Kahramanmaras Sutcu Imam University
Journal of Engineering Sciences

Synthesis and Characterization of Adhesive Obtained from Waste Potato Starch: Its Application on Bobbin Cardboard

Atık Patates Nişastasından Yapıştırıcı Sentezi ve Karakterizasyonu: Karton Masura Üzerine Uygulamaları

Mustafa Dolaz[1]*, Nuran Celikci*[1]*, Cengiz Ayhan Zıba**[2]

[1]University of Kahramanmaras Sutcu Imam, Department of Environmental Engineering, Kahramanmaras, Turkey
[2]University of Kahramanmaras Sutcu Imam, Department of Chemistry, Kahramanmaras, Turkey

*Sorumlu Yazar / Corresponding Author: Cengiz Ayhan ZIBA, caziba@ksu.edu.tr

ÖZET

Atık patates nişastası (WPS) gıda endüstrisinde patates cipsi üreten (sulu ortamda soyularak dilimlendiği aşamada patates nişastası ayrılmaktadır) işletmelerden temin edildi. NaOH ve H_2O_2 ile temizlendikten sonra modifiye atık patates nişastası (MWPS) elde etmek için HCl ile hidroliz edildi. MWPS'lerin yapıları FT-IR ve XRD ile karakterize edildi. DTA-TG ile termal davranışları ve SEM görüntüleri ile yüzey morfolojileri incelenerek viskoziteleri tayin edildi. Bunlara ilaveten MWPS örnekleri ile bobin kartonları üst üste getirilerek yapıştırıldı ve ticari yapıştırma ürünleri ile karşılaştırıldı. Yapışma mukavemetinde en iyi sonuç 12,3 MPa olarak, 1,0 M HCl ile hidrolizinden sentezlenen MWPS örneğinden elde edilmiştir.

Anahtar Kelimeler: Atık patates nişasta, hidrolize nişasta, yapıştırıcı, FT-IR, XRD

ABSTRACT

Waste potato starch (WPS) was obtained from the food industry during slicing, peeling, and washing by producing potato chips. After WPS was purified with H_2O_2 and NaOH, it was hydrolyzed by HCl to obtain modified waste potato starch (MWPS). The MWPS structure was characterized by FT-IR and XRD. Thermal behaviors of MWPSs were investigated by the DTA-TG method and their surface morphology was analyzed by the SEM method. The viscosities of MWPSs were determined. Furthermore, the bobbin cardboard was overlaid and glued by MWPSs. The strength test was applied on the bobbin cardboard and compared with commercial products. The best result was 12.3 MPa on MWPS hydrolyzed 1.0 M HCl.

Keywords : Waste potato starch, Hydrolyzes starch, Adhesive, FT-IR, XRD

1. INTRODUCTION

Starch is of two polysaccharide composed biopolymers which is linear amylose and branched amylopectin. Amylose is a linear molecule in which up to 1000-3000 glucose units are linked to each other by (α-1,4) glycosidic bonds. Also, amylopectin is a branched polymer and is formed by branching with the linkages of glucose units (α-1,6) linked by (α-1,4) bonds and which may have several million glucose units (Delcour *et al.*, 2010; Wang and Copeland, 2012; Wang *et al.*, 2012; Farhad and Richard, 2017). The amylose / amylopectin ratio of starch can be affected via gelatinization and retrogradation properties. The gelation degree of the natural potato starch is understood that can be started to gel form at 59-68°C temperature (Ai and Jane, 2015) when compared to other natural starches. The potato starch has become an important component in food ingredients, textile, paper and other industry. In the light of these investigations, the modified potato starches (MPS) have found unlimited use around the world. Potato starches can be modified easily with help of chemicals and thermal process. The purpose of starch modification is to improve the functional properties of natural starch by altering some of its physical and chemical properties. In this context, MPS is generally used for plating, gelatin, transparence, moisturizing, and stabilization. Moreover, MPS can be produced as glue because of environmentally friendly and low-cost. For a long time, the acid hydrolysis technique has been preferred to modify starch and soluble starch in water (Wang *et al.*, 2012; Wang and Copeland, 2015). The molecular structure and some properties (e.g. paste viscosity or gel strength) of the starch were changed when applied acid treatment on the starch. However, the basic granular structure is preserved while this application (Ulbrich *et al.*, 2016; Abdorreza *et al.*, 2012).

In this study, the waste potato starch (WPS) has been hydrolyzed by diluted hydrochloric acid (HCl) in order to adhesive of bobbin cardboard. The structure of synthesized modified waste potato starch (MWPS) was characterized by FT-IR, XRD, SEM

.

and DTG-TG. After the characterization experiments, the strength tests were applied on the bobbin cardboard and also its adhesive properties was compared with commercial products.

2. EXPERIMENTAL

2.1. Materials

WPS was supplied from Seydisehir-Beysehir Torku Potato Chips Factory, Konya in Turkey. The WPS were purified by using 40% sodium hydroxide and 30% hydrogen peroxide so as to remove impurities comes from cellulose-containing shell and proteins. Subsequently, dried waste potato starch was hydrolyzed by diluted HCl. In order to understand effect of the experimental parameters, temperatures and reaction time were examinated. All experiments were performed in water unless stated otherwise.

2.2. Methods

2.2.1. Acidic modification of waste potato starch

25 g WPS was mixed in 70 mL distillated water with mechanical stirrer. This solution was hydrolyzed at different temperatures (45, 55, 60, 65 and 70°C), various periods of time (5, 10, 15, 20 and 25 min.) and 25 mL HCI (0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0 M). Acid modification process was applied on the potato starches according by Koksel et al., 2007. The solution was subsequently cooled at 25°C. After, the pH of the slurry was changed to the pH around 7 using NaOH. In the last step of the experiments, the obtained product was used as adhesive of bobbin cardboard.

2.2.2. Viscosity of starch

The viscosity of MWPSs was determined using a viscometer (Brookfield Prime DV-I, USA) at 25°C (Babu *et al.*, 2015; Liu *et al.*, 2014). Viscosity values were measured with three different spindles (S1, S2 and S3). The measured viscosity values were shown in Table 1.

2.2.3. Measurement of adhesive

The strength tests were determined according to this method which was used by Emenge at al., 2002. A bobbin cardboard was prepared by the ASTM D638 standards and the area of 2 cm^2 from the middle of the bobbin cardboard was overlaid and glued. All samples were dried at 85 ºC in oven and tested. The strength tests results were demonstrated in Table 2.

3. RESULTS AND DISCUSSION

Waste potato starch (WPS) was obtained from the food industry during slicing, peeling, and washing by producing potato chips. After WPS was purified with H_2O_2 and NaOH, it was modified by HCl to obtain MWPS. It was obtained that for hydrolysis of 25 g WPS, the optimum conditions were recorded at 62 ºC, for 15 min. in 1 M HCl. The MWPS structure was characterized by FT-IR and XRD. Thermal behaviors of MWPSs were investigated by the DTA-TG method and their surface morphology was analyzed by the SEM method. The viscosities of MWPSs were determined. Furthermore, the bobbin cardboard was overlaid and glued by MWPSs. The strength test was applied on the bobbin cardboard and compared with commercial products.

3.1. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

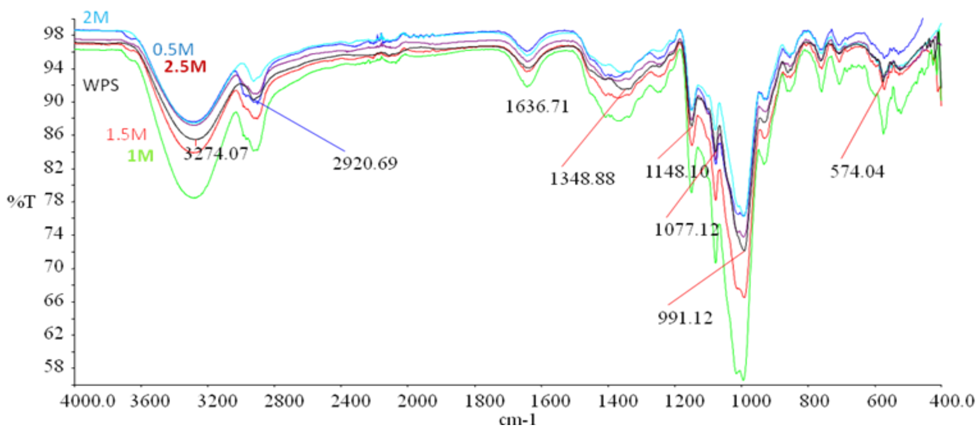
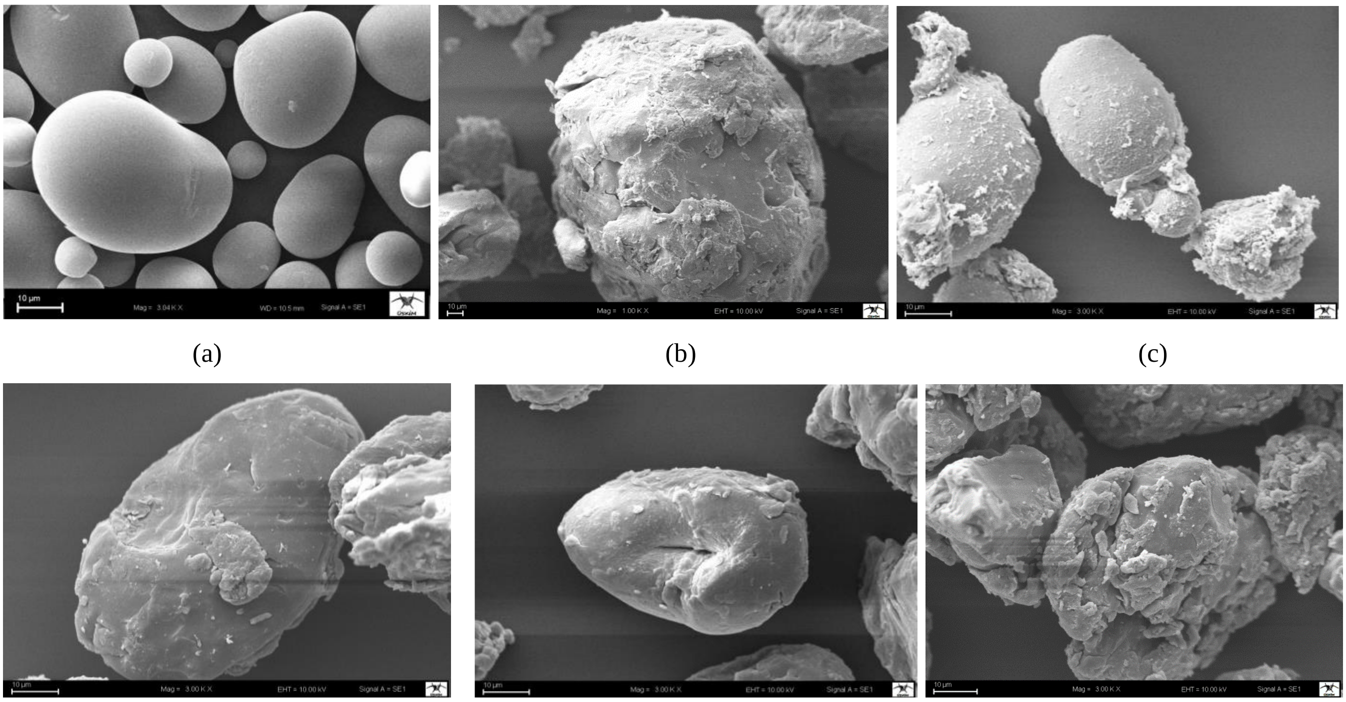


Figure 1. WPS and MWPSs hydrolyzed by 0.5M, 1.0M, 1.5M, 2.0M, 2.5M HCl

WPS and MWPSs were characterized by Fourier transform infrared (ATFT-IR) spectrophotometer (Perkin Elmer Spectrum 400, USA). The FTIR result of non hydrolyzed and hydrolyzed starch was shown in Fig. 1. The spectra shows in Fig. 1 that a broad absorption band at 3274 cm^{-1} for O-H stretching vibrations and a smaller absorption band at 2920 cm^{-1} attributed to C-H stretching vibration. At 1148, 1077 and 991 cm^{-1} wavelengths describe C-O-C stretching (triplet for starch) and of all the starch samples is an evidence for the vibration of the glycosidic linkage. A band at 1636 cm^{-1} corresponds to water molecule (Sangramsingh *et al.*, 2004).

3.2. Scanning Electron Microscopy (SEM) Analysis



(a) (b) (c)

(d) (e) (f)

Figure 2. WPS (a), hydrolyzed MWPS with respectively 0.5M (b), 1.0M (c), 1.5M (d), 2.0M (e), 2.5M (f)

Surface morphologies of WPS and MWPSs granule were examined by a scanning electron microscope (JEAL/NEOSCOPE JCM-5000, Japan). The SEM images of WPS and MWPSs illustrated in Fig. 2. The illustration of starch samples (i.e. WPS and MWPS) showed the presence of starch granules from small to large sizes. While the surface of WPS granules appeared to be smooth with no sign of any fissure, the surface of MWPS roughed and unsmoothed (Babu *et al.*, 2015).

3.3. Thermo-Gravimetric Analyzes (DTA-TG)

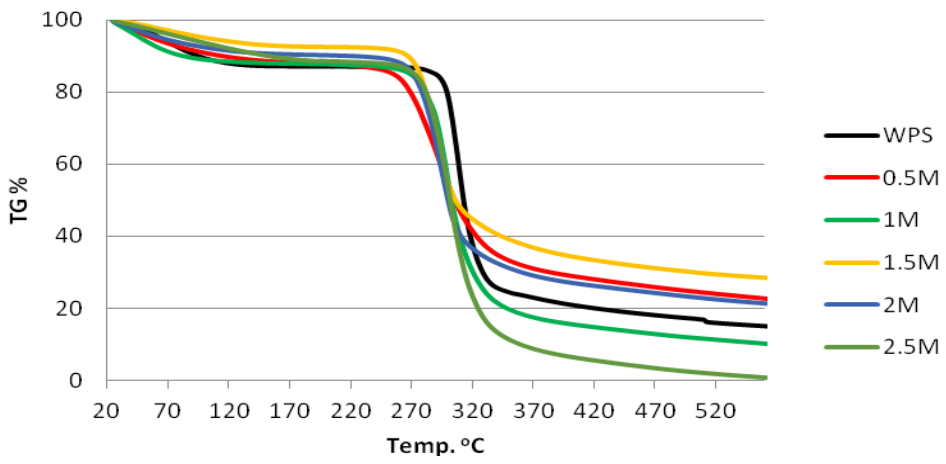


Figure 3. TG Termograms of WPS and hydrolyzed MWPSs

Thermal properties were investigated by SEIKO II TG-DTA. The DTG and TG curves for WPS and MWPSs were presented in Figs 3-4. The thermal analysis proved that the reaction between the components of the blend occurred. The decomposition of WPS occurred in two steps. First step at around 90-100°C was the dehydration of WPS. While second step of WPS showed a prominent effect at 330 °C with about 60% lost of the total weight, MWPSs at 260°C (Fig. 3).

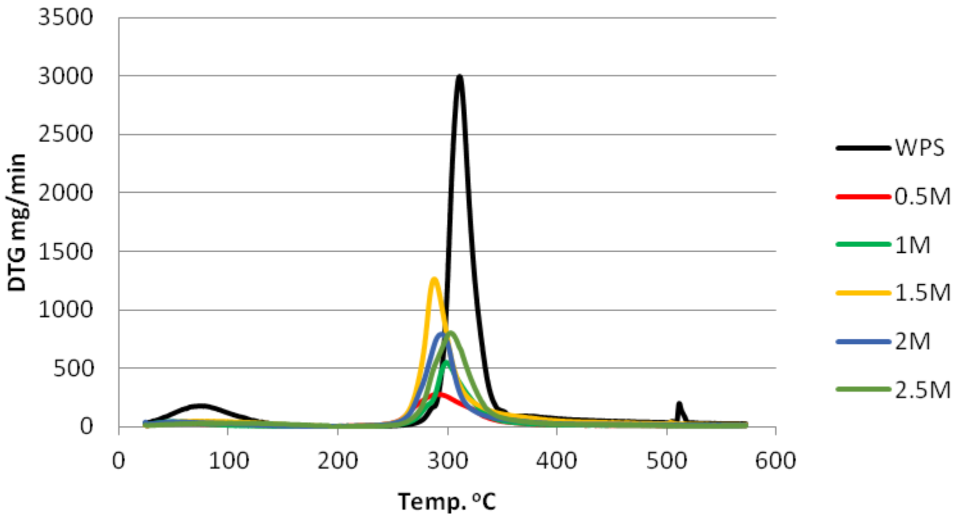


Figure 4. DTG Termograms of Hydrolyzed MWPSs

The DTG curves demonstrated a single peak for this degradation to a carbonaceous residue. Besides, decomposition of hydrolyzed WPS continues from degree 260°C with increasing temperature (Fig. 4). Although WPS decomposed at higher temperature than MWPSs, it lost weight more than the others per minute as microgram (mg/min). As can be seen from the thermograms, it was understood that the least loss of weight was observed in 0.5M sample, while the maximum lost weight was obtained 1.5M.

3.4. X-Ray Diffraction Analyzes (XRD)

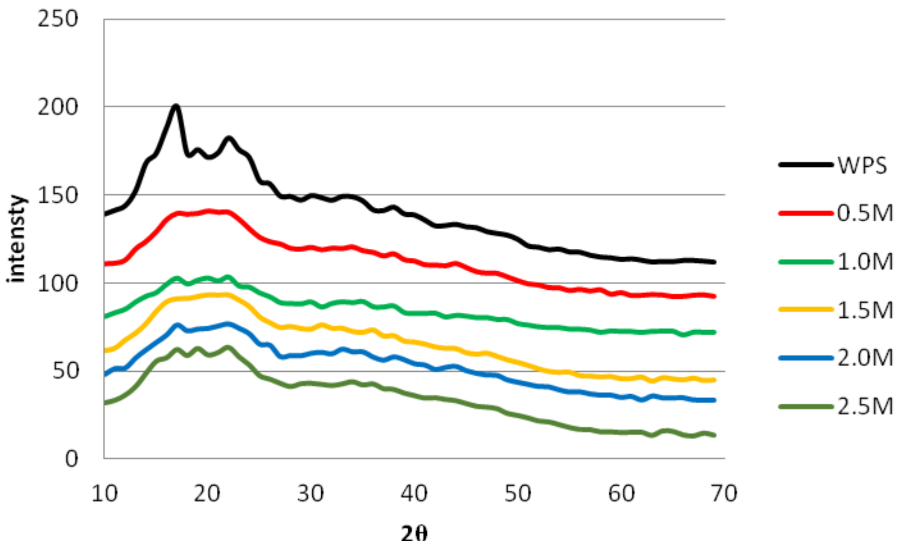


Figure 5. X-ray diffraction patterns of WPS and hydrolyzed MWPSs

The crystalline characteristics of the samples were investigated by X-ray diffraction method (XRD) (model Philips X'Pert PRO). Diffraction patterns of WPS and MWPSs are showed in Fig 5. The diffractogram of WPS exhibits a typical B-type crystallinity pattern (Zhang et al., 2012). It was observed that while the structure of WPS was weak crystalline with amorphous character, the crystallinity was changed after hydrolysis reaction. The loss of crystallinity could be due to the effect of the acid environment during the modification. The breakage of chemical bonds in starch granules with heat treatment was also the possible reason of the loss of crystallinity (Zhang et al., 2012). As a result, formation lost of the crystallinity on MWPSs was verified by thermal characterization by means of DTG and TG.

3.5. Measurement of Viscosity

The viscosity measurement values of MWPSs which dissolved 25 g MWPS in 175 mL were given in Table 1. As shown in Table 1, the highest efficiency of Spindle 1 at 50 rpm was 95% in 1M MWPS comparing with commercial product.

Table 1. Viscosity measurement of MWPS

rpm	Sample	Spindle 1 cP (Efficiency %)	Spindle 2 cP (Efficiency %)	Spindle 3 cP (Efficiency %)
10	Blank	372 (37)	592 (15)	760 (8)
	0.1 M HCl	N/A	N/A	N/A
	0.5 M HCl	23 (2)	28 (1)	50 (0.5)
	1.0 M HCl	481 (48)	756 (19)	364 (9)
	1.5 M HCl	1376 (34)	600 (15)	740 (7)
	2.0 M HCl	N/A	N/A	N/A
	2.5 M HCl	N/A	N/A	N/A
20	Blank	295 (59)	470 (24)	600 (12)
	0.1 M HCl	N/A	N/A	N/A
	0.5 M HCl	17 (3)	22 (1.2)	30 (0.6)
	1.0 M HCl	311 (63)	492 (25)	246 (12)
	1.5 M HCl	954 (47)	412 (20)	495 (10)
	2.0 M HCl	N/A	N/A	N/A
	2.5 M HCl	N/A	N/A	N/A
	Blank	N/A	349 (44)	446 (22)

50	0.1 M HCl	N/A	N/A	N/A
	0.5 M HCl	14 (7)	18 (2)	24 (1.5)
	1.0 M HCl	189 (95)	300 (37)	148 (18)
	1.5 M HCl	584 (72)	148 (31)	300 (15)
	2.0 M HCl	N/A	N/A	N/A
	2.5 M HCl	N/A	N/A	N/A
100	Blank	N/A	283 (71)	357 (36)
	0.1 M HCl	N/A	N/A	N/A
	0.5 M HCl	15 (15)	19 (5)	23 (2.5)
	1.0 M HCl	N/A	206 (51)	100 (25)
	1.5 M HCl	N/A	171 (42)	218 (21)
	2.0 M HCl	N/A	N/A	N/A
	2.5 M HCl	N/A	N/A	N/A

N/A: not applicable; Blank: commercial product

3.6. Measurement of Adhesive

As seen in Table 2, Strength test was applied to the bobbin cardboard glued by MWPS. While the result of the blank sample was 12.00 MPa, the highest value was observed 12.30 MPa in 1N HCI acid modification.

Tablo 2. MWPS based adhesive

Experi. No	Conc.(HCI)	$\sigma_{m(MPa)}$
blank	-	12.00
1	0.25 M	-
2	0.5 M	8.88
3	**1.0 M**	**12.30**
4	1.25	12.10
5	1.5 M	12.00
6	1.75	9.10
7	2.0 M	8.62

4. CONCLUSION

The main purpose of this study is evaluation of waste potato starch, synthesis of hydrolyzed MWPSs and application as adhesive for bobbin cardboard. It was obtained that for hydrolysis of 25 g WPS, the optimum conditions were recorded at 62 ºC, for 15 min. in 1 M HCl. According to the strength tests, waste potato starch which is cheap and easily available is better adhesive than commercial product. The further studies can be carried out new application area for adhesive.

5. ACKNOWLEDGEMENTS

Authors would like to thank to University of Kahramanmaras Sutcu Imam [BAP Project Number: (2017/5-4 YLS)] for supports.

6. REFERENCES

Abdorreza M.N., Robal M., Cheng L.H., Tajul A.Y., Karim A.A. (2012). Physicochemical, Thermal, And Rheological Properties Of Acid Hydrolyzed Sago (Metroxylon Sagu) Starch, *Food Sci. Technol*., 46, 135-141.

Ai Y., Jane J. (2015). Gelatinization And Rheological Properties Of Starch, Review, *Starch/Stärke*, 67: 213-224.

Babu S.,Parimalavalli R., Jagannadham K., Sudhakara RaoJ. (2015). Chemical And Structural Properties Of Sweet Potato Starch Treated With Organic And Inorganic Acids. J Food Sci Technol., 52, 5745–5753.

Babu S., Parimalavalli R., Rudra S.G. (2015).Effect Of Citric Acid Concentration And Hydrolysis Time On Physicochemical Properties Of Sweet Potato Starches, *International Journal of Biological Macromolecules*, 80, 557-565.

Delcour J.A., Hoseney R.C. (2010). Principles Of Cereal Science And Technology (3rd ed.), St. Paul, MN, USA: AACC International (Chapter 2).

Emengo F.N.,Chukwu S.E.R., Mozie J. (2002).Tack And Bonding Strength Of Carbohydrate Based Adhesives From Different Botanical Sources, *International Journal of Adhesion-Adhesives*, 22, 93-100.

Koksel H., Basman A., Kahraman K., Özturk S. (2007). Effect Of Acid Modification And Heat Treatments On Resistant Starch Formation And Functional Properties Of Corn Starch, *International Journal of Food Properties*, 10, 691-702.

Liu J., Guo L., Yang L., Liu Z., He C. (2014)**.** The Rheological Property Of Potato Starch Adhesives, *Advance Journal of Food Science and Technology*, 6, 275-279.

Nazarian F., Richard G.F. (2017). Potato Starch Synthesis: Functions And Relationships, *Biochemistry and Biophysics Reports*,10, 7-16.

Sangramsingh N.M., Patra B.N., Singh B.C., Patra C.M. (2004). Graft Copolymerization Of Methyl Methacrylate Onto Starch Using A Ce (IV)-Glucose Initiator System, *J. Appl. Polym. Sci*., 91, 981-990.

Ulbrich M., Beresnewa-Seekamp T., Walther W., Flöter E. (2016). Acid-Thinned Corn Starch Impact Of Modification Parameters On Molecular Characteristics And Functional Properties, *Starch/Stärke,* 68, 399-409.

Wang S. J. and Copeland L. (2012). New Insights Into Loss Of Swelling Power And Pasting Profiles Of Acid Hydrolyzed Starch Granules, *Starch/ Stärke*, 64, 538-544.

Wang S.J., Blazek J., Gilbert E.P., Copeland L. (2012). New Insights On The Mechanism Acid Degradation Of Pea Starch, *Carbohydr. Polym.,* 87, 1941-1949.

Zhang B., Gong H., Lü S., Ni B., Liu M., Gao C., Huang Y., Han F. (2012). Synthesis And Characterization Of Carboxymethyl Potato Starch And Its Application In Reactive Dye Printing, *International Journal of Biological Macromolecules*, 51, 668– 674.