

# Effect of Propylation on the Characteristics of Corn Starch and Variation of Properties with Different Degrees of Substitution

Sangeeta Garg,<sup>1</sup> Asim Kumar Jana<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, National Institute of Technology, Jalandhar 144 011, Punjab, India

<sup>2</sup>Department of Biotechnology, National Institute of Technology, Jalandhar 144 011, Punjab, India

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**ABSTRACT:** Corn starch was modified by propylation with different degree of substitution (DS). DS of four starch modifications were 0.61, 1.56, 2.27, and 2.51. Samples were characterized by FTIR, XRD, TG-DTA, swelling power, solubility, water binding capacity, and light transmittance. Results of the systematic physico-chemical characterization of the starch modification in comparison with the native starch have been documented in the article. Results showed that during propylation, the crystalline structure of starch got destroyed and surface of the starch was eroded. Propylated starch (DS 2.51) showed 85% weight loss at temperatures from 300 to 400°C, whereas the native starch underwent similar weight loss (83%) from 250 to 300°C. Swelling power and water binding capacity of native starch (DS 0.0) were 3.09 g/g

and 89.8%, respectively. However, in propylated starch at low DS (DS 0.61), swelling power and water binding capacity increased to 10.55 g/g and 136.8% under same conditions. At high DS (DS 2.51), swelling power was similar to native starch at 65°C, whereas solubility and water binding capacity decreased to below that of native starch. Light transmittance of propylated starch with high DS (DS 2.51) increased dramatically compared with native starch. Propylation improved the hydrophobic transformation and thermal stability of starch at high DS. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1383–1392, 2011

**Key words:** Propylated starch; crystallinity; physico-chemical properties; hydrophobic transformation

## INTRODUCTION

Starch is an inexpensive and natural polymer in plants, which has generated interest in its use as a component in plastic formulations. Starch can be used as filler in blends with synthetic polymers from the standpoint of conserving our petrochemical resources and providing biodegradation properties to the end products. Starch based polymers have been used successfully in many packaging industries.<sup>1–3</sup>

However, strong hydrophilicity and poor process ability of starch prevent its application in plastic products.<sup>4–6</sup> Several studies have been carried out on modified starch based blends/films to solve this problem. Different fillers used in the blend were plasticized starch in LDPE,<sup>7</sup> hydroxypropylated starch in polyethylene,<sup>8</sup> crosslinked starch in PVA,<sup>9</sup> methylated-corn starch in PVA<sup>10</sup> and cross linked starch in LDPE.<sup>11</sup> Previous studies revealed that reduction in hydrophilicity of starch increased the

compatibility of blends to some extent. Therefore, it is logical to chemically modify the starch to improve its properties.

One of the common starch modifications is starch acylation, which is actively studied because of specific properties arising from introduction of acyl groups. Acetylated starch having a low DS (0.01 to 0.2) is of commercial interest because of its usage based on properties with respect to film forming, binding, adhesion, thickening, stabilizing, and texturing.<sup>12,13</sup> Acetylated starch with low DS gives product with unique characteristics, such as low gelatinization temperature, high swelling power, and solubility. Acetylated starch with high DS (2.0 to 3.0) has been used in recent years for a number of non-food applications, such as tablet binders, hot melt adhesives, cigarette filters, and coating materials. Chi et al.<sup>14</sup> analyzed structure of acetylated starch by FTIR, <sup>1</sup>H-NMR, X-ray diffraction, and the hydrophobic transformation by contact angle. They reported that during acetylation, crystal structure of the starch was destroyed and contact angle increased from 43.1° to 68.2° indicating the hydrophobic transformation in modified starch. Xu et al.<sup>15</sup> investigated low and high DS starch acetates, for

Correspondence to: A. K. Jana (janaak@nitj.ac.in).

crystalline structure, thermal stability and morphological properties. It revealed that esterification not only happened on the surface but also affected the inner structure of starch. To date no studies have used swelling power, solubility, water binding capacity, and light transmittance as evidence to support hydrophobic transformation of starch after acylation in the entire range of DS particularity at high DS. Also, no report is available for the minimum requirement of DS for satisfactory transformation. The length of the acyl group could be one of the factors which contribute to the properties of the acylated starch.

The objective of the work was preparation of propylated starch samples with low and high DS and study the change in morphological and physicochemical properties of starch. In this study acylation was done using propyl group, which is slightly longer than acetyl group. Substitution of propyl group in starch was done up to high DS to study the entire range.

## EXPERIMENTAL

### 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: –25 to 30% and amylopectin: –70 to 75%), protein –0.4 to 0.5%, fiber < 1%, moisture < 13%, ash < 0.3%. Propionic anhydride was 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.

### Propylation of starch

Propylation of starch was done by propionic anhydride and pyridine as catalyst. Dried starch sample (20 g) was taken in reaction flask followed by 100 mL of pyridine. The flask was then heated to 90°C for 2 h to preactivate the starch. Reflux-condenser was used to prevent the loss of organic liquid. After the preactivation for 2 h, the reaction mixture was cooled to 75°C. Propionic 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.

### Propyl content and degree of substitution (DS)

Propyl content and DS were determined by titration method. Propylated 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 0.5M 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 0.5M HCl using phenolphthalein indicator. The solution was allowed to stand for 2 h and additional alkali which leached from the sample was titrated. A blank was titrated in parallel. The propyl content and DS were calculated by

$$\% \text{ propyl content} = \frac{[(\text{blank, ml} - \text{sample, ml}) \times \text{molarity of HCL} \times 0.057 \times 100]}{\text{sample weight, g}}$$

$$\text{DS} = \frac{(162 \times \text{propyl } \%)}{[57 \times 100 - ((57 - 1) \times \text{propyl } \%)]}$$

where 162 is molecular weight of glucose units and 57 is the formula weight of propyl group.

### Fourier transform infrared (FTIR) spectra

The native and propylated starch were equilibrated at 50°C for 24 h and FTIR spectra of native and propylated starch were recorded by FTIR instrument (Perkin Elmer, Model RX-1) using potassium bromide (KBr) pellets (Sigma Aldrich). FTIR spectra

were recorded at a resolution of 4 cm<sup>-1</sup> and wave number ranged between 400 and 4000 cm<sup>-1</sup>.

### X-ray diffraction studies

X-ray diffraction of native and propylated starch was recorded by X-ray diffractometer (XPRT-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° to 40° (2θ). Intensity ratio and wavelength were 0.50 and 1.54060 Å. Minimum and maximum peak widths were 0° and 1° (2θ), respectively.

### Scanning electron microscopy (SEM)

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

### Thermal analysis

Thermal analysis of the starch samples was performed by DTA-TG instrument (Perkin Elmer, 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 (8–10 mg) were heated from 50 to 650°C with a heating rate of 20°C/min. Nitrogen was used as purge gas at flow rate of 200 mL/min.

### Swelling power, solubility, and water binding capacity

The swelling power and solubility of the starch in water were determined according to the method described by Tsai et al.<sup>16</sup> The native and propylated starch 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. The starch suspension was incubated in a water bath for 1 h at different temperatures from 65 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).

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

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

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

Water binding capacity of dried sample of starch was measured by the procedure described by Sugi-

**TABLE I**  
Propyl Content and DS of Native Starch and Modified Starch

Starch/Pyridine (g/ml)	Propionic anhydride (%)	Propyl content (%)	DS (sites/glucose unit)
1:5	00	00	00
1:5	1.5	17.67	0.61
1:5	2.5	35.63	1.56
1:5	3.5	44.71	2.27
1:5	5.5	47.31	2.51
1:5	6.5	47.32	2.50

moto et al.,<sup>17</sup> 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. Water was decanted and residual starch was weighed ( $W_2$ ). The amount of water held by the starch was determined from the weight difference. The water binding capacity of the starch was calculated by

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

### Light transmittance

The light transmittance of aqueous starch suspension was measured by the method described by Craig et al.<sup>18</sup> 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). The sample was stored for 5 days at 4°C and transmittance was measured after every 24 h over a period of 6 days.

## RESULTS AND DISCUSSION

### Degree of substitution (DS)

Propylated starch samples were prepared with different DS. Table I shows the variation of DS and propyl content at different propionic anhydride concentrations. It was observed that DS and propyl content of starch increased with the increase in concentration of propionic anhydride in reaction medium. With increase in concentration of propionic anhydride from 0 to 5.5 %, DS and propyl content of starch increased from 0 to 2.51 and 0 to 47.31%, respectively. Increase in concentration of propionic anhydride beyond 5.5% did not have any effect on DS.

The reaction equation of propylation of starch is given in Figure 1. The acylation of starch takes place by an addition–elimination mechanism.<sup>19</sup> The three free OH groups of the starch have different

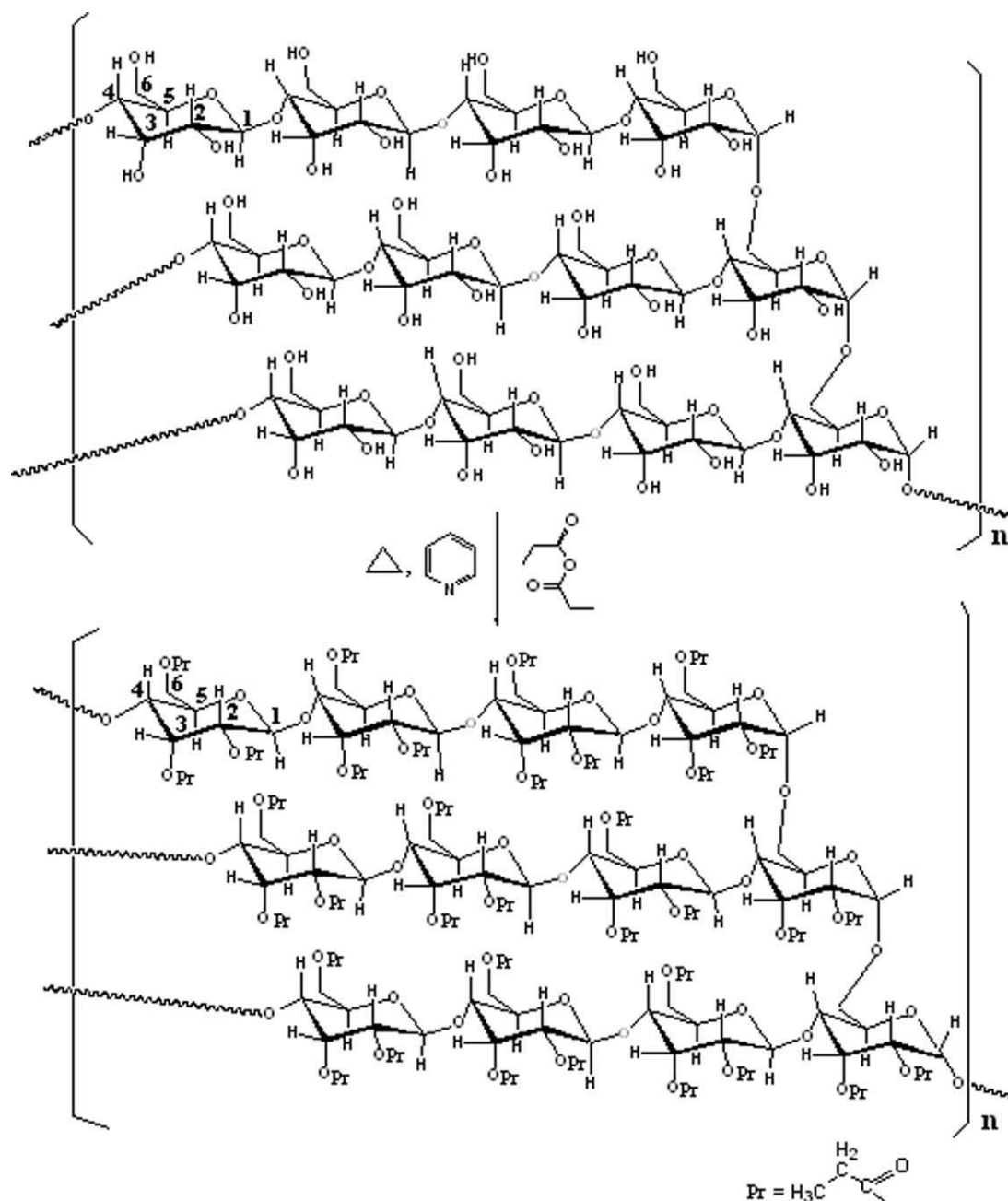


Figure 1 Chemical reaction equation of starch and propionic anhydride.

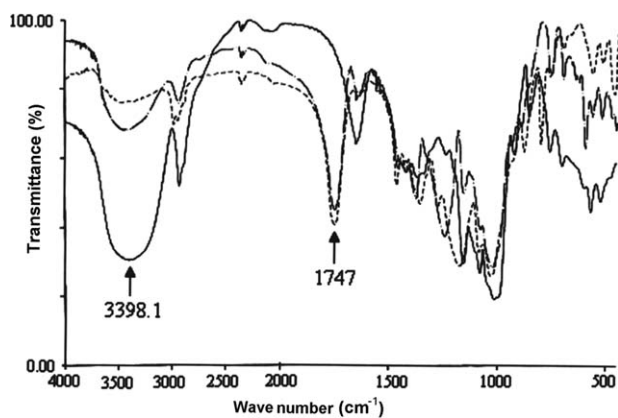
reactivities. The primary C (6) OH is more reactive and is acylated more readily than the secondary ones on C (2) and C (3) because of steric hindrance. Of the two secondary OH groups, the C (2) OH is more reactive than the C (3), mainly because the former is closer to the hemiacetal and more acidic than the later.<sup>20</sup>

At low concentration of propionic anhydride, the numbers of propyl groups were not sufficient to convert the hydroxyl groups. But at high concentration of propionic anhydride, the propyl 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 propionic anhydride and so had unacylated C (2) OH and C (6) OH groups as well. As a result DS was less than 3.0.

#### FTIR spectra

FTIR spectroscopy was used to verify the change in chemical structure of starch molecules after acylation. Spectra of native starch, propylated starch with different DS are shown in Figure 2. In the spectra of native starch (DS 0.0), there were bands at 1158.1, 1081, and 1014  $\text{cm}^{-1}$ , which were attributed to C—O



**Figure 2** FTIR spectra of native starch (DS 0.0) and propylated starch (DS 1.56 & 2.51) DS 0.0(—), DS 1.56(— · —), DS 2.51 (-----).

band stretching. Additional characteristic absorption bands appeared at 928.8, 860.7, 764.6, and 575.1  $\text{cm}^{-1}$ , which were due to anhydroglucose ring stretching vibrations. An extremely broad band because of hydrogen bonded  $-\text{OH}$  groups appeared at 3398.1  $\text{cm}^{-1}$ . FTIR spectra of propylated starch showed new band at 1747  $\text{cm}^{-1}$  assigned to carbonyl  $\text{C}=\text{O}$  vibration. The new absorption band suggested that propylated starch products were formed because of acylation. With the increase in DS of propylated starch from 1.56 to 2.51, the intensity of the peak at 3398.1  $\text{cm}^{-1}$  weakened and almost disappeared at DS 2.51, indicating that hydroxyl groups participated in the reaction.

## PHYSICO-CHEMICAL PROPERTIES

### X-ray diffraction

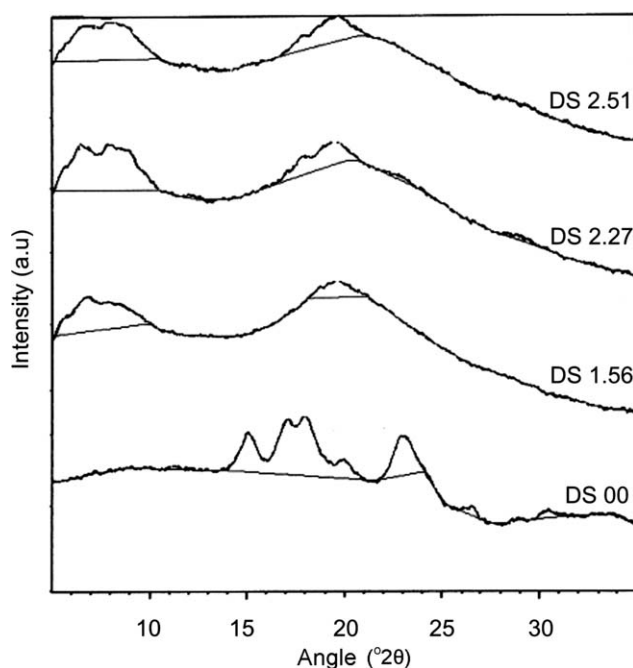
X-ray diffraction was done to check if the chemical modification altered the crystallinity of starch. The X-ray diffraction patterns of native and propylated starch are shown in Figure 3. Variation in intensity of light with angle ( $2\theta$ ) was recorded in the diffractograms. Diffractogram of native starch (DS 0.0) showed five sharp peaks at 15.02°, 17.04°, 17.89°, 19.77°, and 23.12° ( $2\theta$ ) indicating the crystalline structure. However, diffractograms of propylated starch samples showed typical wide peaks near 6 to 8° and 20° ( $2\theta$ ) indicating the amorphous patterns. X-ray diffraction of native starch and propylated starch demonstrated that crystalline structure of native starch got destroyed after propylation.

Starch is a mixture of linear amylose and branched amylopectin. Linear amylose composed of  $\alpha$ -1,4-glucopyranose was responsible for the amorphous region, while large amylopectin contributed to crystalline region. The intramolecular and intermolecular hydrogen bonds were responsible for the highly ordered crystalline structure. The propyl

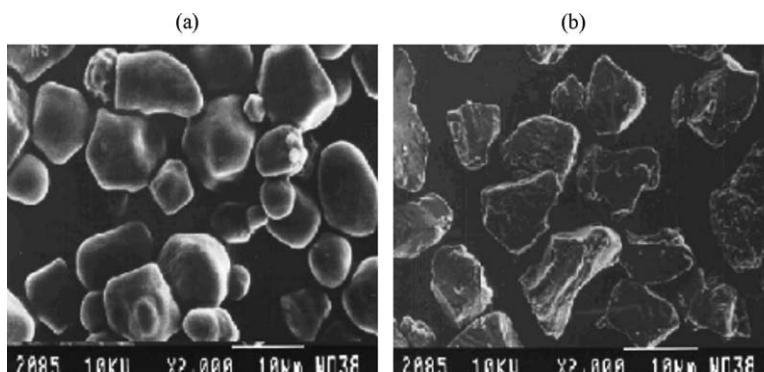
groups in modified starch samples replaced most of the hydroxyl groups on starch, which destroyed the ordered crystalline structure. Semi crystalline nature of starch has also been observed earlier. Starch could adopt different crystalline structures (A, B, C, and V).<sup>21,22</sup> The A, B, and C structures consists of packed double helix. The V-type structure is a single helix structure. The A type is largely present in cereal starches and B type in potato, amylo maize and in retrograded starches. Each type of structure give typical characteristic peaks described by various researchers.<sup>14,15</sup> Chi et al.,<sup>14</sup> described that A pattern of cereal starch exhibited sharp peaks at 15°, 17°, 18°, and 23°. Xu et al.,<sup>15</sup> 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.

### SEM

SEM studies were done to examine the morphological changes occurred in starch particles due to propylation. SEM micrographs of native starch (DS 0.0) and propylated starch (DS 2.51) are shown in Figure 4. Micrographs showed that the surface of the starch particles became rough and eroded after propylation. The granular structure of starch was lost. Increased roughness of starch surface could improve the adhesion of starch with synthetic polymers



**Figure 3** X-Ray diffraction patterns of native starch (DS 0.0) and propylated starch (DS 1.56, 2.27 and 2.51).



**Figure 4** SEM (2000 $\times$ ) of (a) native starch (DS 0.0) and (b) propylated starch (DS 2.51).

because of increased surface area for bonding and mechanical interlocking.

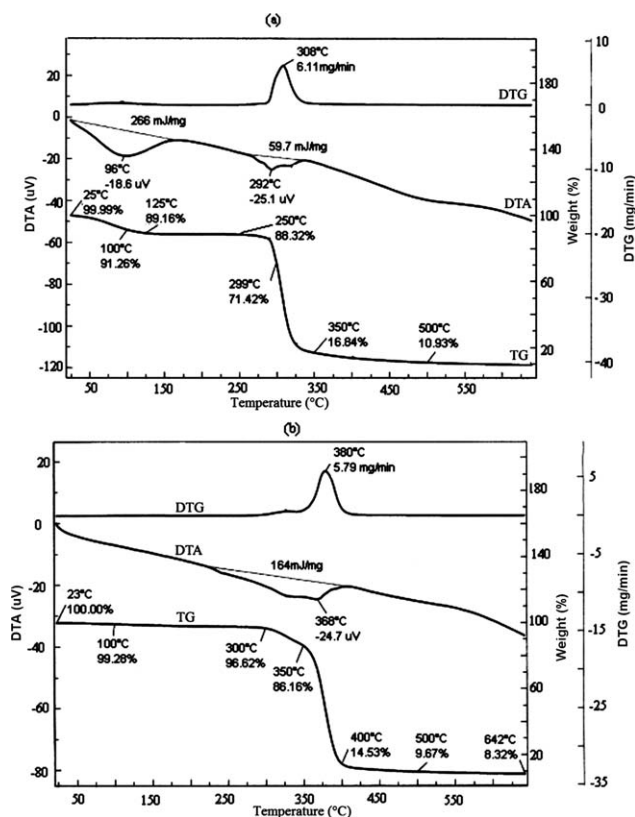
### Thermal analysis

Thermal analysis test was conducted to examine the change in thermal properties of the starch caused by propylation. Thermo gravimetric analysis (TG), derivative thermo gravimetric analysis (DTG), and differential thermal analysis (DTA) curves of native (DS 0.0) and propylated starch (DS 2.51) are shown in Figure 5. TG thermo gram of native starch (DS 0.0) showed a two stage weight loss below 500 $^{\circ}$ C with the first minor one corresponding to loss of water around 50 to 120 $^{\circ}$ C with a weight loss of 11%. Once dehydrated, the native starch was stable up to 250 $^{\circ}$ C. With increase in temperature from 250 to 350 $^{\circ}$ C, the thermal decomposition took place with a weight loss of 83%. Further heating up to 500 $^{\circ}$ C resulted in carbonization and ash formation. The main product of decomposition below 300 $^{\circ}$ C was formation of water by intermolecular or intramolecular condensation of starch hydroxyls.<sup>23</sup> Results showed that the decomposition temperature of propylated starch was higher than native starch. TG thermo gram of propylated starch (DS 2.51) showed single stage decomposition from 300 $^{\circ}$ C to 400 $^{\circ}$ C with a weight loss of 85%.

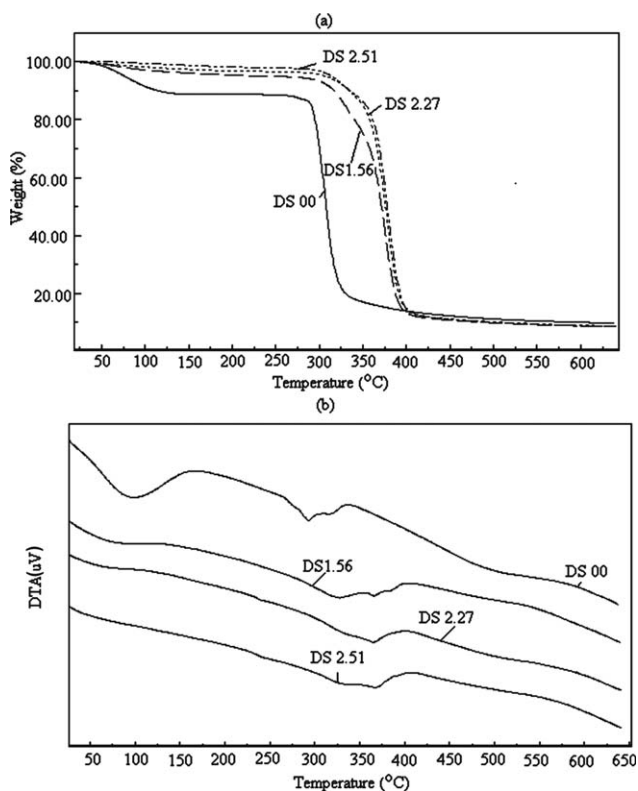
DTA curve of native starch showed two endothermic peaks with first one corresponding to loss of water at 96 $^{\circ}$ C with energy absorbed 266 mJ/mg followed by a stage of decomposition at 292 $^{\circ}$ C with energy absorbed 59.7 mJ/mg. But the curve of propylated starch (DS 2.51) showed one decomposition peak at 368 $^{\circ}$ C with energy absorbed 164 mJ/mg. DTG data showed the rate of weight change of starch with temperature. It showed that native starch degraded maximum at 308 $^{\circ}$ C and propylated starch (DS 2.51) at 380 $^{\circ}$ C.

Figure 6 shows the comparative TG–DTA curves of native and propylated starch at different DS. TG curves revealed that all the propylated starch sam-

ples decomposed at higher temperatures than the native starch. DTA results also demonstrated that as the DS increased from 1.56 to 2.27, the intensity of the first peak decreased and temperature of the second endothermic peak shifted towards right. At DS 2.51, the first peak disappeared and maximum temperature of second peak increased to a noticeable value. The propylated starch was thermally more stable than native starch. The increase in thermal stability with increase in DS was due to low amount of remaining hydroxyl groups in starch molecules after propylation. The increase in molecular weight and covalent bonding due to the propylation of



**Figure 5** TG, DTA, and DTG curves of (a) native starch (DS 0.0) and (b) propylated starch (DS 2.51).



**Figure 6** (a) TGA curves of native starch (DS 0.0) and propylated starch at different DS and (b) DTA curves of native starch (DS 0.0) and propylated starch at different DS.

hydroxyl groups were also responsible for the increased thermal stability. In an earlier study also, 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.<sup>24</sup>

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

Swelling power of native (DS 0.0) and propylated starch is shown in Figure 7. Figure 7(a) showed that the swelling power of native and propylated starch increased with temperature. With increase in temperature from 65°C to 75°C, swelling power of native starch (DS 0.0) increased significantly from 3.09 to 11.43 g/g. Propylated starch at low DS (DS 0.61) showed swelling power 10.55 g/g at 65°C which was much higher than native starch (DS 0.0). But it was comparable to the native starch at 95°C. Swelling power of the propylated starch at high DS (DS 2.51) was similar to native starch (DS 0.0) at 65°C but did not increase with increase in temperature as it was in native starch.

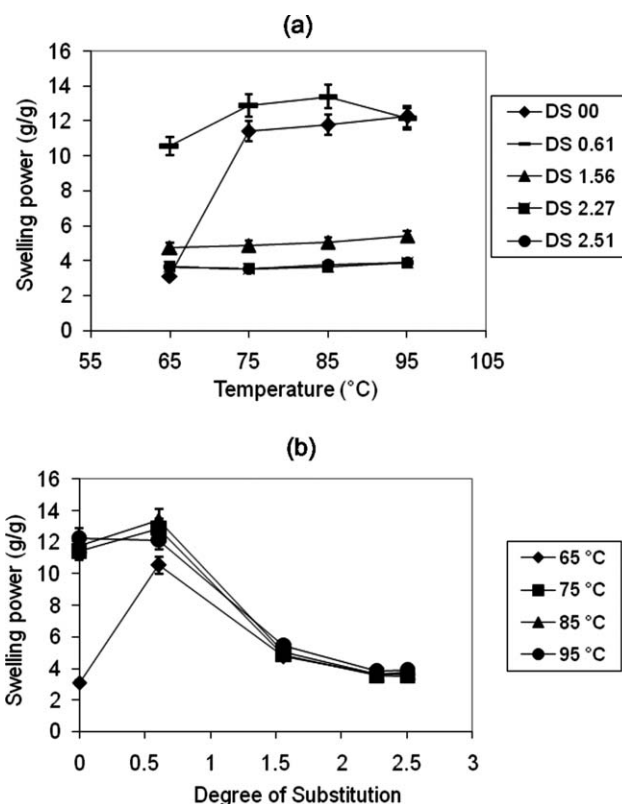
Figure 7(b) demonstrated that the propylated starch at low DS (DS 0.61) showed higher swelling power than native starch at all temperatures except 95°C. But at high DS (DS 2.27 and 2.51), the swelling

power of propylated starch was lower than native starch (DS 0.0) except at 65°C.

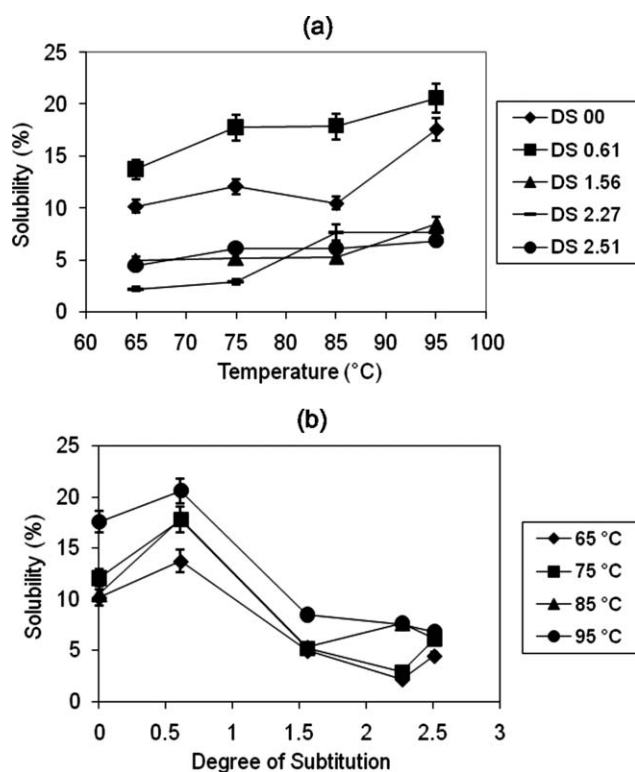
Solubility is contributed by extent of amylose in the starch. Solubility of native and propylated starch is shown in Figure 8. The solubility of all the samples increased with increase in temperature [Figure 8(a)]. The changes in solubility of starch with DS are shown in Figure 8(b). Solubility of propylated starch at low DS (DS 0.61) was higher than native starch (DS 0.0) at all temperatures. With increase in DS from 1.56 to 2.51, solubility decreased. The solubility of native starch was 17.58% at 95°C. Propylated starch at high DS (DS 2.51) showed solubility 6.83% under same temperature, which was lower than native starch.

Water binding capacity of native and propylated starch is shown in Figure 9. The water binding capacity of native starch (DS 0.0) was 89.76%. It increased to 136.77% in propylated starch at low DS (DS 0.61). At DS 1.56 water binding capacity decreased to 120.4 %, which was still higher than native starch. But at high DS (DS 2.51), the water binding capacity decreased to 77.4% that was below native starch.

Starch is comprised of amylose and amylopectin chains. Due to structure of the starch, it can not dissolve in water at normal temperature. The starch



**Figure 7** Swelling power of starch (a) as a function of temperature at different DS and (b) as a function of DS at different temperatures.

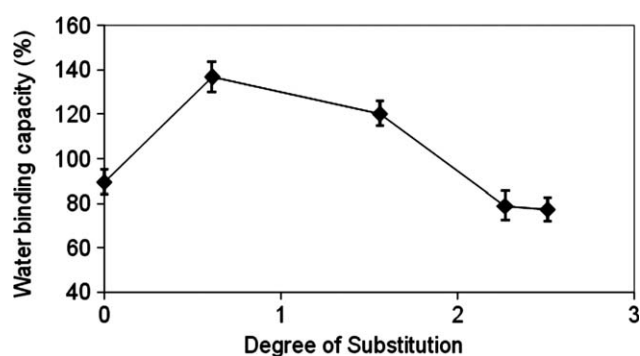


**Figure 8** Solubility of starch (a) as a function of temperature at different DS and (b) as a function of DS at different temperatures.

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 propyl groups. At high DS, the propyl groups replaced most of hydroxyl groups on starch and interaction with water decreased. Therefore, 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. Jae-Hong-Jeong et al.<sup>25</sup> observed that introduction of acetyl groups into polymer chains resulted in destabilization of granular 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.<sup>26–28</sup>

#### Light transmittance

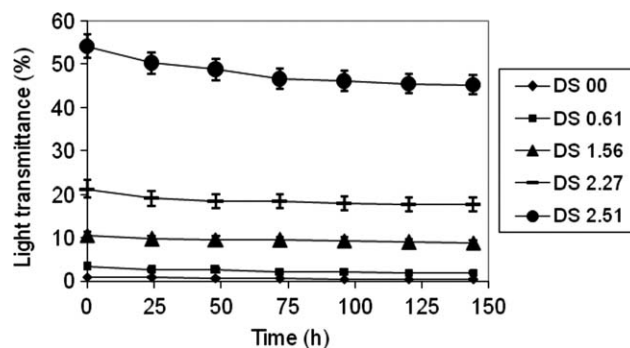
Figure 10 shows the light transmittance of native and propylated starch suspension during 144 h of storage period. Results showed that propylation



**Figure 9** Variation of water binding capacity with DS.

increased the light transmittance. At low DS (DS 0.61), the propylated starch showed slightly higher light transmittance than native starch (DS 0.0). But at high DS (DS 2.51), it showed drastic increase in light transmittance. There was gradual and slight decrease in the light transmittance of the native and propylated starch during 144 h of storage period. The transmittance decreased from 1.1 to 0.5% in native starch (DS 0.0) and from 54.3 to 45.4% in propylated starch (DS 2.51) after 144 h.

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 light transmittance is due to Rayleigh 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.<sup>17</sup> 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.



**Figure 10** Variation of light transmittance at different DS.



**TABLE II**  
**Comparative Study of the Properties of Starch After Acylation**

Reference	Modification (DS)	Morphology	TGA/DTA	Swelling power at 95°C (g/g)	Solubility at 95°C (%)	Water binding capacity (%)
Singh et al. <sup>12</sup>	Acetylation (DS 0.0)	–	–	10.3	0.125	95.60
	Acetylation (DS 0.150)	Starch molecules coalesce together after acetylation	–	13.10	0.150	80.50
Sodhi et al. <sup>13</sup>	Acetylation (DS 0.0)	–	–	13.03	17.30	–
	Acetylation (DS 0.144)	Slight aggregation of granules after acetylation	–	14.28	18.21	–
Xu et al. <sup>15</sup>	Acetylation (DS 0.0)		First decomposition temperature = 60 to 100°C, second decomposition temperature = 325°C with 50% weight loss	–	–	–
	Acetylation (DS 2.95)	At high DS starch almost fell in pieces and lost their individuality and smoothness	Decomposition temperature = 328 to 372 °C with 50% weight loss	–	–	–
This study	Propylation (DS 0.0)		First decomposition temperature = 50 to 120°C. second decomposition temperature = 250 to 350°C with 83% weight loss	12.26	17.58	89.76
	Propylation (DS 0.61)	–	–	12.14	20.60	136.77
	Propylation (DS 2.51)	Surface of the starch particles become rough and eroded after propylation	Decomposition temperature = 300 to 400°C with 85% weight loss	3.90	6.83	77.39

**Comparison with earlier studies**

Singh et al.<sup>12</sup> prepared acetylated starch with low DS and observed that swelling power and solubility increased but water binding capacity decreased after acetylation. Sodhi et al.<sup>13</sup> evaluated the morphology, swelling power and solubility of acetylated rice cultivars. It showed that swelling power and solubility increased at low DS. Xu et al.<sup>15</sup> studied the morphology and TGA/DTA properties of acetylated starch samples up to DS 2.95. The comparison of the properties of the starch after acylation reported earlier with properties of starch after propylation in the present study is shown in Table II. Singh et al.<sup>12</sup> showed swelling power increased by 27% and solubility by 20% with the increase in DS from 0 to 0.15. Sodhi et al.<sup>13</sup> found that with increase in DS from 0 to 0.144, swelling power and solubility increased by 10% and 5% respectively. However, in present case with the increase in DS from 0 to 0.61, the swelling power did not change appreciably and solubility increased by 17%. At high DS, swelling power and solubility decreased by 68% and 61% respectively

which confirmed the hydrophobic transformation in corn starch.

**CONCLUSIONS**

Changes in physico-chemical properties of propylated starch were observed when compared with native starch. The crystal structure of native starch got destroyed and surface of starch became rough during propylation. Thermal stability of propylated starch increased due to decrease in number of hydroxyl groups. DS of propylated starch governed the swelling power, solubility, water binding capacity and light transmittance of starch. At low DS (DS 0.61) swelling power, solubility and water binding capacity increased. At DS of about 2.15, swelling power, solubility and water binding capacity decreased than native starch. Changes in physico – chemical properties of propylated starch at high DS confirmed the hydrophobic transformation in corn starch. It could be used for blending of starch with synthetic polymers.

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