

# Water solubility, thermal characteristics and biodegradability of extruded starch acetate foams<sup>☆</sup>

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## Abstract

Starch based foams have been studied as replacements for non-degradable expanded polystyrene (EPS) as loose-fill packaging material because of starch's total degradation and low cost. However, starch's hydrophilicity, poor mechanical properties and dimensional stability limited their applications. Acetylated starch with a high degree of substitution (DS) is an alternative. Starch acetates with DS 1.11, 1.68, and 2.23 were extruded with either water or ethanol as solvents. The effects of DS and type of solvent on the starch acetate foam's water absorption index (WAI), water solubility index (WSI), thermal behavior (glass transition temperature [ $T_g$ ], melting temperature [ $T_m$ ], and thermal decomposition temperature), and biodegradability were investigated. There was a significant interaction ( $P < 0.05$ ) between solvent type and DS on WAI and WSI of the foams. As DS increased from 1.11 to 2.23, WAI and WSI increased when ethanol was used as solvent and decreased when water was used as solvent. The  $T_g$  values of starch decreased with acetylation and with increasing DS, but increased with extrusion. Acetylation and extrusion increased the thermal stability of the foams. The rate of biodegradation of the foams decreased with increasing DS. The foams, extruded with ethanol, had higher degradation rates than those with water.

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## 1. Introduction

Loose-fill packaging materials offer effective protection for fragile products by absorbing or isolat-

ing impact energy during transportation and handling (Fang and Hanna, 2000). Generally, expanded polystyrene (EPS) is a popular material for this application due to its low cost and excellent physical and mechanical properties. However, its resistance to microbial degradation and potential products of its eventual degradation are environmental concerns. Therefore, efforts have been made to find alternatives.

Of the natural biopolymers, starch has received more attention because of its low cost, availability, and total degradation after usage. Some studies have been done on the use of starch foam to replace

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synthetic foams (Altieri and Lacourse, 1990; Wang and Shogren, 1997). However, starch has the disadvantages of hydrophilicity, poor mechanical properties and dimensional stability, especially in presence of water and humid environments. Chemical modification is a way to overcome these shortcomings.

Starch acetylation is a modification technique that can be performed on starch with relative ease. Starch acetates with high degree of substitution ( $DS > 1$ ) have been studied for 60 y with the aim of replacing cellulose acetate (Mullen and Pacsu, 1942; Whistler and Hilbert, 1944; Wolff et al., 1951). The properties of whole starch and waxy maize starch acetates were inferior to those of their cellulose counterpart because of the presence of significant amounts of branched amylopectin, which adversely influenced the mechanical and physical properties. Although amylose acetates possessed properties competitive with cellulose acetate, the high costs of fractionation and purification of amylose were detrimental to their wide use.

Recently, the availability of starch that contains 70% amylose makes commercial production of starch acetate more likely. Moreover, Mark and Mehlretter (1972) developed a simple method to produce a relatively undegraded starch triacetate using 50% NaOH as the catalyst and without pretreatment. Miladinov and Hanna (1999, 2001) used that method to prepare starch acetates ( $DS$  2.0 and 3.0), and then extruded and compared the effects of temperature and solvent types on their functional properties.

It is well known that starch becomes water-resistant after acetylation and this hydrophobicity increases with increasing  $DS$ , which increases their suitability as packaging materials. Nevertheless, the challenge with high  $DS$  starch acetate is their higher cost and reduced degradability. Rivard et al. (1992, 1995) and Derradji-Serghat et al. (1999) determined the aerobic and anaerobic degradation of acetylated starch and found the common hydrolysis of native starch to glucose and maltose was slowed down, and was inhibited further with increased incorporation of the acetyl groups. In a previous study (unpublished data), we determined the physical, mechanical, and morphological characteristics of starch acetate foams ( $DS$  from 0.5 to 2.5) extruded with either water or ethanol. Significant interaction between  $DS$  and solvent type occurred on the functional properties of the foams. The objectives of this study was to produce starch

acetate foams with  $DS$  of 1.0–2.5 by extrusion with either water or ethanol and to measure the water absorption, thermal, and degradation characteristics for their potential as biodegradable materials.

## 2. Materials and methods

### 2.1. Synthesis of starch acetates

Starch acetylation was carried out by a modification of the procedure of Mark and Mehlretter (1972). Prior to acetylating, cornstarch with 70% amylose (American Maize Products Co., Hammond, IN), first was dried at 40–50 °C for 24 h to decrease the moisture content (<2%). Starch (20 kg, dry basis) was mixed with acetic anhydride (Aldrich Chemical Co., Milwaukee, WI) at 1:2 ratio (w/w) in a 1100 L steam jacketed reactor. After stirring for 5 min, 50% of an aqueous NaOH solution (0.2 (g/g) starch) was added. The temperature was increased to 123 °C within 15 min, and then held at this temperature for 90, 110, and 155 min to obtain starches with  $DS$  of 1.11, 1.68, and 2.23, respectively. The reaction was terminated by adding excess cold water to the reactor. White starch acetates were obtained by thoroughly rinsing the reaction products with tap water and drying them at about 50 °C. The dried products were ground prior to extrusion.

### 2.2. Extrusion

About 500 g of the dried acetylated starches were mixed with either distilled water or ethanol to adjust the solvent content to 18% (w/w). Talc (5% (w/w) starch) was added as a nucleating agent to ensure the uniformity of the cell void spaces. The mixture was blended in a Hobart mixer (Model C-100, Hobart Corp., Troy, OH) and allowed to equilibrate for 12 h at 25 °C, and then extruded. The extrusion was performed in a laboratory twin screw extruder with co-rotating mixing screws (Model CTSE-V, C.W. Brabender, Inc., S.Hackensack, N.J.). The conical screws had diameters decreasing from 43 to 28 mm along their length of 365 mm from the feed end to exit. Temperatures in the feeding, metering, and die sections were held at 50, 140, and 140 °C, respectively. A 4-mm-diameter die nozzle was used to produce cylindrical foams. The screw speed was maintained

at 140 rpm. The foams were cut into finite lengths or ground to powder for the following tests.

### 2.3. Determination of degree of substitution (DS)

DS value was determined according to the method of Miladinov and Hanna (2000) with some modifications. NaOH was used to hydrolyze the acetyl groups from starch molecules. The remaining NaOH was back titrated with HCL.

DS was calculated as:

$$DS = \frac{162 \times (M_{NaOH} \times V_{NaOH} - M_{HCL} \times V_{HCL})}{1000 \times W - 42 \times (M_{NaOH} \times V_{NaOH} - M_{HCL} \times V_{HCL})}$$

where  $M_{NaOH}$  is the molar of NaOH,  $V_{NaOH}$  is the volume of NaOH,  $M_{HCL}$  is the molar of HCL using to back titrate,  $V_{HCL}$  is the volume of HCL using to back titrate, and  $W$  is the sample weight (g).

### 2.4. Water absorption index (WAI) and water solubility index (WSI)

WAI and WSI of the foams were measured by a procedure similar to AACC method 56-20 (1983). To determine WAI and WSI, the foams were ground to pass through a #80 sieve. The samples (about 1 g) were dispersed in 30 ml of distilled water in pre-weighed centrifuge tubes. The centrifuge tubes were placed in a shaking water bath at 30 °C for 30 min, and then centrifuged at 5000 ×  $g$  for 10 min. The supernatants were decanted carefully into pre-weighed aluminum dishes, dried at 103 °C for 12 h, cooled and weighed. The remaining sediment with tube was weighed. WAI and WSI were calculated as

$$WAI = \frac{\text{weight of tube with sedi} - \text{weight of tube}}{\text{weight of sample (d.b.)}}$$

$$WSI = \frac{\text{weight of dish with solids} - \text{weight of dish}}{\text{weight of sample (d.b.)}} \times 100\%$$

### 2.5. Thermal stability analysis

#### 2.5.1. Differential scanning calorimetry (DSC)

DSC measurements were performed with a Perkin-Elmer DSC7 (Norwalk, CT, USA). About

10 mg of the dried samples (< 2% moisture) were placed in stainless steel DSC pans (Perkin-Elmer), and the pans were sealed. The instrument was calibrated with indium. The samples were heated from 20 to 250 °C with a heating rate of 10 °C/min in a nitrogen atmosphere. The glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) were taken as the inflection point of the increment of special heat capacity and as the peak value of the endothermal process in the DSC curves, respectively.

#### 2.5.2. Thermogravimetry analysis (TGA)

The thermogravimetric analyzer (Perkin-Elmer TGA 7, Norwalk, CT, USA) was calibrated with nickel. Samples of about 3 to 6 mg were placed in the balance system and heated from 50 to 650 °C with a heating rate of 20 °C/min in a nitrogen atmosphere. The initial degradation temperature was calculated using a TGA7 software.

### 2.6. Biodegradability

Biodegradabilities of starch acetate foams were measured according to the method of Ghorpade et al. (2001). Samples (50 g) were placed in the laboratory composting system for 3 months. Humidified air was passed through flowmeters (mean air velocity 25 mL/min) and then into the composting vessels. External heat was applied to maintain a constant temperature of 65 °C. The exhaust air was directed through a two-way valve attached to a gas chromatograph (GC) (Perkin-Elmer, Norwalk, CT, USA) to measure each eluted gas concentration three times each week. At an interval of once a week, compost samples were removed from the vessels and water was added to maintain the moisture content of the samples between 20 and 56%. Biodegradation was expressed as CO<sub>2</sub> percentage in eluted gas and the mean value per week was obtained by averaging each measurement within one week.

### 2.7. Statistical analysis

Synthesis and extrusions were made using a randomized complete block design (RCBD) with three blocks representing the replications. The results of water absorption and solubility were analyzed by SAS version 8.0 statistical software (SAS Institute Inc.,

Cary, NC) and were reported by the means of three replications. An analysis of variance (ANOVA) was employed to estimate the significant ( $P < 0.05$ ) influences of the solvent type and DS. Factorial response curves were developed to fit the regression line.

### 3. Results and discussion

#### 3.1. Water absorption index (WAI) and water solubility index (WSI)

WAI and WSI reflect a foam's solubility in water. Low WAI and WSI enhance the foam's dimensional stability, thus improving its suitability as a packaging material. Changes in WAI of starch acetate foams, extruded with either water or ethanol, with increasing DS are illustrated in Fig. 1. Opposite trends were found for WAI of the foams with these two solvents. As DS of starch acetate increased from 1.11 to 2.23, WAI of the foam increased when ethanol was used as the solvent and decreased when water was used as the solvent. The ANOVA results indicated there was a significant interaction ( $P = 0.0239$ ) between solvent type and quadratic effect of DS, implying that WAI of the foam response to DS depended on the solvent type. Therefore, two different regression equations were fitted to the changes in WAI with DS for the two solvents.

$$\text{Water : WAI} = 1.2807 + 9.0477 \times \text{DS} - 3.7648 \times \text{DS}^2 \quad (R^2 = 0.9988) \quad (1)$$

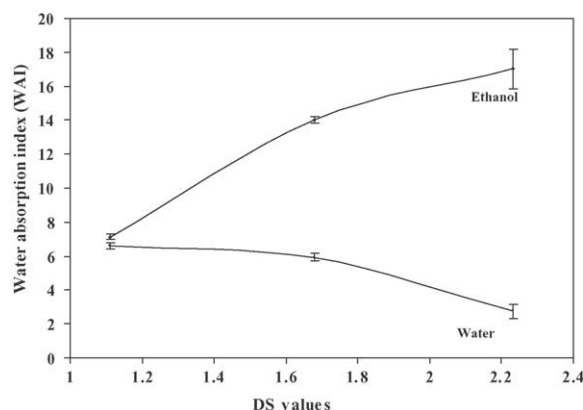


Fig. 1. Changes in water absorption index (WAI) of starch acetate foams with DS and solvent type.

$$\text{Ethanol : WAI} = -18.8168 + 30.8627 \times \text{DS} - 6.7168 \times \text{DS}^2 \quad (R^2 = 0.9997) \quad (2)$$

The changes in WAI of the foams with DS were considered to relate to the morphology of the foams (Miladinov and Hanna, 2001). In a previous study (unpublished data), when the DS 1.11 starch acetate was extruded with water, great numbers of interconnected cells with thin walls were observed. However, when the DS of starch acetate increased to 2.23, the numbers of cells were reduced, accompanied by an increase in cell wall thickness. Conversely, when ethanol was the solvent and the DS of starch acetate increased from 1.11 to 2.23, uniform cells with thin cell walls were observed, which gave the samples higher surface areas per unit weight than those extruded with water. This difference in the surface area was responsible for the difference in WAI of the foams with the two solvents. The samples extruded with ethanol provided greater surface area, thus resulting in higher water absorption. Actually, after acetylation, starch became more hydrophobic as the result of reducing the possibility of forming hydrogen bonds between the hydroxyl groups in the starch and water (Thiebaud et al., 1997). Consequently, water could not penetrate into the material, but interacted only on the surface (Miladinov and Hanna, 2001). DS of starch acetate seemed to be a main factor affecting the water uptake. The DS 2.23 starch acetate extruded with water showed a significantly ( $P = 0.006$ ) lower WAI (2.74) than that with DS 1.11 (6.62).

With respect to WSI of the foams, there was a significant interaction ( $P = 0.009$ ) between quadratic effect of DS and the type of solvent. Similarly, two different regression equations were offered to explain changes in WSI of the foams with DS of starch acetate for the two solvents.

$$\text{Water : WSI} = 42.3157 - 40.8200 \times \text{DS} + 10.2260 \times \text{DS}^2 \quad (R^2 = 0.9963) \quad (3)$$

$$\text{Ethanol : WSI} = 14.8303 - 19.9733 \times \text{DS} + 9.2120 \times \text{DS}^2 \quad (R^2 = 0.9979) \quad (4)$$

Graphical representations of the changes in WSI of the foams, as functions of DS for the two solvents, are given in Fig. 2. When water was used as solvent, WSI of the foams decreased with increasing DS. When

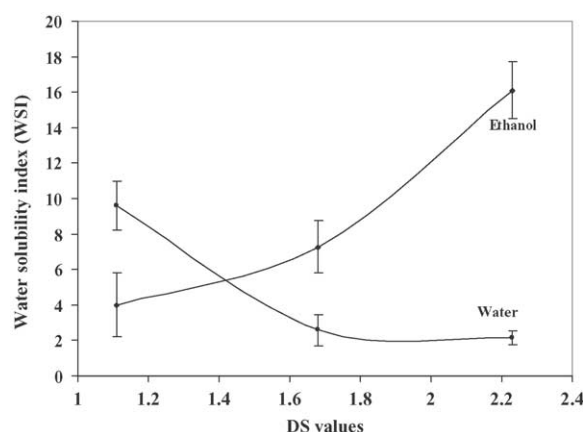


Fig. 2. Changes in water solubility index (WSI) of starch acetate foams with DS and solvent type.

DS of starch acetate was 1.11, approximately two hydroxyl groups on each anhydroglucose unit remained, making the sample hydrophilic. As a result, it swelled and was extracted partially by water (Aburto et al., 1999). With further increase in DS of starch acetate, the samples became more hydrophobic reducing the chances of water extraction.

### 3.2. Thermal analyses

#### 3.2.1. DSC

The  $T_g$  and  $T_m$  of native starch were changed by esterification reaction (Sagar and Merrill, 1995) and consequent extrusion process (Miladinov and Hanna, 1999, 2001). DSC plots of DS 2.23 starch acetate be-

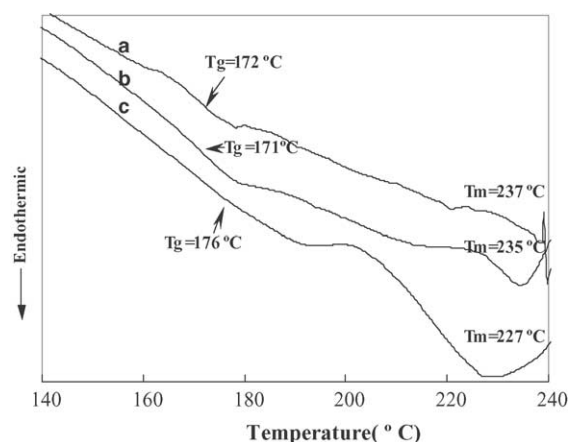


Fig. 3. DSC thermographs of starch acetate, with DS 2.23, extruded with (a) ethanol; (b) before extrusion; and (c) extruded with water.

fore extrusion and extruded with water or ethanol are presented in Fig. 3. The data for all measurements are given in Table 1. Although starch used in this study contained 70% amylose (largely amorphous), there was approximately 30% amylopectin in the molecules, which was responsible for the crystalline area in starch molecules. In Table 1, it is shown that the  $T_g$  of native starch was 224 °C and the DS 1.11 starch acetate was 192 °C, which is 32 °C lower than its unmodified counterpart. The  $T_g$  decreased to 171 °C for DS 2.23 starch acetate and the  $T_g$  of starch decreased with increasing acetylation. This agreed with the results of Shogren (1996). These changes can be explained by the fact that the intermolecular hydrogen bonds, which stiffened the macromolecular chain, decreased

Table 1  
Thermal data for starch acetate (SA) before and after extrusion

Sample	DS	DSC measurement		TGA measurement	
		$T_g$ (°C)	$T_m$ (°C)	Initial degradation Temperature (°C)	Weight loss (%)
Native starch	0	224	237	297	70.46
SA (no extruded)	1.11	192	225	299	44.15
SA extruded with water	1.11	195	228	301	47.98
SA extruded with ethanol	1.11	191	225	304	48.58
SA (no extruded)	1.68	182	236	347	37.92
SA with water	1.68	186	232	354	43.01
SA extruded with ethanol	1.68	183	231	358	45.51
SA (no extruded)	2.23	171	235	354	33.46
SA extruded with water	2.23	170	227	356	35.22
SA extruded with ethanol	2.23	172	237	360	44.53



with partial replacement of hydroxyl groups by acetyl groups. Moreover, the increase in free volume within the molecules, due to the introduction of bulk groups that allowed more molecular mobility, also contributed to the reduction in the  $T_g$  of starch with acetylation (Aburto et al., 1999). The higher the DS value of the starch acetate, the greater the free volume the molecules. Regarding the  $T_m$  values of starch acetates, it was found that  $T_m$  decreased slightly with acetylation and ranged from 225 to 237 °C.

As far as the changes in  $T_g$  after extrusion were concerned, it was found that the  $T_g$  of the extruded foams increased compared with those before extrusion. The  $T_g$  values of the samples extruded with water were slightly greater than those of samples with ethanol. Actually, after extrusion, the samples presented some crystalline structures (Xu and Hanna, unpublished data), likely due to the realignment of starch acetate molecules during extrusion. However, enough bulky groups within the molecules (for example DS 2.23 starch acetate foam) inhibited the recrystallization, thus its  $T_g$  remained lower even after extrusion.

### 3.2.2. TGA

TG curves were used to examine the changes in thermal stability caused by acetylation and subsequent extrusion. The TGA thermograms of native starch and starch acetate with DS 2.23 before extrusion and extruded with water or ethanol are shown in Fig. 4 and while the data for all measurements are given in

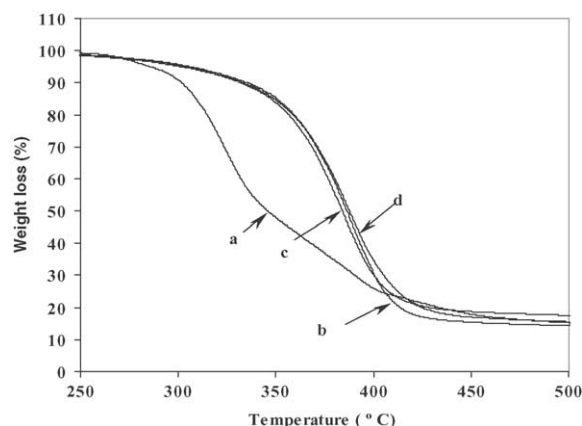


Fig. 4. TGA thermograms of (a) native starch and starch acetates, (b) with DS 2.23, before extrusion; (c) extruded with water; and (d) extruded with ethanol.

Table 1. The initial degradation of native starch began at 297 °C with a weight loss of 70.7%. Further heating, up to 650 °C, resulted in carbonization and ash formation (Thiebaud et al., 1997). After acetylation, and as DS of starch acetate increased from 1.11 to 2.23, thermal degradation onset temperature increased from 299 (for DS 1.11) to 358 °C (for DS 2.23). This increase in thermal stability with increasing DS was attributed to the low amount of remaining hydroxyl groups in starch molecules after acetylation. The decomposition of starch was a result of the inter- or intra-molecular dehydration reactions of starch molecules with water as a main product of decomposition (Thiebaud et al., 1997). The opportunity for this condensation reaction was reduced with substitution of hydroxyl group by acetyl group. The resultant weight loss was reduced noticeably. Therefore, a high DS had a beneficial effect on the thermal stability of the sample.

After extrusion, regardless of which solvent was used, initial degradation temperature of the foams increased compared with that of the non-extruded counterparts. The foams extruded with ethanol had slightly higher thermal decomposition temperatures than those with water. As mentioned above, crystalline structures in the foams increased during extrusion process. Well-ordered structure might resist the foam's thermal decomposition by preventing syneresis. A little higher weight losses in the extruded foams than in those before extrusion can be explained by degradation of some molecules during extrusion.

### 3.3. Biodegradability

Biodegradability of starch acetate foams is a critical functionality issue for their application. The aerobic bioconversion results of starch acetate foams having different DS values are displayed in Fig. 5. Different degradation kinetics were found for each sample, and were affected not only by DS values, but also by solvent type. Obviously, in the foams extruded by water, increasing DS of starch acetate from 1.11 to 2.23 led to a considerable decrease in the production of CO<sub>2</sub>. When DS was 1.11, the production of CO<sub>2</sub> was 25.7% after one week and increased to 41.8% after 12 weeks. Rapid degradation happened after 8 weeks. When DS increased to 1.68, the rate of biodegradation was reduced as indicated by the initial CO<sub>2</sub> amount of 12.7% after 1 week and 38.8% after 12 weeks. With

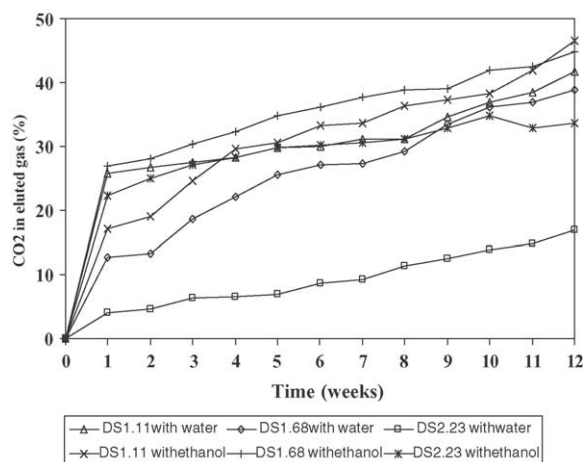


Fig. 5. Aerobic biodegradation of starch acetate foams.

further increase in DS to 2.23, the production of CO<sub>2</sub> after one week was only 4.1% and slowly increased to 17.0% after 12 weeks. It was demonstrated that the biodegradability of the starch acetate foams was inhibited at high DS. Native starch foam was reported to experience rapid degradation, and complete degradation took place after 15–20 days because the enzyme released by microorganisms in the compost hydrolyzed the starch backbone. The bulky groups introduced by acetylation increased the starch chain's hydrophobicity and inhibited the catalytic action of enzyme, thus reducing starch acetate foam's biodegradation (Aburto et al., 1999).

Different trends were observed for the starch acetate foams extruded with ethanol. The DS 1.68 foam had a higher degradation rate (an onset CO<sub>2</sub> of 26.9%) than those with DS 1.11 (17.1%) and DS 2.23 (22.3%), which can be explained by the difference in morphology of the foams. The DS 1.11 foams extruded with ethanol had small cells, surrounded by relatively thick and broken cell walls. However, uniform large cell sizes having smooth thin cell walls were observed for those foams having DS 1.68 and 2.23 (Xu and Hanna, unpublished data). These large size cells increased the sites accessibility to microbial attack, thus increasing rate of degradation. However, increases in hydrophobicity of the foams and steric hindrance within molecules, with increasing DS, were detrimental to microbial attack, thus reducing the rate of degradation of the DS 2.23 foams. Generally, the foams extruded

with ethanol had higher degradation rates than those extruded with water.

#### 4. Conclusions

Starch acetate foams were prepared by extruding starch acetates, degrees of substitution (DS) of 1.11, 1.68 and 2.23, with water and ethanol. The changes in water absorption of the foams were not only related to DS of starch acetates, but also to the foam's morphology. Acetylation decreased starch's glass transition temperature ( $T_g$ ) but increased their thermal stability because the number of the hydroxyl groups in starch molecules decreased with acetylation. The consequent extrusion increased the foam's  $T_g$  due to the realignment of starch acetate molecules. Biodegradation rates of starch acetates foams, extruded with water, decreased with increasing DS, whereas the DS 1.68 foam extruded with ethanol, had higher biodegradation rate than foams with DS 1.11 and 2.23.

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