

Effect of Acids with Different Chain Lengths Modified by Methane Sulfonic Acid and Temperature on the Properties of Thermoplastic Starch/Glycerin Blends

Chi-Yuan Huang, Mei-Chuan Kuo, Ching-Yi Hsiao

Abstract—In this study, acids with various chain lengths (C_6 , C_8 , C_{10} and C_{12}) modified by methane sulfonic acid (MSA) and temperature were used to modify tapioca starch (TPS), then the glycerol (GA) were added into modified starch, to prepare new blends. The mechanical properties, thermal properties and physical properties of blends were studied. This investigation was divided into two parts. First, the biodegradable materials were used such as starch and glycerol with hexanedioic acid (HA), suberic acid (SBA), sebacic acid (SA), decanedioic acid (DA) manufacturing with different temperatures (90, 110 and 130 °C). And then, the solution was added into modified starch to prepare the blends by using single-screw extruder. The FT-IR patterns indicated that the characteristic peak of C=O in ester was observed at 1730 cm^{-1} . It is proved that different chain length acids (C_6 , C_8 , C_{10} and C_{12}) reacted with glycerol by esterification and these are used to plasticize blends during extrusion. In addition, the blends would improve the hydrolysis and thermal stability. The water contact angle increased from 43.0° to 64.0°. Second, the HA (110 °C), SBA (110 °C), SA (110 °C), and DA blends (130 °C) were used in study, because they possessed good mechanical properties, water resistances and thermal stability. On the other hand, the various contents (0, 0.005, 0.010, 0.020 g) of MSA were also used to modify the mechanical properties of blends. We observed that the blends were added to MSA, and then the FT-IR patterns indicated that the C=O ester appeared at 1730 cm^{-1} . For this reason, the hydrophobic blends were produced. The water contact angle of the MSA blends increased from 55.0° to 71.0°. Although break elongation of the MSA blends reduced from the original 220% to 128%, the stress increased from 2.5 MPa to 5.1 MPa. Therefore, the optimal composition of blends was the DA blend (130 °C) with adding of MSA (0.005 g).

Keywords—Chain length acids, methane sulfonic acid, tapioca starch, tensile stress.

I. INTRODUCTION

At present, plastics have enormous demands in industry and convenience goods. However, plastics cannot always break down for reuse, bringing about a large ecological problem instead [1]. The development of biodegradable thermoplastic starch can solve the increasingly important environmental issues arising from plastic [2], [3]. Therefore, a lot of scholars have researched biodegradable composites.

Over the past two decades, biodegradable polymers have more and more interests in the basic research as well as in the chemically modified. The chemical modification of

biodegradable starch has been not only considerable studied but also reviewed for a long time [4].

Starch is an abundant, inexpensive, naturally renewable polysaccharide. Besides, it could biodegrade in soil easily. In sum, starch is applied widely in diverse areas of polymer science [5]. But the starch which used in biodegradable plastics often encountered a few problems. For example, starch is hydrophilic, and this property will influence compatibility in starch and biodegradable plastics. It will decline the compatibility in the mixture.

High intermolecular forces of starch make biodegradable compounds quite brittle. Therefore, it is necessary to use plasticizers for obtaining appropriate polymeric effect. For this purpose, glycerol is commonly used for this purpose [6], [7]. Glycerol is added to the starch, which can increase agility of hydroxyl groups and intra- and intermolecular interactions [8].

Modified starch has high flow ability and hydrophobicity. Chemically modified by treatment with reagents, such as anhydride, it introduces a substituent via reaction with the hydroxyl groups in the starch molecules [9].

Esterification with organic acids (from acetic to fatty acids) is known for result in thermoplastic and hydrophobic materials. Long-chain fatty acid moieties introduced into starch improved the thermoplastic character and thermal stability of the resulting starch esters [10]. The introduction of an ester group into polysaccharides constitutes an important synthetic task, because it permits to modify their original hydrophilic nature and to obtain enhanced or new thermal and mechanical properties [11].

In this study, eight series of composites were prepared with glycerol(GA) mixed with HA, SBA, SA, DA, MSA and the solution join with starch (ST) and then the modified starch by single screw extruder to produced thermoplastic starch materials.

II. EXPERIMENTAL METHODS

A. Blending

Section1: The blends were prepared by eight-step procedure. First, HA (1.5g) was dissolved in glycerol (75g) that used different temperature (90,110,130°C) and then mixed with TPS (250g) about 15 minutes. Second, SBA (1.75g) was dissolved in glycerol (75g) that used different temperature (90,110,130°C) and then mixed with TPS (250g) about 15 minutes. Third, SA (2g) was dissolved in glycerol (75g) that used different temperature (90,110,130°C) and then mixed with

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TPS (250g) about 15 minutes. Fourth, DA (2.3g) was dissolved in glycerol (75g) that used different temperature (90,110,130°C) and then mixed with TPS (250g) about 15 minutes.

Section 2: Fifth, HA (1.5g) was dissolved in glycerol (75g) and joined MSA (0.005, 0.01, 0.02g) that used 110°C and then mixed with TPS (250g) about 15 minutes. Sixth, SBA (1.75g) was dissolved in glycerol (75g) and joined MSA (0.005, 0.01, 0.02g) that used 110°C and then mixed with TPS (250g) about 15 minutes. Seventh, SA (2g) was dissolved in glycerol (75g) and joined MSA (0.005, 0.01, 0.02g) that used 110°C and then mixed with TPS (250g) about 15 minutes. Eighth, DA (2.3g) was dissolved in glycerol (75g) and joined MSA (0.005, 0.01, 0.02g) that used 110°C and then mixed with TPS (250g) about 15 minutes. The ratio of glycerol to TPS (w/w) was 30:100. Finally, the blends were prepared by single screw extruder ($\phi=25\text{mm}$, $L/D=32$). The extrusion process was controlled at four-step temperatures: 100, 105, 110, 105°C (from feed zone to die end) with a screw speed was maintained constant at 20 rpm. The samples were extruded a round with the diameter 6mm holes. The detail compositions of abbreviations of SATPS blends were shown in Tables I and II

In this final part, the HA110, SBA110, SA110, DA130 was used in study, because they possessed good mechanical properties, water resistances and thermal stability. In this part, the various contents (0, 0.005, 0.010, 0.020g) of MSA were also used to modify the mechanical properties of blends. And then, we hoped that the blends were modified to improve the esterification, further the blends were improved in water resistance and thermal stability.

TABLE I
ABBREVIATIONS OF ST/GA BLENDS

Sample Names	Starchb(g)	Glycerol (g)	HA (g)	Temperature (°C)
TPS			0	25
HA090,SBA090,SA090,DA090	250	75		090
HA110,SBA110,SA110,DA110			1.5	110
HA130,SBA130,SA130,DA130				130

TABLE II
ABBREVIATIONS OF ST/GA BLENDS

Sample Names	Starch (g)	Glycerol (g)	HA (g)	MSA (g)
HA110,SBA110,SA110,DA130				0
HM005,SMB005,SM005,DA005	250	75	1.5	0.005
HM010,SMB010,SM010,DA010				0.010
HM020,SMB020,SM020,DA020				0.020

B. Tensile Test

The tensile test was according to the standard procedure described by ASTM D638-99. The tensile strength and elongation of the blends were measured by Hung Ta Instrument Testing Machine (HT-9101). The load of cross-head was 100kg and the test speed was 20mm/min.

C. Fourier Transform Infrared Spectrometry

The different composition of grafting starches and raw starch

was subjected to FTIR spectroscopy in the range of 400-4000 cm^{-1} as KBr powder and the sample was mixed. FTIR-DR spectroscopy was operated at a resolution of 4 cm^{-1} and accumulation 100 times in the range of 400-4000 cm^{-1} .

D. Water Contact Angle Analysis

The water contact angles (WCA) on the original and the modified specimens such as plasma-deposited, were measured by the sessile drop method with distilled water and were recorded by a CCD camera (Goni-meter type G-1 made by ERMA Optical Works Co. LTD.) at room temperature. Each WCA value was the average of four measurements. If the contact angles of water increased, it means that the surface of the material was more hydrophobic.

E. Scanning Electron Microscope (SEM) Imaging

To observe the broken surface morphologies of samples, the strip samples were cooled in liquid nitrogen, and then broken. Specimens were dried in a vacuum oven for 12 hours. All broken surfaces of specimens were vacuum-coated with a thin layer of gold for 180 seconds and monitored by SEM (JEM-5600).

III. RESULTS AND DISCUSSION

Fig. 1 shows the FT- IR spectra of DA added blends from 1050 to 1800 cm^{-1} . In Fig. 1, curve A shows that the absorption peaks of TPS at 1649 cm^{-1} , 1203 cm^{-1} , 1149 cm^{-1} and 1077 cm^{-1} . The absorption peak at 1649 cm^{-1} in Fig. 1 curves B~D attribute to δ -OH bend from free water [12]. The broad absorption peak around 1203 cm^{-1} is attributed to C-O deformation vibration of glycerol [13]. The absorption peaks of HA, SBA, SA and DA blends observed slightly absorption peak at 1730 cm^{-1} is the C=O and two broad absorption peaks at 1149 and 1077 cm^{-1} stretching vibration, and two broad absorption peaks could be seen at 1149 and 1077 cm^{-1} , which can attribute to the C-O groups of the ester [13]. And then, we could see absorption peak at 1730 cm^{-1} , which improved the degree of esterification that attributed to C=O shifted to the high wavenumber.

The cryo-fractured surface morphology of various starch blends was photographed by SEM. Fig. 2 shows the SEM of HA added blends. Fig. 3 shows the SEM of SBA added blends. Fig. 4 shows the SEM of SA added blends. Fig. 5 shows the SEM of DA added blends. In Figs. 2 (a)-5 (a), they show the starch particles not average distribution, size and shape irregular. However, the starch particles can improve distribution, size and shape that different chain length acid was added in the blends, we can easily observe in Figs. 2 (b)-5 (b), Figs. 2 (c)-5 (c), and Figs. 2 (d)-5 (d). The particles of starch can distribute in average, because a deagglomeration process was originated from the surface modification of the starch particles and taking place in the mixing phase of the extrusion [14].

The starch particles can be more rounded in shape, because of a consequence of the chemical modification procedure [15]. We observe in Figs. 2 (b)-5 (b), Figs. 2 (c)-5 (c), and Figs. 2

(d)-5 (d), we can find the blends added the long chain acids and can find that the more chains, the more rounded starch granules.

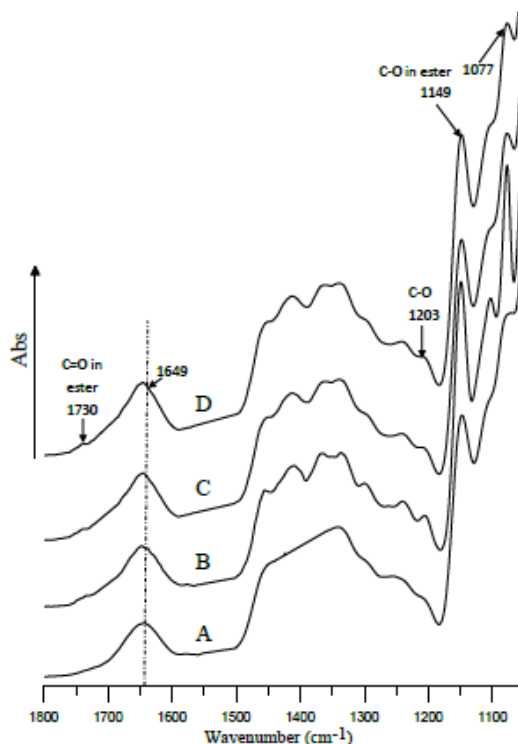


Fig. 1 The FT-IR spectra of DA series blends: (A) TPS (B) DA090 (C) DA110 (D) DA130

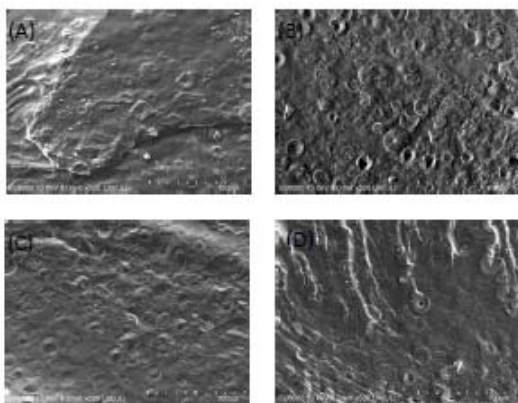


Fig. 2 SEM micrograph of various blends: (a) TPS (b) HA090 (c) HA110 (d) HA130

The data of contact angle measurement were given in Table III. The starch was hydrophilic, and glycerol possesses three $-OH$ groups. These results in starch blends possessed poor water resistance. In the Table III, showed the TPS not a good hydrophobic material, its water contact angle was only 43.0° . In Table III, we observed that adding long chain acids could increase the water resistance of the materials, because the long chain acids had the hydrophobic chain. And then, in the Table IV, it could be found that the contact angle of HA and

SBA blends were higher than those of SA and DA blends. The contact angle of HA and SBA blends were almost over 60.0° . The water contact angle of SA and DA blends were almost over 55.0° . Because of the esterification reaction in the range C6–C10 of acids, reaction conditions were appropriate for successful reaction with starch [16].

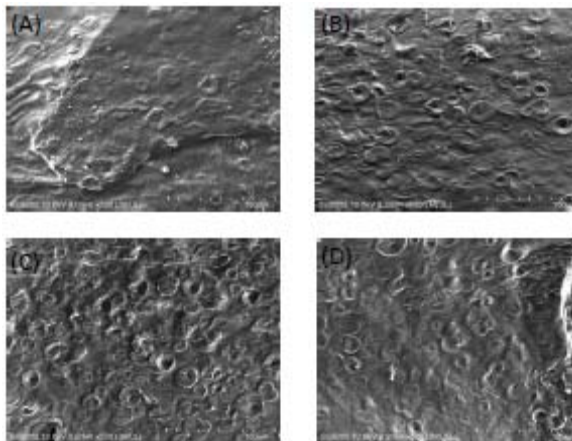


Fig. 3 SEM micrograph of various blends: (a) TPS (b) SBA090 (c) SBA110 (d) SBA130

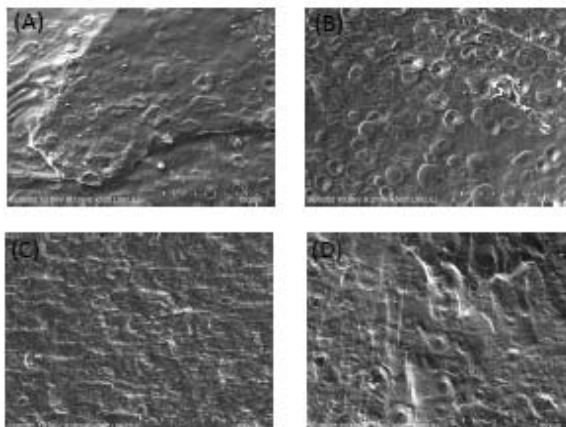


Fig. 4 SEM micrograph of various blends: (a) TPS (b) SA090 (c) SA110 (d) SA130

In Fig. 6, we observed to the HA blends added to the MSA result of the blends became brittle. The MSA added to the HA and GA compounds, its tensile strength increasing from 2.5MPa to 4.6MPa. However, the elongation was at break decreasing from 220% to 62%. Because HA110 might have the better degree of esterification, the MSA was added to the blends form excess acids that caused the blends brittle.

In Figs. 7 and 8, as the MSA was added to SA or DA blends. The tensile strength and elongation of blends were increased. Its tensile strength of SM005 was increased from 4.3 MPa to 4.6 MPa and the elongation at breaks increased from 84% to 123%. In addition, the MSA was added to the SA and GA compounds. Its tensile strength increased from 4.8 MPa to 5.1MPa and the elongation at breaks increased from 93% to

128%, because the MSA could let blends improve the degree of esterification.

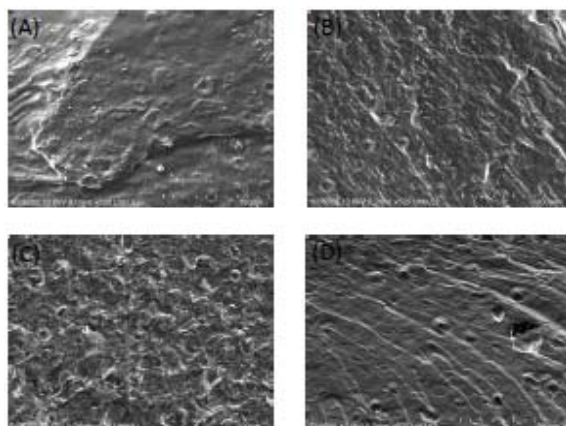


Fig. 5 SEM micrograph of various blends: (a) TPS (b) DA090 (c) DA110 (d) DA130

TABLE III
WATER CONTACT ANGLE ANALYSIS OF VARIOUS BLENDS

Samples	Contact Angle (°)
TPS	43.0
HA90	58.0
HA110	64.0
HA130	66.0
SBA90	62.0
SBA110	63.0
SBA130	58.0
SA90	60.0
SA110	56.0
SA130	53.0
DA90	60.0
DA110	51.0
DA130	55.0

TABLE IV
WATER CONTACT ANGLE ANALYSIS OF VARIOUS BLENDS

Samples	Contact Angle (°)
HA110	64.0
HM005	66.0
HM010	68.0
HM020	72.0
SBA110	63.0
SBM005	65.0
SBM010	67.0
SBM020	66.0
SA110	56.0
SM005	70.0
SM010	55.0
SM020	67.0
DA130	55.0
DM005	71.0
DM010	67.0
DM020	61.0

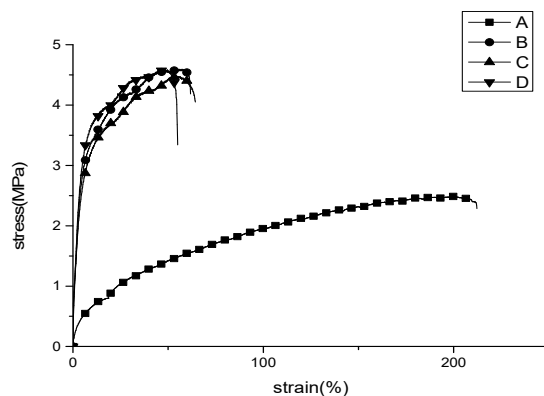


Fig. 6 Stress-Strain curves of various blends: (A) HA110 (B) HM005 (C) HM010 (D) HM020

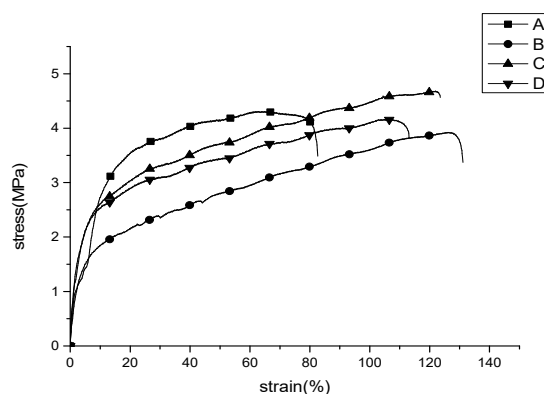


Fig. 7 Stress-Strain curves of various blends: (A) SA110 (B) SM005 (C) SM010 (D) SM020

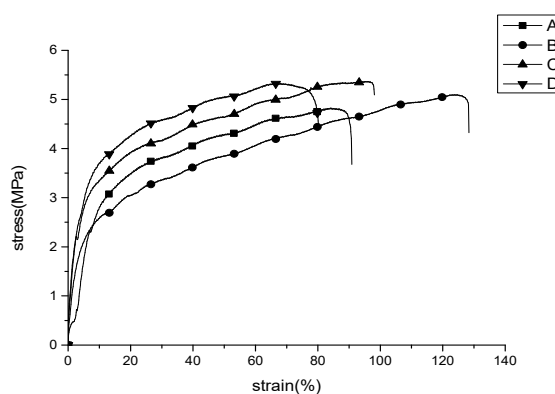


Fig. 8 Stress-Strain curves of various blends: (A) DA130 (B) DM005 (C) DM010 (D) DM020

IV. CONCLUSIONS

In Section I, we added different long-chain acids (C6, C8, C10 and C12) into glycerin at different temperatures (90°C, 110°C and 130°C) that would be formed to esterification. We observed that the blends were added to long-chain acids, and then the FT-IR patterns indicated the C=O in ester was appeared at 1730 cm⁻¹ present. In addition, the blends would

improve the hydrolysis and thermal stability. The water contact angle increased from 43.0° to 64.0°. The TGA curves shifted to the right. Although stress reduced from the original 3.5 MPa to 2.5 MPa, the break elongation increased from 160 to 220%. Consequently, the optimal composition of blends was HA110.

In Section II, the MSA was added to HA110, SBA110, SA110 and DA130 to increase the esterification of blends. The FT-IR patterns indicated that the esterification occurred. For this reason, the hydrophobic blends were produced. The water contact angle of blends increased from 43.0° to 71.0°. Although break elongation reduced from the original 220% to 128%, the stress increased from 2.5 MPa to 5.1 MPa. According to the results of this research, adding long-chain acids into TPS can efficiently improve the water resistance property of TPS.

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REFERENCES

- [1] H. Szymanowski et al., "New biodegradable material based on RF plasma modified starch", *SURFACE & COATINGS TECHNOLOGY*, vol. 200,1-4, pp539-543, 2005
- [2] L. YU, G. J. Christie," Microstructure and mechanical properties of orientated thermoplastic starches",*J MATER SCI*, vol. 40 , pp.111, 2005.
- [3] P. P. Kampeerappun, A. O. Duangdao, P. K. Duanghathai, K. Srikulkit," Preparation of cassava starch/montmorillonite composite film". *CARBOHYD POLYM*, vol.67,2 , pp.155-163, 2007
- [4] N. Nishat and A. Malik., "Synthesis, spectral characterization thermal stability, antimicrobial studies and biodegradation of starch–thiourea based biodegradable polymeric ligand and its coordination complexes with (Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)) metals", *J SAUDI CHEM SOC*,20, pp.S7–S15, 2016
- [5] H. Chi et al., "Effect of acetylation on the properties of corn starch", *FOOD CHEM* , vol.106, 3, pp.923-928, 2008.
- [6] H. M Park, W. K Lee, C. Y. Park, W. J. Cho, C. S Ha, "Environmentally friendly polymer hybrids Part I Mechanical, thermal, and barrier properties of thermoplastic starch/clay nanocomposites", *J MATER SCI*, vol. 38, 5,pp.909-915, 2003.
- [7] Y. T. Wen,The study of compounding process and mechanical properties of biodegradable polyester/starch plastics, M. S. Thesis, Department of Bioengineering, TTU,2015.
- [8] A. Heydaria, I. Alemzadeha, M. Vossoughia, "Functional properties of biodegradable corn starch nanocomposites for food packaging applications", *MATER DESIGN* , vol.50, pp.954-961,2013
- [9] C. H. Lu, Develop Anti-Yellowing agent for TPU, Department of Molecular Science and Engineering, NTUT, 2009
- [10] Y. Shinozaki, T. Watanabe, T. Nakajima-Kambe, HK. Kitamoto, "Rapid and simple colorimetric assay for detecting the enzymatic degradation of biodegradable plastic films", *J BIOSCI BIOENG*, vol.115, 1, pp. 111-114, 2013
- [11] .A. Soroudi and I. Jakubowicz, "Recycling of bioplastics, their blends and biocomposites: A review", *EUR POLYM J*, vol.49,10, pp. 2839-2858,2013
- [12] J. M Fang, "The preparation and characterisation of a series of chemically modified potato starches", *CARBOHYD POLYM*, vol.47, 3, pp.245-252, 2002
- [13] J. G. Yu, N. Wang, X. F Ma, "The Effects of Citric Acid on the Properties of Thermoplastic Starch Plasticized by Glycerol", *STARCH-STARKE*, vol.57, 10, pp. 494-504, 2005
- [14] H. Szymanowska, M. Kaczmareka, M. Gazicki-Lipmana, L. Klimeka, B. Woźniakb, "New biodegradable material based on RF plasma modified starch", *SURFACE & COATINGS TECHNOLOGY*, vol. 200(1-4), pp.539-543,2005
- [15] C,C,Chang, "Effect of Sebacic Acid Modification and Titanate Coupling Agent Treated Calcium Carbonate on the Properties of Thermoplastic Starch", M. S. Thesis, Department of Materials Engineering, TTU, 2010
- [16] J.M Fanga, P.A Fowlera, C Sayersb, P.A Williamsb, "The chemical modification of a range of starches under aqueous reaction conditions", *CARBOHYD POLYM*, vol.55, 3, pp.283-289, 2004.