starch macromolecule using biophysical techniques (Govindaraju et al., 2020).

There was no esterification and etherification reactions conducted to convert the modified starch into biodegradable plastics in this study, however microstructural and composition analysis offers valuable information that can be benefited in bioplastic production relatively. Experimental over theoretical consistency ratios of carbon besides oxygen were calculated using the elemental composition design modeling analysis, and the calculation results of carbon ratio was determined as 0.99, and oxygen ratio was outcome as 0.29 in glucose molecule of starch biopolimer.

4. Conclusions

Adana origin native maize starch granules were modified with thermal, acidic and amylase enzyme breakdown processes and examined using FEG-SEM for the microstructure analysis and composition design modeling. The starch microstructural image and components were significantly elucidated advantageous information offering for the starch manufacturing and utilizing. The degradation and stretches of the amylopectin polymer layers on the shape surface of the starch nanoparticle were principally shown in astounding precision. The experimental obviousness modeling of the elemental ratios of carbon and oxygen of glucose molecule were approximated as 0.99 and 0.29 respectively. Further all, this starch microstructural image observation was significantly elucidated beneficial information offering for the starch manufacturing and utilizing than the formerly starch structural visualization surveys found in the numerous related literature. The structure of starch granules is susceptible to breakdown under thermal, chemical and biochemical operations to make starch more useful for food and non-food industries. Value of native starch polymer properties are improved through physical and chemical modifications to expand textural characteristics to provide functional performances as flexibility, solubility and adhesion properties for industrial uses. Starch biopolymers can be degraded under high temperatures, and hydrolyzed in acidic or enzymatic breakdown applications. Potential use of interest in this case, the heat degraded starch is named as modified starch that the amylose and amylopectin molecules are degraded resulting more useful decomposed structure. Glucose bonds in starch polymer are fragmented by acid or enzyme hydrolysis process to obtain complete yield to dextrose molecules which are used for the production of sweets as dextrose, maltose and fructose syrups or syrup mixtures such as high fructose corn syrup blends, commonly used as nutrition supplement for drinks, meals or serum production (Bachler et al., 1970; Robyt, 2008). It is greatly practiced study to investigate microstructure and composition of starch biopolimers to be benefited more efficiently and productively in relation to its applications in the industry. Morphology of untreated native or treated modified starch varieties systematically and extensively examined for the structure and constituent exploration by electron microscopy.

References

Bachler, M.J., Strandberg, G.W., & Smiley, K.L. (1970). Starch conversion by immobilized glucoamylase. Biotechnology and Bioengineering 1:12(1):85–92. https://doi.org/10.1002/bit.260120108

BeMiller, J.N. (2009). Starch: Chemistry and Technology, 3rd Ed. Academic Press

Bertoft, E. (2017). Understanding Starch Structure: Recent Progress. Agronomy 7(3):56. https://doi.org/10.3390/agronomy7030056

Castillo, L.A., López, O.V., Garcia, M.A., Barbosa, S.E., & Villar, M.A. (2019). Crystalline morphology of thermoplastic starch/talc nanocomposites induced by thermal processing. Heliyon 1:5(6):e01877. https://doi.org/10.1016/j.heliyon.2019.e01877

Chakraborty, I., Pallen, S., Shetty, Y., Roy, N., & Mazumder, N. (2020). Advanced microscopy techniques for revealing molecular structure of starch granules. Biophysical Reviews 16:12(1):105–22. https://doi.org/10.1007/s12551-020-00614-7

Chen, Y.F., Kaur, L., & Singh, J. (2018). Chemical modification of starch. In: Elsevier eBooks 283–321. https://doi.org/10.1016/b978-0-08-100868-3.00007-x

Chen, P., Yu, L., Chen, L., & Li, X. (2006). Morphology and Microstructure of Maize Starches with Different Amylose/Amylopectin Content. Starch-starke 1:58(12):611–5. https://doi.org/10.1002/star.200500529

Fannon, J.E., Hauber, R.J., & BeMiller, J.N. (1992). Surface pores of starch granules. Cereal

Chemistry 69:284-288.

Govindaraju, I., Chakraborty, I., Baruah, V.J., Sarmah, B., Mahato, K.K., & Mazumder, N. (2020). Structure and morphological properties of starch macromolecule using biophysical techniques. Starch-starke 12:73(1–2). https://doi.org/10.1002/star.202000030

Hall, D., & Sayre, J.G. (1973). A comparision of starch granules as seen by both scanning electron and ordinary light microscopy. Starch-starke 1;25(4):119–23. https://doi.org/10.1002/star.19730250404

Hill, R.D., & Dronzek, B.L. (1973). Scanning Electron Microscopy Studies of Wheat, Potato and Corn Starch during Gelatinization. Starch-starke 1:25(11):367–72. https://doi.org/10.1002/star.19730251104

Jane, J. (1995). Starch Properties, Modifications, and Applications. Journal of Macromolecular Science 32(4):751-757. https://doi.org/10.1080/10601329508010286.

Li, P., Ben-Shan, Z., Shen, Q., Hu, X., & Li, W. (2010). Preparation and structure analysis of noncrystalline granular starch. International Journal of Food Engineering 26:6(4). https://doi.org/10.2202/1556-3758.1900

Liu, Y., Xie, H., & Shi, M., (2016). Effect of ethanol–water solution on the crystallization of short chain amylose from potato starch. Starch - Stärke, 68:683-690. https://doi.org/10.1002/star.201500300

Nikuni, Z. (1978). Studies on Starch Granules. Starch 30(4):105-111. https://doi.org/10.1002/star.19780300402

Olawoye, B. et al. (2023). Modification of Starch. In: Sharanagat, V.S., Saxena, D.C., Kumar, K., Kumar, Y. (eds) Starch: Advances in Modifications, Technologies and Applications. Springer, Cham. https://doi.org/10.1007/978-3-031-35843-2_2

Pfister, B., Zeeman, S.C., Rugen, M.D., Field, R.A., Ebenhöh, O., & Raguin, A. (2020). Theoretical and experimental approaches to understand the biosynthesis of starch granules in a physiological context. Photosynthesis Research 18:145(1):55–70. https://doi.org/10.1007/s11120-019-00704-y

PubChem. (2023). Compound Summary for CID 439207 Amylopectin, National Library of Medicine (US), National Center for Biotechnology Information. https://pubchem.ncbi.nlm.nih.gov/compound/Amylopectin

Robyt, J. (2008). Starch: Structure, Properties, Chemistry, and Enzymology. In: Fraser-Reid BO, Tatsuta K, Thiem J, Glycoscience. Springer, 1437–1472. https://doi.org/10.1007/978-3-540-30429-6_35.

Rolbiecki, R., Yücel, A.G., Kocięcka, J., Atilgan, A., Markovć, M., & Liberacki, D. (2022). Analysis of SPI as a Drought Indicator during the Maize Growing Period in the Çukurova Region (Turkey). Sustainability Mar 21:14(6):3697. https://doi.org/10.3390/su14063697

Shi, M., Yue, J., Liu, Y., Huang, X., Wang, H., & Yan, Y. (2019). Structure and physicochemical properties of malate starches from corn, potato, and wrinkled pea starches. Polymers 19:11(9):1523. https://doi.org/10.3390/polym11091523

Say, S.M., & Erdogan, Y., (2011). Energy use pattern of first crop maize production: Case study for Cukurova region in a sample farm. Journal of Food, Agriculture and Environment 9(2):309-312.

Vilpoux, O.F., & Silveira, J.F.S. (2023). Global production and use of starch. In: Elsevier eBooks 43–66. https://doi.org/10.1016/b978-0-323-90058-4.00014-1