Carbohydrate Polymers 83 (2011) 1623–1630

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Characterization and evaluation of acylated starch with different acyl groups and degrees of substitution

Sangeeta Garg[a], Asim Kumar Jana[b,*]

[a] Department of Chemical Engineering, National Institute of Technology, Jalandhar 144 011, Punjab, India
[b] Department of Biotechnology, National Institute of Technology, Jalandhar 144 011, Punjab, India

ARTICLE INFO

Article history:
Received 14 July 2010
Received in revised form 3 October 2010
Accepted 8 October 2010
Available online 15 October 2010

Keywords:
Starch
Acylation
Crystallinity
Thermal stability
Hydrophobic transformation

ABSTRACT

Corn starch was modified with acetyl, propionyl and butyryl groups at four different degrees of substitution (DS). FTIR, X-RD, TG–DTA, SEM, swelling power, solubility, water binding capacity and light transmittance techniques were used to characterize the samples. Effect of DS and acyl groups on physico-chemical properties of starch was studied. During acylation, the crystalline structure of starch got destroyed and starch surface was eroded. Acylated starch was thermally stable than native starch. Amylose content of the starch samples increased slightly after acylation. Swelling power and water binding capacity of native starch were 3.09 g/g and 89.8%, respectively. In acetylated, propionylated and butyrylated starch at low DS, these properties increased. But at high DS, these decreased to below that of native starch. Butyrylated starch at DS of 1.75 showed lower swelling power, and water binding capacity than acetylated starch at DS 2.55. Increase in DS and acyl group chain length from acetyl to butyryl group improved hydrophobic transformation of starch.

1. Introduction

Recently interest is increasing in the development of biodegradable polymers for packaging materials in order to reduce the environmental pollution caused by plastic waste (Betancur & Chel, 1997; Kim & Lee, 2002). Starch has been one of the best choices as blending material in plastics because of its easy availability and low cost. Starch remains in granular form in plastic matrix and may act as filler in blends. Microbial removal of starch from starch–plastic blend composition can cause severe reduction in the mechanical strength of the remaining films i.e. non-biodegradable portion, causing it to disintegrate readily into smaller pieces (Potts, Clendinning, Ackart, & Niegisch, 1973; Rutenberg & Solarek, 1984).

However, the use of starch as a blending material has been challenged by some limitations including strong hydrophilicity and poor process ability. Different ways of modification of starch, in starch based films have been adopted by researchers to solve the problem. Various modifications were plasticized starch in LDPE (Bikiaris et al., 1997), plasticized starch in polyethylene (Soundararajan, Palanivalu, & Sharma, 2002), hydroxypropionylated starch in polyethylene (Kim, 2003), methylated-corn starch in poly-vinyl alcohol (Guohua et al., 2006), cross-linked starch in PVA (Lee, Youn, Yun, & Yoon, 2006) and cross-linked starch in LDPE (Garg & Jana, 2007). It was found that starch modification overcame the shortcomings of starch to some extent by altering the structure and affecting the hydrogen bonding of amylose and amylopectin in a controllable manner.

Of various modifications, starch acetylation can be performed with relative ease to improve significantly the physico-chemical and functional properties of starch. Acetylated starch having low DS (0.01–0.2) gives product with characteristics such as high swelling power, solubility, and low gelatinization temperature (Singh, Chawla, & Singh, 2004; Sodhi & Singh, 2005). Recently, acetylated starch with high DS (2.0–3.0) has received attention for a number of non-food applications such as tablet binders, hot melt adhesives, cigarette filters and coating materials. Phillips, Huijum, Duohai, and Harold (1999) found that the extent of change in physico-chemical properties of acetylated starch was proportional to the degree of acetylation of the starch molecules. Chi et al. (2007) studied structural characterization of acetylated starch by FTIR, ^{1}H NMR and X-ray diffraction. Acylation could be an effective way for hydrophobic transformation of starch and to improve compatibility of starch based plastic materials. Acylation of starch with increased length of the acyl group could be one of the factors which contribute to the properties of the acylated starch. To date no studies have used swelling power, solubility, water binding capacity and light transmittance as evidence to support hydrophobic transformation of starch with different acyl groups and DS.

The objective of the study was preparation of acetylated, propionylated and butyrylated starch samples with low and high DS. Effect of different acyl groups and DS on morphological, thermal and physico-chemical properties of starch was examined.

---

* Corresponding author. Tel.: +91 181 2690301; fax: +91 181 2690320.
E-mail address: janaak@nitj.ac.in (A.K. Jana).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.10.015

2. Materials and methods

2.1. Materials

Starch (corn starch) used in the study was made by Sukhjit Starch and Chemicals Limited, Phagwara (India). The characteristic composition of starch was: carbohydrates – 98% (amylose content: 23.56%), protein – 0.4 to 0.5%, fiber <1%, moisture <13%, and ash <0.3%. Acetic anhydride, propionic anhydride, and butyric anhydride were purchased from High Media Chemicals, India. Pyridine, ethanol, potassium hydroxide, hydrochloric acid and phenolphthalein indicator used in the study were reagent grade chemicals obtained from s.d. Fine Chemicals Limited, Mumbai, India.

2.2. Acylation of starch

Acylation of starch was done using acetic anhydride, propionic anhydride and butyric anhydride separately. Dried starch sample (20 g) was taken in a reaction flask followed by 100 ml of pyridine. The flask was then heated to 90 °C for 2 h to pre-activate the starch. Reflux-condenser was used to prevent the loss of organic liquid. After the pre activation for 2 h, the reaction mixture was cooled to 75 °C. Acyl anhydride was added drop-wise and the reaction continued for 22 h to ensure reaction equilibrium. The content of the reaction mixture was coagulated by adding 100 ml of isopropanol. The product was filtered and washed with methanol three times. Finally, product was dried in an oven at 70 °C for 24 h.

2.3. Acyl content and degree of substitution (DS)

Acyl content and DS were determined by titration method. Acylated starch (1.0 g) was taken in a 250 ml flask and 75% ethanol (50 ml) was added. The solution was stirred at 50 °C for 30 min at 40 rpm in shaker cum incubator and cooled to room temperature and then 0.5 M KOH (40 ml) was added with swirling. The flask was stoppered and allowed to stand for 72 h with stirring at 40 rpm for 10 min after every 2 h interval for complete saponification. The excess of alkali was back titrated with 0.5 N HCl using phenolphthalein indicator. The solution was allowed to stand 2 h and additional alkali which might leach from the sample was titrated. A blank was titrated in parallel. The acyl content and DS was calculated by

$$\%\,\text{Acyl content} = \frac{[(V_B - V_S) \times \text{molarity of HCl} \times M_{\text{acyl}} \times 10^{-3} \times 100]}{\text{Sample weight } (g)} \tag{1}$$

V_B in ml is the volume of 0.5 N HCl used to titrate the blank; V_S in ml is the volume of 0.5 N HCl used to titrate the sample; M_{acyl} is the formula weight of acyl group:

$$DS = \frac{(162 \times \text{Acyl}\,\%)}{[M_{\text{acyl}} \times 100 - ((M_{\text{acyl}} - 1) \times \text{Acyl}\,\%)]}$$
$$(M_{\text{acetyl}} = 43,\ M_{\text{propionyl}} = 57,\ M_{\text{butyryl}} = 71) \tag{2}$$

where 162 is the molecular weight of glucose units.

2.4. Fourier transform infrared (FTIR) spectra

The native and acylated starch samples were equilibrated at 50 °C for 24 h and FTIR spectra of native and acylated starch samples were recorded by FTIR instrument (PerkinElmer, Model RX-1, USA) using potassium bromide (KBr) pellets (Sigma–Aldrich). FTIR spectra were recorded at a resolution of 4 cm^{-1} and wave number ranged between 400 and 4000 cm^{-1}.

2.5. X-ray diffraction studies

X-ray diffraction of native and acylated starch samples was recorded by X-ray diffractometer (XPERT-PRO PW 3064, Philips, Japan). Tube Anode was Cu, tube voltage was 40 kV and generator current was 35 mA. The range of diffraction angle was 5–40° (2θ). Intensity ratio and wavelength were 0.50 and 1.54 Å. Minimum and maximum peak widths were 0° and 1° (2θ), respectively.

2.6. Scanning electron microscopy (SEM)

Surface scanning of starch particles was done by the SEM (JEOL JSM-6100, Jeol Ltd., Tokyo, Japan). The range of accelerating voltage was 0.3–30 kV. The samples were first sputter coated with a thin layer of gold and then observed at magnification range of 200–2000×.

2.7. Thermal analysis

Thermal analysis of starch samples was performed in TG–DTA apparatus (PerkinElmer, Pyris Dimond). Change in weight of sample against temperature (thermogravimetric analysis, TG), rate of change of weight against temperature (derivative thermogravimetric analysis, DTG) and heat evolved or absorbed in the sample because of exothermic or endothermic activity in the sample (differential thermal analysis, DTA) were measured. Samples (8 to 10 mg) were heated from 50 °C to 650 °C with a heating rate of 20 °C/min. Nitrogen was used as purge gas at flow rate of 200 ml/min.

2.8. Amylose content

Amylose content of native and acylated starch samples were determined according to the method described by Williams, Kuzina, and Hlynka (1970). The principle of the test lies in the blue color developed by the addition of an iodine reagent to a solution containing the amylose under standardized conditions. Starch sample (20 mg) was dissolved in 10 ml of 0.5 N KOH. The suspension was mixed thoroughly. The dispersed starch sample was transferred to 100 ml volumetric flask and diluted to the mark with distilled water. An aliquot (10 ml) of starch solution was pipetted into 50 ml volumetric flask and 5 ml of 0.1 N HCl was added followed by the 0.5 ml of iodine reagent. The volume was diluted to 50 ml and the absorbance was measured at 625 nm. The measurement of amylose was determined from a standard curve.

2.9. Swelling power, solubility and water binding capacity

The swelling power and solubility of starch in water were determined according to the method described by Tsai, Li, and Lii (1984). The native and acylated starch samples were dried at 60 °C for 24 h up to constant weight (moisture content 5.21%). Dried starch sample (0.1 g) was taken in centrifuge tube with 10 ml of distilled water. Then the starch suspension was incubated in a water bath for 1 h at different temperatures from 65 °C to 95 °C with a working churn. After cooling the sample to room temperature, the tube was centrifuged at 3000 rpm for 20 min to separate out the insoluble starch particles. Insoluble starch was separated from supernatant and weighed (W_p). Both phases were dried at 105 °C for 24 h. The dry solid in insoluble starch (W_{ps}) and supernatant (W_s) were weighed. Swelling power was calculated as the ratio of the weight of hydrated insoluble starch granule (g)/weight of dry granule in insoluble starch (g):

$$\text{Swelling power} = \frac{W_p}{W_{ps}} \tag{3}$$

The solubility was calculated as the percentage of dry mass of soluble in supernatant (W_s) to the dry mass of whole starch sample (W_o):

$$\text{Solubility} = \frac{W_s}{W_o} \times 100\% \tag{4}$$

Water binding capacity of the dried starch was measured by the procedure described by Sugimoto, Nishihara, and Fuwa (1986) at room temperature (25 °C). Starch (1.0 g) (W_1) was added to 15 ml distilled water in a conical flask. The flask was agitated for 1 h, and then centrifuged for 15 min at 16,000 rpm. The starch was weighed after the water was decanted (W_2). The amount of water held by the starch was determined from the weight difference. The water binding capacity of the starch was calculated by

$$\text{Water binding capacity} = \frac{(W_2 - W_1) \times 100}{W_1} \tag{5}$$

2.10. Light transmittance

The light transmittance of aqueous starch suspension was measured by the method described by Craig, Maningat, Seib, and Hoseney (1989). Aqueous suspension of starch (1%) was heated in a water bath at 90 °C for 1 h with constant stirring. The starch suspension was cooled for 1 h to 30 °C and light transmittance was measured against water blank at 640 nm by spectrophotometer (La Motte Company, Chestertown, USA). The sample was stored for five days at 4 °C and transmittance was measured at every 24 h over a period of 6 days.

3. Results and discussion

3.1. DS

Acetylated, propionylated and butyrylated starch samples with different DS were prepared. Table 1 shows the variation of DS and acyl content at different acyl anhydride concentrations. It was observed that DS of starch increased with the increase in concentration of acyl anhydride in the reaction medium. With increase in concentration of acyl anhydride from 0% to 5.5%, DS of acetylated, propionylated and butyrylated starch increased from 0 to 2.55, 0 to 2.51 and 0 to 1.75, respectively. The DS of the acylated starch appeared to be dependent on the length of the aliphatic chain attached to the acid anhydride. Butyrylated starch had low DS as compared to acetylated and propionylated starch at the same concentration of acyl anhydride.

The reaction equation of acylation of starch is given in Scheme 1. The acylation of starch takes place by an addition–elimination mechanism (Yixiang, Miladinov, & Hanna, 2004). The three free OH groups of the starch have different reactivities. The primary C (6) OH is more reactive and is acylated more readily than the secondary ones on C (2) and C (3) due to steric hindrance. Of the two secondary OH groups, the C (2) OH is more reactive than the C (3), mainly because the former is closer to the hemi-acetal and more acidic than the later (Fedorova & Rogovin, 1963).

At low concentrations of acyl anhydride, the numbers of acyl groups were not sufficient to convert the hydroxyl groups but at high concentration of acyl anhydride, the acyl groups were sufficient to associate at the hydroxyl sites. As the reaction was not a homogeneous one, it was likely that some glucose units were completely inaccessible to the acyl anhydride and so had unacylated C (2) OH and C (6) OH groups as well. As a result DS was less than 3.0.

3.2. FTIR

FTIR spectroscopy was used to verify the change in chemical structure of starch molecules after acylation. Spectra of acetylated, propionylated and butyrylated starch samples at similar DS in comparison to the native starch are shown in Fig. 1. In the spectra of native starch (NS 0.0), there were bands at 1158.1, 1081, and 1014 cm^{-1} which were attributed to C–O band stretching. Additional characteristic absorption bands appeared at 928.8, 860.7, 764.6, and 575.1 cm^{-1} which were due to anhydroglucose ring stretching vibrations. An extremely broad band due to hydrogen bonded –OH groups appeared at 3398.1 cm^{-1}. FTIR spectra of acetylated, propionylated and butyrylated starch (Ac 1.45, Pr 1.56, and Bu 1.41) showed new band at 1749 cm^{-1}, assigned to carbonyl C=O vibration. The new absorption band suggested that acylated starch products were formed due to acylation. The intensity of the peak at 3398 cm^{-1} weakened after acylation indicating hydroxyl groups participated in the reaction.

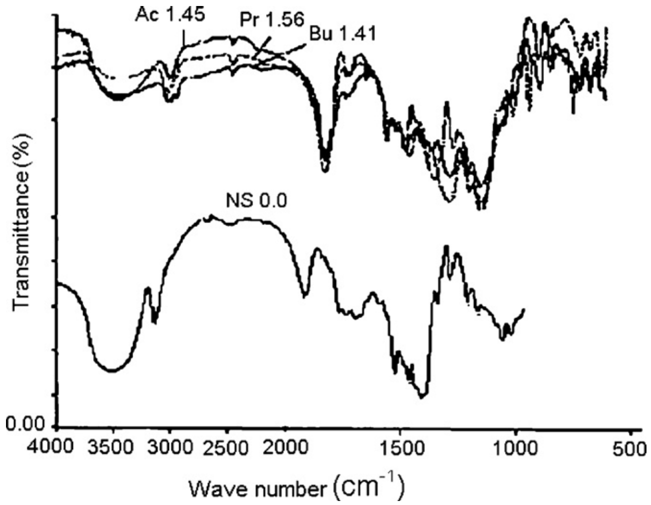


Fig. 1. FTIR spectra of native starch (NS 0.0), acetylated, propionylated and butyrylated starch (Ac 1.45, Pr 1.56 and Bu 1.41).

3.3. Physico-chemical properties

3.3.1. X-ray diffraction

X-ray diffraction was done to check if the chemical modification altered the crystallinity of starch. The X-ray diffraction patterns of native and acylated starch samples are shown in Fig. 2. Variation in intensity of light with angle (2θ) was recorded in the diffractrograms. Diffractrogram of native starch (NS 0.0) showed five sharp peaks at 15.02°, 17.04°, 17.89°, 19.77° and 22.86° (2θ) indicating the crystalline structure. However, diffractograms of acetylated, propionylated and butyrylated starch at similar DS ~ 1.45 showed typical wide peaks near 6–8° and 20° (2θ) indicating amorphous pattern. X ray diffraction of native and acylated starch demonstrated that crystalline structure of native starch got destroyed after acylation.

Starch is a mixture of linear amylose and branched amylopectin. Linear amylose composed of α-1,4-glucopyranose was responsible for amorphous region, while large amylopectin contributed to crystalline region. The intra- and intermolecular hydrogen bonds were responsible for the highly ordered crystalline structure. The acyl groups in modified starch samples replaced most of the hydroxyl groups on starch. The negligible intermolecular hydrogen bonds remained which destroyed the ordered crystalline structure. Semi crystalline nature of the starch has also been observed earlier and could adopt different crystalline structures (A, B, C, and V) (Rioux, Ispas-Szabo, Ait-Kadi, Mateescu, & Juhasz, 2002; Zobel, 1964). The A, B and C structures consisted of packed double helix. The V-type structure was a single helix structure. The A type is largely present in cereal starches and B type in potato, amylomaize and in retro-

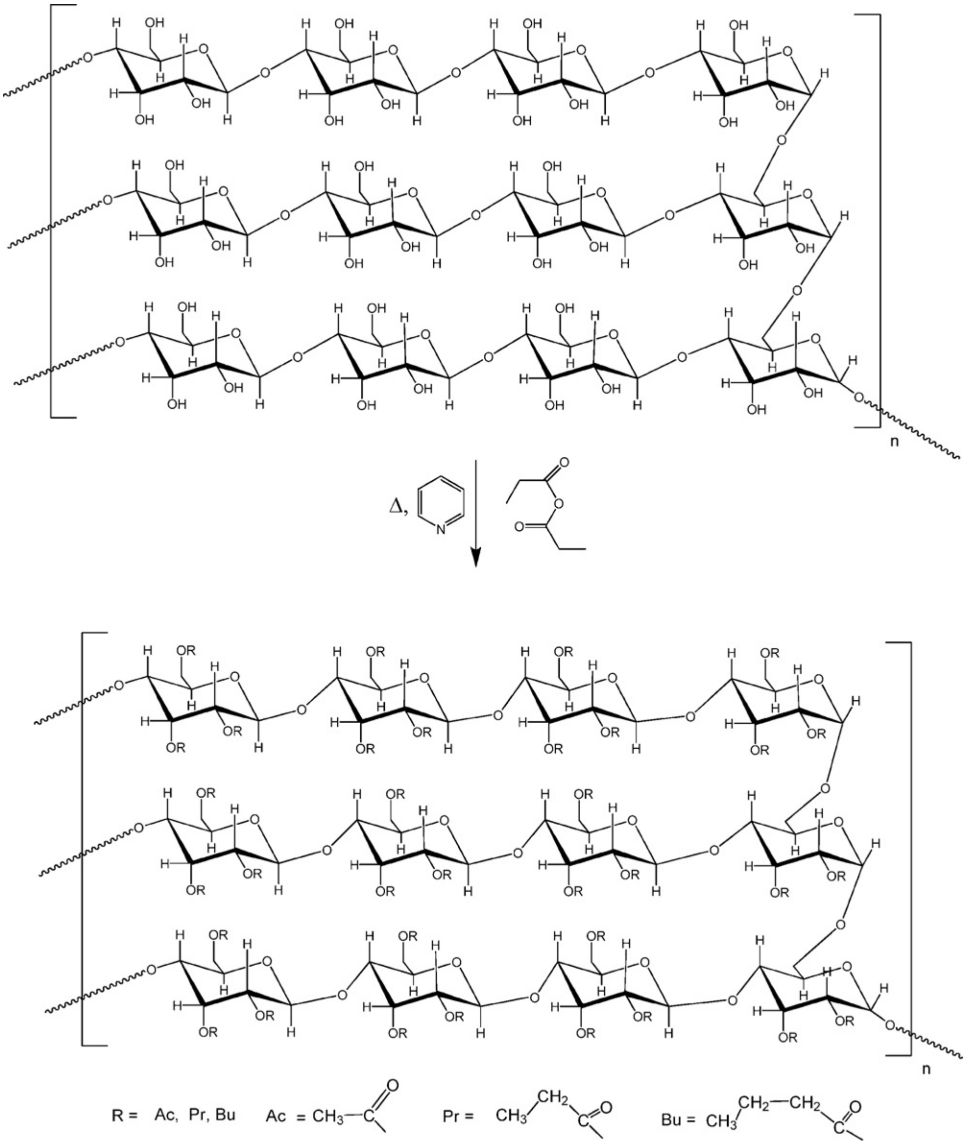
Table 1
Acyl content and DS of native starch and modified starch.

Acetylated starch			Propionylated starch			Butyrylated starch		
Acetyl (%)	DS	Sample	Propionyl (%)	DS	Sample	Butyryl (%)	DS	Sample
–	–	NS 0.0	–	–	NS 0.0	–	–	NS 0.0
13.76	0.60	Ac 0.60	17.67	0.61	Pr 0.61	12.78	0.34	Bu 0.34
27.95	1.45	Ac 1.45	35.63	1.56	Pr 1.56	28.76	0.92	Bu 0.92
36.41	2.13	Ac 2.13	44.71	2.27	Pr 2.27	38.34	1.41	Bu 1.41
40.75	2.55	Ac 2.55	47.31	2.51	Pr 2.51	43.67	1.75	Bu 1.75

graded starches. Each type of structure gives typical characteristic peaks described by various researchers (Chi et al., 2007; Xu et al., 2008). Chi et al. (2007) described that A pattern of cereal starch exhibited sharp peaks at 15°, 17°, 18° and 23°. Xu et al. (2008) reported that peak at 5.68° was the characteristic peak of B type structure and peak at 27.01° was indicative of A type structure. C type was a mixture of A and B type structures. The peaks observed in present study showed that the native corn starch has A type of structure.

3.3.2. SEM

Surface scanning of starch was done to examine the morphological changes occurred in starch particles due to acylation. SEM micrographs of native starch (NS 0.0) and acylated starch samples (Ac 2.55, Pr 2.51, and Bu 1.75) are shown in Fig. 3. It was observed that the surface of the starch became rough and eroded after acylation which was attributed to substitution of acyl groups in starch. The granular structure of starch was lost. Increased roughness of starch could improve the adhesion of starch with synthetic poly-



Scheme 1. Chemical reaction equation of starch and acyl anhydride.

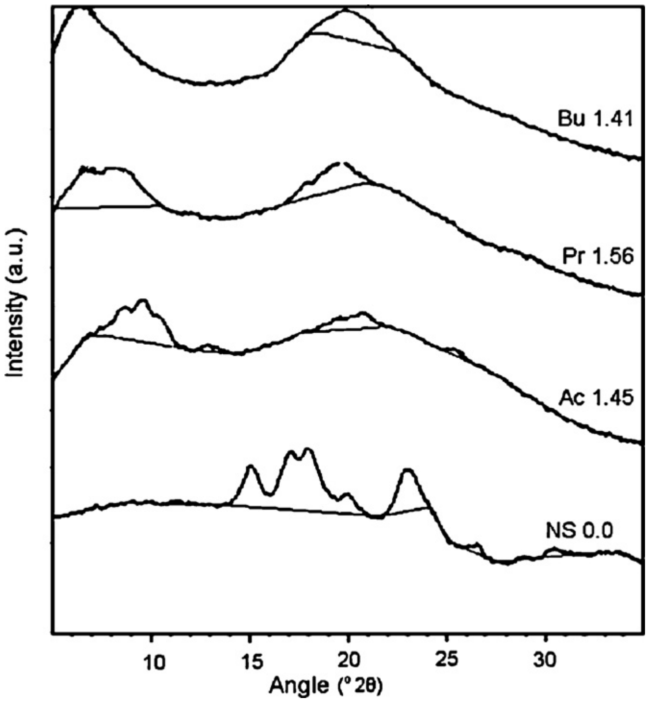


Fig. 2. X-ray diffraction patterns of native starch (NS 0.0), acetylated, propionylated and butyrylated starch (Ac 1.45, Pr 1.56 and Bu 1.41).

mers due to increased surface area for bonding and mechanical interlocking.

3.3.3. Thermal analysis

Thermal analysis test was conducted to examine the change in thermal properties of the starch caused by acylation. Table 2 shows the results of thermogravimetric analysis (TG), differential thermal analysis (DTA) and derivative thermal analysis (DTG) of native (NS 0.0) and acylated starch. TG results of native starch showed a two stage weight loss with the first minor one corresponding to loss of water around 50 °C to 125 °C with a weight loss of 11%. Once dehydrated, the native starch sample was stable up to 250 °C. With increase in temperature from 250 to 350 °C, the thermal decomposition took place with a weight loss of 83%. The main product of decomposition below 300 °C was formation of water by intermolecular or intra-molecular condensation of starch hydroxyls (Thiebaud et al., 1997). Acylated starch also showed two stage weight loss but the 1st stage weight loss due to dehydration of starch was very less as compared to native starch. 2nd stage decomposition temperature of acylated starch at low DS (Ac 0.60, Pr 0.61, and Bu 0.34) was 272–380 °C, 279–382 °C and 278–385 °C with a weight loss of 84.6%, 86.6% and 84.4%, respectively. At high DS (Ac 2.55, Pr 2.51 and Bu 1.75) decomposition temperature increased to 295–397 °C, 300–400 °C, and 310–405 °C with a weight loss of 84.4%, 86.7%, and 84.8%, respectively. Thus, it was evident from TG data that acylated starch was thermally more stable than native starch and decomposition temperature increased with the increase in DS. Comparative TG–DTA curves of native and acylated starch at similar DS are shown in Fig. 4. TG thermo gram of acylated starch (Ac 1.45, Pr 1.56, and Bu 1.41) showed single stage decomposition from 278–392 °C, 285–395 °C and 297–394 °C, respectively. Results showed that decomposition temperature of butyrylated starch was higher than acetylated and propionylated starch.

DTA result of native starch (NS 0.0) also showed two endothermic peaks with first one corresponding to loss of water at 96 °C with energy absorbed 266 mJ/mg followed by stage of decomposition at 292 °C with energy absorbed 59.7 mJ/mg. Acylated samples Ac 0.60, Ac 1.45, Ac 2.55, Pr 0.61, Pr 1.56, Pr 2.51, Bu 0.34, Bu 1.41 and Bu 1.75 had endothermic decomposition at higher temperature 301 °C, 324 °C, 361 °C, 326 °C, 345 °C, 368 °C, 312 °C, 358 °C and 370 °C (Table 2), respectively. At similar DS, decomposition temperature of butyrylated starch curve shifted towards right (Fig. 4). Butyrylated starch (Bu 1.41) exhibited higher decomposition temperature

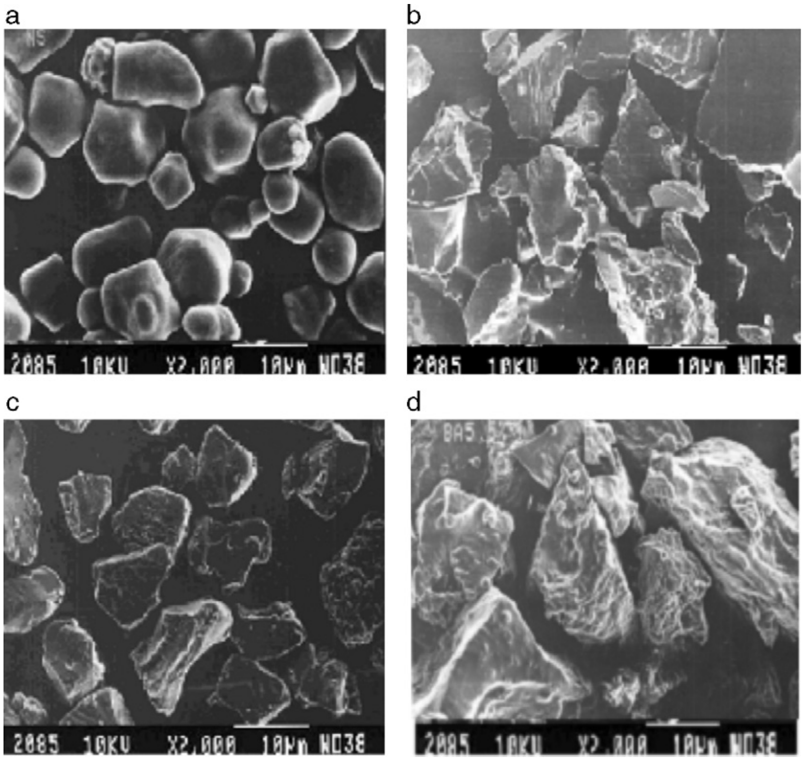


Fig. 3. SEM (2000×) of (a) native starch (NS 0.0), (b) acetylated starch (Ac 1.90), (c) propionylated starch (Pr 2.51), and (d) butyrylated starch (Bu 1.75).

Table 2
TG–DTA studies of native starch and modified starch.

Sample	TG				DTA		DTG	
	1st stage		2nd stage					
	T_D (°C)	Weight loss (%)	T_D (°C)	Weight loss (%)	T_E (°C)	Energy absorbed (mJ/mg)	T_D (°C)	Rate of weight loss (mg/min)
NS 0.0	50–125	11	250–350	83	96, 292	266, 59.7	308	6.11
Ac 0.60	26–100	4.3	272–380	84.6	301	162	371	4.33
Ac 1.45	20–100	4.0	278–392	84.2	324	91.7	376	4.56
Ac 2.55	23–100	2.7	295–397	84.4	361	121	376	4.13
Pr 0.61	24–100	2.9	279–382	86.6	326	170	376	4.77
Pr 1.56	19–100	2.9	285–395	85.8	366	86.8	379	4.37
Pr 2.51	25–100	0.7	300–400	86.7	368	164	380	3.96
Bu 0.34	17–100	2.1	278–385	84.5	312	180	325	4.14
Bu 1.41	24–101	2.2	297–394	85.6	333	250	376	4.26
Bu 1.75	–	–	310–405	84.8	348	180	377	3.85

T_D = decomposition temperature; T_E = endothermic peak temperature.

at 358 °C as compared to acetylated (Ac 1.45) and propionylated starch (Pr 1.56).

DTG analysis of native starch and acylated starch was studied as a function of rate of weight loss (mg/min) vs. temperature. In native starch decomposition took place at 308 °C with a rate of 6.11 mg/min weight loss. However, acylated starch samples had higher decomposition temperatures with lower rate of weight loss. DTG results revealed that the rate of decomposition of native starch was higher as compared to acylated starch.

The acylated starch samples were thermally more stable than native starch. The increase in thermal stability was due to low amount of remaining hydroxyl groups in starch molecule after modification. The increase in molecular weight and covalent bonding due to the acylation of hydroxyl groups were also responsible for the increased thermal stability. In the earlier study, thermal properties of starch succinates showed that the fewer the number of hydroxyl groups remained, the better was the thermal stability of the starch esters (Rudnik, Matuschek, & Milanov, 2005).

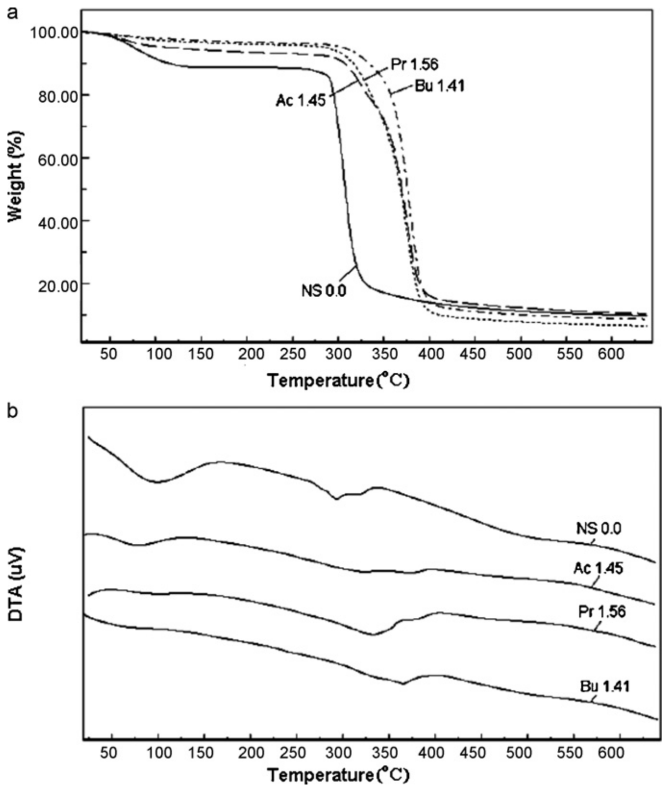


Fig. 4. (a) TGA curves of native, acetylated, propionylated and butyrylated starch (NS 0.0, Ac 1.45, Pr 1.56 and Bu 1.41); (b) DTA curves of native, acetylated, propionylated and butyrylated starch (NS 0.0, Ac 1.45, Pr 1.56 and Bu 1.41).

3.3.4. *Amylose content*

The amylose content of the native corn starch was 23.56%. It was observed that the amylose content of starch increased after acylations, but the increase was not significant. In acylated starch samples at high DS (Ac 2.55, Pr 2.51, and Bu 1.75), the amylose content increased to 24.81%, 25.75% and 26.28%, respectively. The increase in the amylose content after acylation was because of the interference of acyl groups with the functioning of amylose and amylopectin fractions of starch and affected the absorption of iodine during testing (Betancur & Chel, 1997). Gonzalez and Perez (2002) observed that the introduction of acyl groups also affect the helical structure of amylose by sterical hindrance and formation of amylase–iodine complex.

3.3.5. *Swelling power, solubility and water binding capacity*

Swelling power of native and acylated starch samples is shown in Fig. 5a. It was observed that the swelling power increased with temperature. With increase in temperature from 65 °C to 75 °C, swelling power of native starch (NS 0.0) increased significantly from 3.09 to 12.26 g/g. At low DS, swelling power of acetylated, propionylated and butyrylated starch (Ac 0.60, Pr 0.61, and Bu 0.33) was higher than native starch at 65 °C. But it was comparable to native starch at 95 °C. At high DS, acylated starch (Ac 2.55, Pr 2.51, and Bu 1.75) showed swelling power similar to native starch at 65 °C but it did not increase with increase in temperature as it was in native starch.

Fig. 5b demonstrates that swelling power of acylated starch decreased with the increase in DS. At high DS, swelling power of the propionylated and butyrylated starch was lower than acetylated starch. Swelling power of acetylated starch (Ac 2.55) was 5.75 g/g. It decreased by 32% in propionylated starch (Pr 2.51) and by 34% in butyrylated starch (Bu 1.75).

Solubility is contributed by extent of amylose in the starch. Solubility of native and acylated starch samples is shown in Fig. 5c. The solubility of all the samples increased with increase in temperature (Fig. 5c). At low DS, acetylated and propionylated starch (Ac 0.60 and Pr 0.61) had higher solubility than native starch at all temperatures. But in butyrylated starch (Bu 0.33) it was lower than native starch except at 95 °C. At high DS, solubility of acylated starch samples decreased than native starch. The changes in solubility of starch with DS at 95 °C are shown in Fig. 5d. Results showed that solubility decreased with the increase in DS. The solubility of acetylated starch (Ac 2.55) was 8.5%. Propionylated (Pr 2.51) and butyrylated starch (Bu 1.75) showed solubility 6.83% and 6.42%, respectively, under same temperature, which was lower than that of acetylated

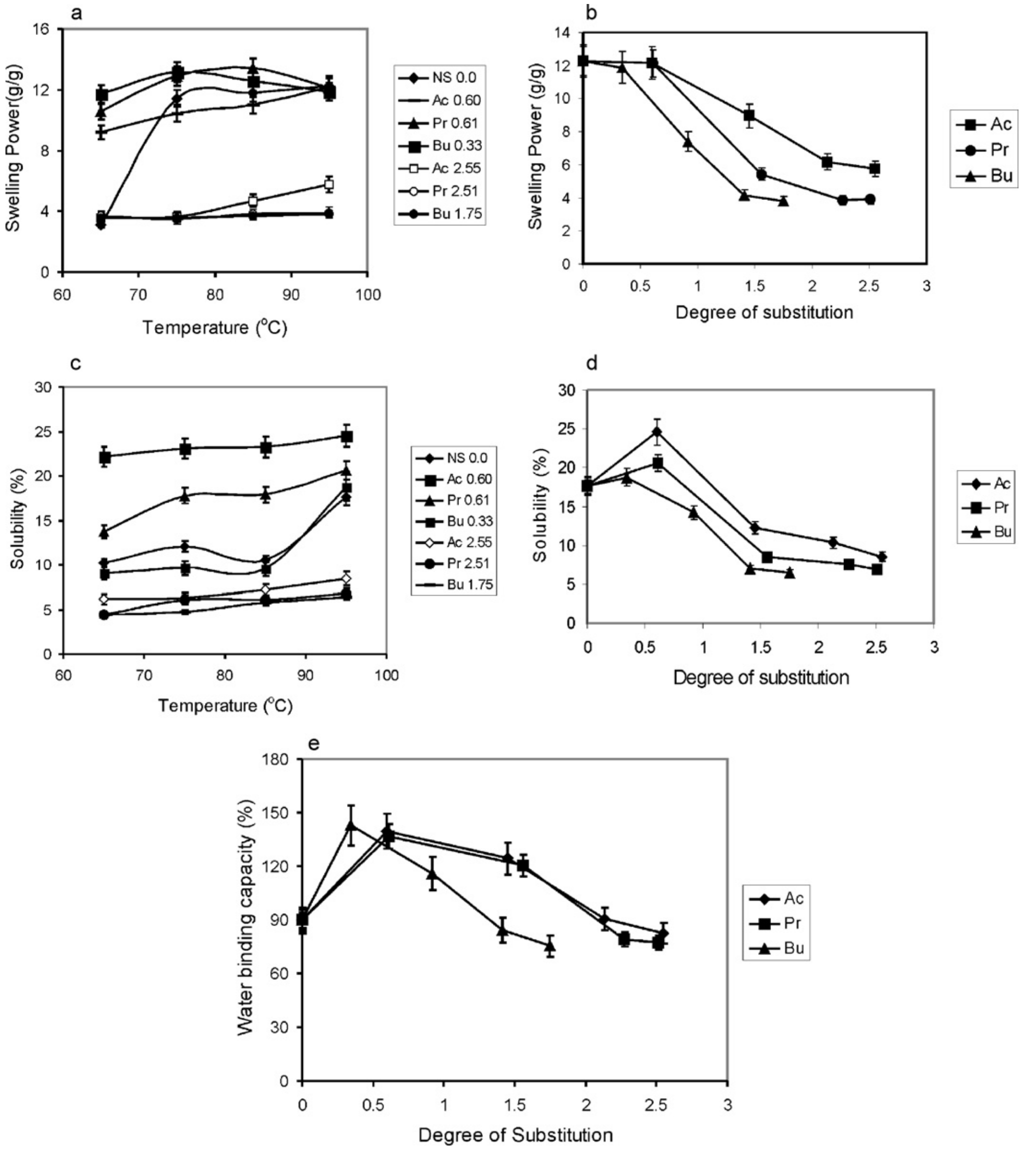


Fig. 5. Swelling power (a) as a function of temperature at different DS, (b) as a function of DS at 95 °C; solubility (c) as a function of temperature at different DS, (d) as a function of DS at 95 °C; (e) variation of water binding capacity with DS.

starch. At high DS, butyrylated starch had lowest solubility among all the samples.

Water binding capacity is the amount of water held by the starch. Water binding capacity of native and acylated starch samples is shown in Fig. 5e. The water binding capacity for native starch (NS 0.0) was 89.76%. In acylated starch at low DS (Ac 0.60, Pr 0.61, and Bu 0.33), it increased than native starch. But at high DS, water binding capacity decreased to below that of native starch. Water binding capacity of acetylated starch and propionylated starch at high DS (Ac 2.55 and Pr 2.51) decreased to 81% and 77%, respectively. However, in butyrylated starch (Bu 1.75) it decreased to minimum 75%.

Starch is comprised of amylose and amylopectin chains. Due to structure of starch, it could not be dissolved in water at normal temperature. The starch granules start integrating with water at high temperature. At low level of DS, the acyl groups were not sufficient to change the behavior of hydroxyl groups. There was weakening of intermolecular hydrogen bonds in starch with the introduction of acyl groups. At high DS, the acyl groups replaced most of hydroxyl groups on starch and interaction with water decreased. At high DS, swelling power, solubility and water binding capacity decreased to below that of native starch. Results showed that swelling power, solubility and water binding capacity depended on two opposing effects: (i) the opening up of the starch structure at low level of acylation, rendering it more accessible to water and (ii) the increasing hydrophobic character of polymer chains which gradually became the predominant effect with increase in the DS. Wotton and Bamunuarachchi (1979) observed that introduction of acetyl groups into polymer chains resulted in destabilization of granule structure of starch. At high DS, the difference in degree of availability of water binding sites among the starch samples contributed to the variation in water binding capacity (Fringant, Desbrieres, & Rinaudo, 1996; Hoover & Sosulski, 1986; Paronen et al., 1997; Soni, Sharma, Bisen, Srivastava, & Gharia, 1987). Butyrylated starch showed lower swelling power, solubility, and water binding capacity as compared to acetylated and propionylated starch may be because of high molecular weight groups and covalent bonding causing increased hydrophobicity of starch.

3.3.6. *Light transmittance*

Fig. 6 shows the light transmittance of native and acylated starch suspension during 144 h of storage period. Results showed

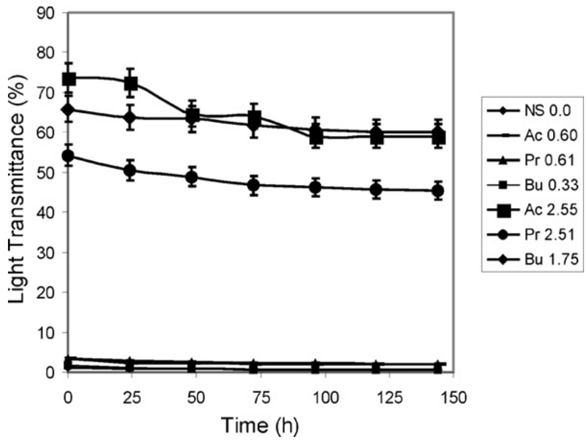


Fig. 6. Variation of light transmittance at different DS.

that acylation increased the light transmittance. Light transmittance of native starch (NS 0.0) was 1.1%. At low DS, butyrylated starch (Bu 0.33) showed comparable light transmittance as native starch. But acetylated and propionylated starch (Ac 0.60 and Pr 0.61) showed slightly higher light transmittance than native starch. But at high DS, acylated starch samples showed dramatic increase in light transmittance. At high DS, light transmittance of acetylated (Ac 2.55), propionylated (Pr 2.51) and butyrylated (Bu 1.75) starch increased to 73.6%, 54.3%, and 65.8%, respectively. There was gradual and slight decrease in light transmittance of native and acylated starch samples during 144 h of storage period.

Light transmittance provides the information on the clarity of starch in light and depends upon the swollen and non-swollen granule particles. At low DS, the starch granules swell after interaction with water and more light begins to pass through the granules instead of being reflected. At high DS, the starch granules prevent its molecules from association with water due to substitution of hydroxyl groups, thus contributing to a molecular dispersion in solution. There is no significant reflection to impede the light through the paste. One of the factors that lead to higher% transmittance is due to Raleigh light scattering. This occurs when the suspended particles, in this case starch molecule, are so small that their diameter is comparable to the wavelength of the incident light (Sugimoto et al., 1986). The scattering involves not only ordinary reflection but also a kind of diffraction in which each particle in the light path behaves as if it was a secondary light source.

4. Conclusion

Acylated, propionylated and butyrylated starch with different DS were prepared. Changes in physcio-chemical properties of acetylated, propionylated and butyrylated starch were observed as compared to native starch. DS of acetylated, propionylated and butyrylated starch varied from 0.60 to 2.55, 0.61 to 2.51 and 0.34 to 1.75 under same conditions. The crystal structure of native starch got destroyed and surface of starch became rough during acylation. Thermal stability of acylated starch increased due to decrease in number of hydroxyl groups. DS and length of the acyl group controlled the swelling power, solubility, water binding capacity and light transmittance of starch. In acetylated, propionylated and butyrylated starch at low DS (DS 0.60, DS 0.61, and DS 0.34) swelling power, solubility and water binding capacity increased. These properties decreased to below that of native starch at DS of about 1.65, 2.15 and 1.41 in acetylated, propionylated and butyrylated starch. With increase in chain length from acetyl to butyryl group at high DS, swelling power and water binding capacity decreased by 34% and 8%. Changes in physico-chemical properties of acylated starch at high DS confirmed the hydrophobic transformation in corn starch. An increase in length of the acyl group from acetyl to butyryl group increased the hydrophobic character of starch.

References

Betancur, A. D., & Chel, G. L. (1997). Acid hydrolysis and characterization of *Canavalia ensiformis* starch. *Journal of Agricultural and Food Chemistry*, *45*, 4237–4241.

Bikiaris, D., Prinos, J., Koutsopoulos, K., Vouroutzis, N., Pavlidou, E., & Frangis, N. (1997). LDPE/plasticized starch blends containing PE-g-MA copolymer as compatibilizer. *Polymer Degradation and Stability*, *59*, 287–291.

Chi, H., Xu, K., Wu, X., Chen, Q., Xue, D., Song, C., et al. (2007). Effect of acetylation on the properties of corn starch. *Food Chemistry*, *106*, 923–928.

Craig, S. A. S., Maningat, C. C., Seib, P. A., & Hoseney, R. C. (1989). Starch paste clarity. *Cereal Chemistry*, *45*, 378–382.

Fedorova, A. F., & Rogovin, Z. A. (1963). Relative reactivity of cellulose hydroxyls on esterification in an acid medium. *Vysokomolekulyamye Soedieneiya (Abstr.)*, *5*, 519–523.

Fringant, C., Desbrieres, J., & Rinaudo, M. (1996). Physical properties of acetylated starch based materials: Relation with their molecular characteristics. *Polymer*, *37*, 2663–2673.

Garg, S., & Jana, A. K. (2007). Studies on the properties and characteristics of starch–LDPE blend films using cross-linked, glycerol modified, cross-linked and glycerol modified starch. *European Polymer Journal*, *43*, 3976–3987.

Gonzalez, Z., & Perez, E. (2002). Effect of acetylation on some properties of rice starch. *Starch*, *54*, 148–154.

Guohua, Z., Ya, L., Cuilan, F., Min, Z., Caiqiong, Z., & Zongdao, C. (2006). Water resistance, mechanical properties and biodegradability of methylated-cornstarch/poly(vinyl alcohol) blend film. *Polymer Degradation and Stability*, *91*, 703–711.

Hoover, R., & Sosulski, F. (1986). Effect of cross linking on functional properties of legume starches. *Starch*, *38*, 149–155.

Kim, M. (2003). Evaluation of degradability of hydroxypropionylated potato starch/polyethylene blends films. *Carbohydrate Polymers*, *54*, 173–181.

Kim, M., & Lee, S. (2002). Characteristics of cross-linked potato starch and starch filled linear low-density polyethylene films. *Carbohydrate Polymers*, *50*, 331–337.

Lee, W., Youn, Y. N., Yun, Y. H., & Yoon, S. D. (2006). Physical properties of chemically modified starch (RS4)/PVA blend films. *Journal of Environmental Polymer Degradation*, *61*, 1–18.

Paronen, P., Peltonen, S., Urtti, A., & Nakari, J. (1997). Starch acetate composition with modifiable properties, method for preparation and usage thereof. *US Patent Office*, Pat. No. 5,667,803.

Phillips, D. L., Huijum, L., Duohai, P., & Harold, C. (1999). General application of Raman spectroscopy for the determination of level of acetylation in modified starches. *Cereal Chemistry*, *76*, 439–443.

Potts, J. E., Clendinning, R. A., Ackart, W. B., & Niegisch, W. D. (1973). *Polymer and ecological problems*. New York: Plenum Press.

Rioux, B., Ispas-Szabo, P., Ait-Kadi, A., Mateescu, M., & Juhasz, J. (2002). Structure–properties relationship in cross-linked high amylase starch cast films. *Carbohydrate Polymers*, *4*, 371–378.

Rudnik, E., Matuschek, G., & Milanov, N. (2005). Thermal properties of starch succinates. *Thermochimica Acta*, *427*, 163–166.

Rutenberg, M. M., & Solarek, D. (1984). Starch derivatives: Production and uses. In E. F. Whistler, E. F. Whistler, et al. (Eds.), *Starch chemistry and technology* (pp. 311–388). New York: Academic Press.

Singh, N., Chawla, D., & Singh, J. (2004). Influence of acetic anhydride on physico-chemical, morphological and thermal properties of corn and potato starch. *Food Chemistry*, *86*, 601–608.

Sodhi, N. S., & Singh, N. (2005). Characteristics of acetylated starches prepared using starches separated from different rice cultivars. *Journal of Food Engineering*, *70*, 117–127.

Soni, P. L., Sharma, H. W., Bisen, S. S., Srivastava, H. C., & Gharia, M. M. (1987). Unique physicochemical properties of sal (*Shorea robusia*) starch. *Starch*, *23*, 8–11.

Soundararajan, S., Palanivalu, K., & Sharma, S. K. (2002). Studies on starch filled PE (film) and PP (sheet). *Plastic Process Uses*, *47*, 80–83.

Sugimoto, Y., Nishihara, K., & Fuwa, H. (1986). Some properties of taro and yam starch. *Journal of Japanese Society of Starch Science*, *33*, 169–176.

Thiebaud, S., Aburto, J., Alric, I., Borredon, E., Bikiaris, D., Prinos, J., et al. (1997). Properties of fatty-acid esters of starch and their blends with LDPE. *Journal of Applied Polymer Science*, *65*, 705–721.

Tsai, M. L., Li, C. F., & Lii, C. Y. (1984). The modified alkaline steeping method for the isolation of rice starch. *Food Science*, *11*, 158–162.

Williams, P. C., Kuzina, F. D., & Hlynka, I. (1970). A rapid colorimetric procedure for estimating the amylose content of starches and flours. *Cereal Chemistry*, *47*, 411–420.

Wotton, M., & Bamunuarachchi, A. (1979). Application of DSC to starch gelatinization. *Starch*, *31*, 201–204.

Xu, W., WenYuan, G., LiMing, Z., PeiGen, X., LiPing, Y., Yi, L., et al. (2008). Study on morphology, crystalline structure and thermal properties of yam starch acetates with different degrees of substitution. *Science in China Series B: Chemistry*, *51*, 859–865.

Yixiang, X., Miladinov, V., & Hanna, M. A. (2004). Synthesis and characterization of starch acetates with high substitution. *Cereal Chemistry*, *81*, 735–740.

Zobel, H. F. (1964). *Methods in carbohydrate chemistry*. New York: Academic Press.