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Physical, Mechanical, and Morphological Characteristics of Extruded Starch Acetate Foams

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Starch acetates with degrees of substitution (DS) of 0.57, 1.11, 1.68, and 2.23 were prepared and extruded with either water or ethanol. The microstructure, physical properties (radial expansion ratio [RER] and unit density), mechanical properties (spring index [SI] and compressibility), and crystalline structure of the foams were investigated. The functional properties were a function of DS and blowing agent type. When water was used as the blowing agent and DS increased, the foams were pale yellow, with rough and uneven surfaces. The cells were dense, with thick cell walls. Lower RER and SI, with higher DS, were associated with high unit density and compressibility. When ethanol was used as the blowing agent, contrary results were observed. The snow-white foams had smooth surfaces, uniform cells, and smooth cell walls. High RER and SI, and low unit density and compressibility were observed. The changes in SI and compressibility with RER also were examined and found to depend on the type of solvent. A crystalline pattern was observed because of the formation of well-ordered structures during extrusion.

KEY WORDS: Starch acetate foam; microstructure; physical and mechanical properties; crystalline.

INTRODUCTION

Since the 1950's when the petroleum industry grew rapidly, synthetic plastics have occupied a dominant position in the packaging industry. However, the excessive use of synthetic plastics has caused environmental problems associated with their disposal. Synthetic plastics require hundreds of years to degrade. It has been reported that municipal solid wastes consist of 7.2% by weight or 18% by volume of plastics [1], most of which end up in overburdened landfills. Expanded polystyrene (EPS) is currently a popular loose-fill packaging material used to protect fragile products during transportation and handling. EPS has excellent physical and mechanical properties after foaming and also is inexpensive. However, concern over its negative effect on the environment has prompted researchers to seek alternatives from natural agricultural products.

Of the natural biopolymers, starch has received the most attention because of its low cost, availability, and total degradation after usage. Studies have been done on the use of starch foam to replace synthetic foams [2–5]. However, starch has disadvantages of being hydrophilic, having poor mechanical properties, and having poor dimensional stability, especially in aqueous environments.

Starch acetylation is a modification technique that can be performed with relative ease. Starch acetates with high degrees of substitution (DS > 1) have been studied for 60 years with the aim of replacing cellulose acetate [6–8]. However, the

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properties of whole starch and waxy maize starch acetates were found to be inferior to those of the cellulose counterpart, because of the presence of a significant amount of branched amylopectin, which adversely influenced the mechanical and physical properties. Although amylose acetate had properties that were competitive with cellulose acetate, the high cost of fractionation and purification of amylose deterred its use.

More recently, the availability of starch that contains 70% amylose makes commercial production of starch acetate more likely. Shogren [9] prepared starch acetate (DS = 2.5) based foams and discussed their mechanical properties. Miladinov and Hanna [10] compared the physical and molecular properties of starch acetates (DS = 2.0 and 3.0) extruded with water or ethanol. However, no work has been published on starch acetate foams with a broader DS range (from 0.5 to 2.5). Water was selected as blowing agent to increase the volume of the foam. However, it is well known that the hydrophobicity of starch acetate increased as DS increased. Ethanol, another blowing agent, is more hydrophobic than water. The objectives of this study were (1) to extrude starch acetates having DS between 0.5 and 2.5 with either water or ethanol, (1) to investigate the interaction between DS and blowing agent type; and (3) to evaluate the foams as loose-fill packaging by measuring the physical, mechanical, and morphological properties.

MATERIALS AND METHODS

Synthesis of Starch Acetates

Starch acetylation was carried out by a modification of the procedure of Mark and Mehltretter [11]. Prior to acetylating, 70% amylose corn starch (American Maize Products Co., Hammond, IN) was dried (<2%) at 40–50°C for 24 h. 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 held at this temperature for 45, 90, 110, and 155 min. to obtain starches with DS of 0.57, 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.

Extrusion

About 500 g of the dried acetylated starches were mixed with either distilled water or ethanol to adjust the blowing agent 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, Horbart 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-shaped foams. Screw speed was maintained at 140 rpm. The foams were cut into finite lengths or ground to powder for the following tests.

Determination of DS

DS value was determined according to the method of Miladinov and Hanna [12] with some modification. Excess NaOH was used to hydrolyze acetyl groups from starch molecules. The remaining NaOH was back titrated with HCl.

DS was calculated as:

$$\mathrm{DS} = \frac{162 \times (N_{\mathrm{NaOH}} \times V_{\mathrm{NaOH}} - N_{\mathrm{HCL}} \times V_{\mathrm{HCl}})}{1000 \times W - 42 \times (N_{\mathrm{NaOH}} \times V_{\mathrm{NaOH}} - N_{\mathrm{HCl}} \times V_{\mathrm{HCl}})} \tag{1}$$

where N_{NaOH} was the normality of NaOH, V_{NaOH} was the volume used of NaOH, N_{HCl} was the normality of HCl used to back titrate, V_{HCl} was the volume of HCl used to back titrate, and W is the sample weight (g).

Scanning Electron Microscopy (SEM)

The morphologies of starch acetates extruded with either water or ethanol were observed under a SEM (Hitachi S-3000N, Tokyo, Japan). Before testing, the samples were mounted on SEM stubs with double-sided adhesive tape, and then coated with platinum to a thickness of about 10 nm under vacuum to make the sample conductive. Micrographs were recorded at different magnifications to assure clear images.

Physical Properties

Radial Expansion Ratio (RER)

RER of the foams were calculated according to the method of Bhatnagar and Hanna [13]. The mean cross-sectional area of the foams was divided by the cross-sectional area of the die nozzles. Each mean value was the average of 20 observations.

Unit Density

Unit density of the foams was determined using a glass bead displacement method [2]. Glass beads of 0.1-mm diameter were used as the displacement media to determine the volume of the foams. Unit density was obtained by dividing the mass by the volume of foams. Five replications were used to obtain mean values.

Mechanical Properties

Spring Index (SI)

SI measurements were carried out using an Instron universal testing machine (model 5566, Instron Engineering Corp., Canton, MA). A 6-cm diameter cylindrical probe was used to compress the sample to 80% of its original dimension at a loading rate of 30 mm/min [4]. The sample was recompressed 1 min after releasing the load from the first compression. SI was calculated by dividing the recompression force by the initial force of compression and had an ideal value of nearly 1. The mean value was obtained by averaging five replications.

Compressibility

Compressibility was calculated using the same data collected for SI test. It was calculated by dividing the peak force required to achieve a deformation of 80% of the original dimension by the axial cross-section area of the sample [3].

X-ray Diffraction

X-ray patterns of starch acetate foams were analyzed between $2\theta = 3$ and 40° using an X-ray diffractometer (Rigaku D/Max-B, Tokyo, Japan) with Cu-Kα radiation and voltage of 40 KV and 30 mA. Prior to testing, the samples were ground into powder.

Statistical Analysis

All results were reported using the means of three or more replicates. Starch acetate syntheses and extrusions were made using randomized complete block design (RCBD) with three blocks representing the replicates. Physical and mechanical properties were analyzed with SAS version 8.0 statistical software (SAS Institute Inc., Cary, NC). An analysis of variance (ANOVA) was employed to estimate the significant ($p < 0.05$) influence of each factor. Factorial response curves were developed to fit the regression line.

RESULTS AND DISCUSSION

Microstructures of Starch Acetate Foams

Figure 1 shows differences in the surface structures of starch acetates having different DS values, when extruded with water or ethanol. The samples extruded with water were pale yellow, and had rough and uneven surfaces, especially those from high-DS starch acetates. Conversely, those extruded with ethanol were snow-white, and had smooth surfaces. Differences in the stereoscopic structural and textural properties also were determined, using SEM micrographs of cross sections of the foams as illustrated in Figs. 2 and 3. The textural differences in starch acetates foams having different DS values were affected strongly by type of blowing agent. When starch acetates were extruded with water, large dead-end cells [14] with some broken cell walls were found in DS 0.57 starch acetate. Increasing DS to 1.11 resulted in great numbers of interconnected cells with thin walls, and lighter foams. However, further increasing DS to 2.23 led to a reduction in the number of cells and thicker cell walls, so that the foams became denser. Totally different changes were found for the samples extruded with ethanol. Starch acetate with DS 1.11 had small cells, surrounded by relatively thick and broken cell walls. When DS was increased to 2.23, uniform cell sizes accompanied by smooth thin cell walls were observed.

The morphologies of the foams depended on cell growth and cell nucleation, which were influenced partially by the compatibility between the blowing agent and the starch acetate. Higher com-

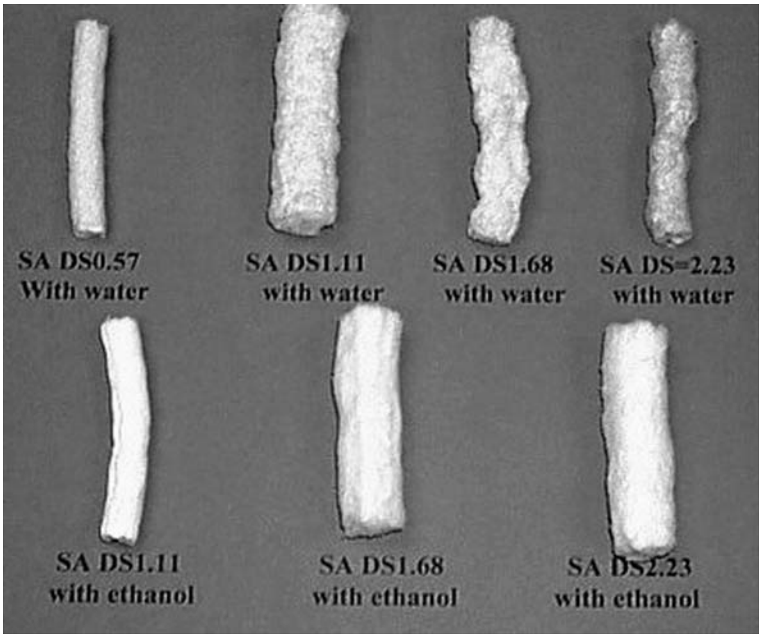

Fig. 1. Photographs of starch acetates (SA) having different DS extruded with water or ethanol.

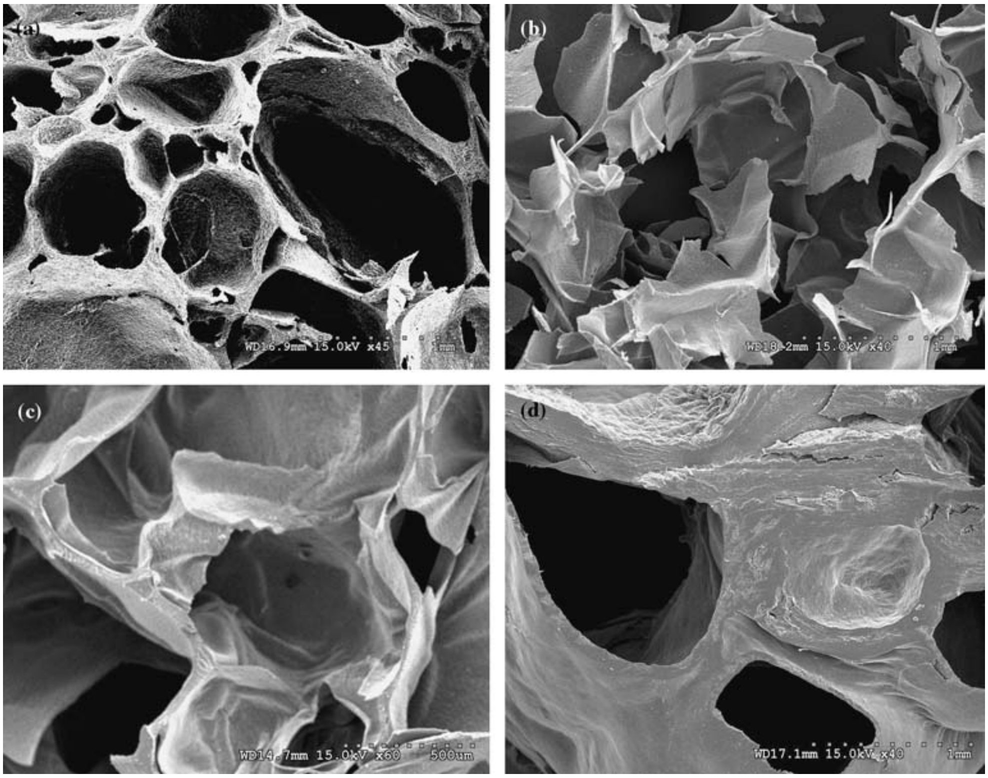

Fig. 2. SEM micrographs of starch acetates (a) DS 0.57, (b) DS1.11, (c) DS 1.68, and (d) DS 2.23 extruded with water.

patibility between blowing agent and starch acetate resulted in even distribution of the blowing agent in the starch acetate matrix. Consequently, uniformly sized cell was formed. It was known that when DS of the starch acetate was increased, the compatibility between water and starch acetate would

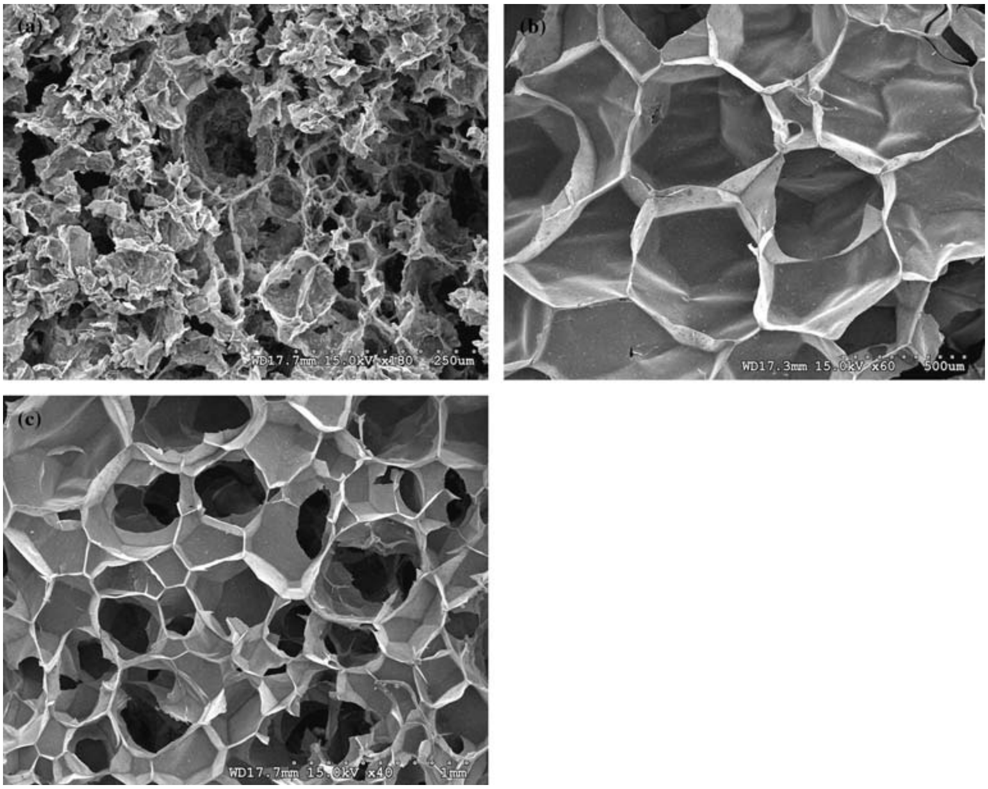

Fig. 3. SEM micrographs of starch acetates (a) DS1.11, (b) DS1.68, and (c) DS 2.23 extruded with ethanol.

decrease, with the reverse being true for ethanol and starch acetate [9, 10]. As a result, the cell sizes of the foams extruded with water were less uniform than those extruded with ethanol. In addition, low compatibility between blowing agent and starch acetate led to fewer cells and bigger cells since the low melt viscosity, caused by low compatibility, increased the chance of cell collapse and cell merging. The two blowing agents have different surface tensions, which played an important role in cell nucleation according to the equation (2) developed by Lee [15].

$$\mathrm{Ca} = \frac{R_c \eta \gamma}{4\sigma} \tag{2}$$

where Ca is capillary number, η is the melt viscosity, γ is the average shear rate, and σ is surface tension.

Lower surface tension led to higher nucleation speed, hence forming the uniform cell size. It is known that the surface tension of water is 78 dyn/cm while that of ethanol is 27 dyn/cm. As a result, the cell sizes of foam extruded with ethanol were much smaller than that of foam extruded with water.

RER and Unit Density

RER and unit density are important physical parameters of extruded foams used as loose-fill packaging. High RER and low unit density are ideal for foams because of the reduced cost. The ANOVA results indicated that the changes in RER of the foams with DS were dependent on the blowing agent type ($p < 0.001$). Therefore, two quadratic regression equations were applied to the changes in RER (γ) with DS for two blowing agents.

$$\text{Water: } \gamma = -8.9540 + 35.0368^{*}\mathrm{DS} - 13.2294^{*}\mathrm{DS}^2 \tag{3}$$

$$\text{Ethanol: } \gamma = -27.8618 + 40.5836^{*}\mathrm{DS} - 9.0679^{*}\mathrm{DS}^2 \tag{4}$$

For unit density, as with RER, there was a strong interaction ($p < 0.001$) between the blowing agent type and DS. Separate quadratic regression equations were developed for the changes in unit density (ρ) with DS for the two blowing agents.

$$\text{Water: } \rho = 0.5390 - 0.6640^{*}\text{DS} + 0.2580^{*}\text{DS}^2 \quad (5)$$

$$\text{Ethanol: } \rho = 0.6566 - 0.6380^{*}\text{DS} + 0.1622^{*}\text{DS}^2 \quad (6)$$

Graphical representations of changes in RER and unit density with DS for both blowing agents are given in Fig. 4. When water was the blowing agent, RER of the foams increased to a maximum value of 18.1, and unit density decreased to a minimum value of 0.07 g/cm^3 when DS increased from 0.57 to 1.11. Further increasing DS from 1.11 to 2.23 resulted in a decrease in RER to 4.9, and an increase in unit density to 0.32 g/cm^3. In contrast, continuous increases in RER from 6.0 to 17.6 and decreases in unit density from 0.15 to 0.04 g/cm^3 were found when DS changed from 1.11 to 2.23 with ethanol as blowing agent. The unit density of the foams depended mainly on how much vaporized gas the molten starch acetate could hold. Higher compatibility between blowing agent and starch acetate increased the viscosity of the molten starch acetate, which allowed it to hold more vaporized gas and, therefore, expand more.

Figure 5 shows the relationship of RER and unit density. As expected, unit density (ρ) decreased with an increase in RER (γ). However, this decrease was dependent on the blowing agent type, and followed a non-linear pattern.

$$\text{Water: } \rho = 1.679\gamma^{-1.0912} \quad R^2 = 0.9854 \quad (7)$$

$$\text{Ethanol: } \rho = 1.5045\gamma^{-1.2945} \quad R^2 = 0.9835 \quad (8)$$

SI and Compressibility

SI relates to resiliency, and refers to the ability of a material to recover its original shape after it has been deformed. A greater SI indicates a greater degree of rebound of a material after being compressed. Compressibility describes the cushioning ability of a material, and is related to its relative softness or hardness. High SI and low compressibility are desirable for loose-fill packaging material [13]. When changes in SI with DS were evaluated, there was a significant interaction ($p < 0.001$) between DS of starch acetates and blowing agents. Separate quadratic regression equations were developed for the changes in SI (λ) with DS for both the blowing agents

$$\text{Water: } \lambda = 0.6490 + 0.4261^{*}\text{DS} - 0.1441^{*}\text{DS}^2 \quad (9)$$

$$\text{Ethanol: } \lambda = 0.7579 + 0.2091^{*}\text{DS} - 0.05085^{*}\text{DS}^2 \quad (10)$$

Blowing agent type also was found to have a significant ($p < 0.001$) effect, along with DS, on compressibility of the foams. The regression equations for compressibility (δ) of starch acetates are

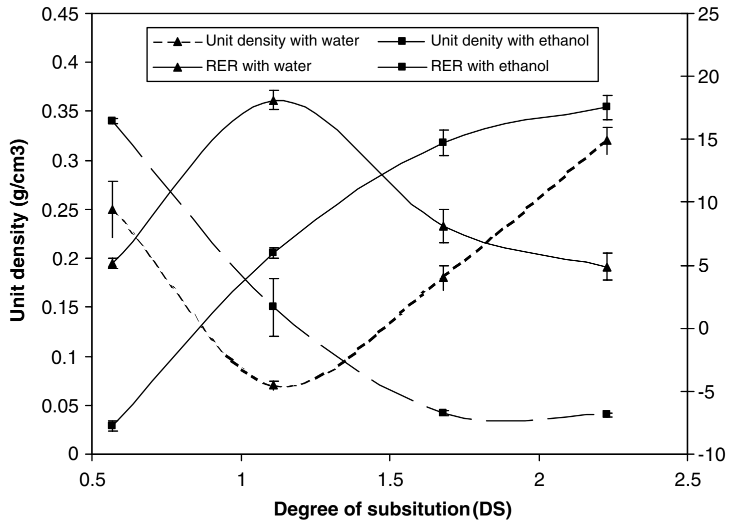

Fig. 4. Unit density and radial expansion ratio as functions of DS with different blowing agents.

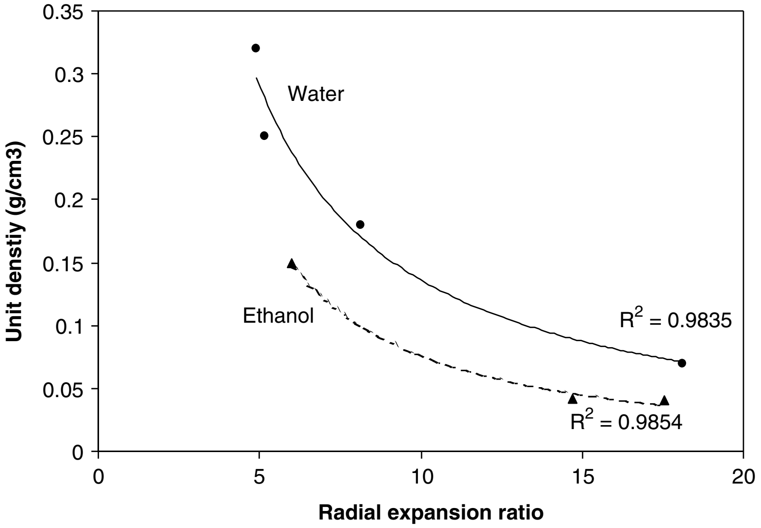

Fig. 5. Relationship between radial expansion ratio and unit density.

$$\text{Water: } \delta = 46.9231 - 62.9448^{*}\text{DS} + 22.3067^{*}\text{DS}^2 \tag{11}$$

$$\text{Ethanol: } \delta = 73.9759 - 74.905^{*}\text{DS} + 19.0025^{*}\text{DS}^2 \tag{12}$$

Figure 6 shows the changes in SI and compressibility as a function of DS. With water as the blowing agent, SI of the foams increased from 0.84 to a maximum value of 0.95 while compressibility decreased from 19.02 MPa to a minimum value of 2.46 MPa when DS increased from 0.57 to 1.11. A further increase in DS from 1.11 to 2.23 resulted in a decrease in SI to 0.89 and an increase in compressibility to 20.12 MPa, respectively. These results implied that the mechanical properties of starch acetates extruded with water were improved in the low DS range. Increasing DS was detrimental to the mechanical properties. On the other hand, with ethanol as the blowing agent, an increase in SI from 0.93 to 0.97 and a decrease in compressibility from 14.25 to 1.44 MPa were found when DS changed from 1.11 to 2.23, indicating that high DS had

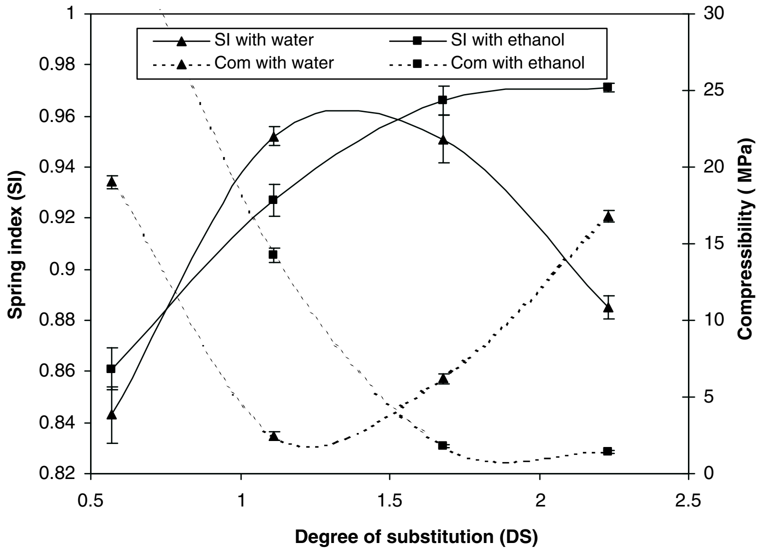

Fig. 6. Spring index and compressibility as functions of DS with different solvents.

favorable effects on the mechanical properties of starch acetates extruded with ethanol. The relationships between SI and compressibility are shown in Fig. 7. Compressibility (δ) decreased as SI (λ) increased. However, this decrease depended on the blowing agent. Extruded with water, this decrease was in the form of a quadratic and was expressed as:

$$\delta = -1268.7\lambda^2 + 2141.4\lambda - 884.62 \quad R^2 = 0.9689 \tag{13}$$

Extruded with ethanol, the decrease was linear

$$\delta = -302.13\lambda + 294.25 \quad R^2 = 0.9934 \tag{14}$$

Relationships between Mechanical Properties and RER

Mechanical properties were related to physical properties. Figure 8 shows the effects of RER on SI and compressibility of the foams extruded with water and ethanol, respectively. When extruded with water, with RER increasing from 4.9 to 5.2, SI and compressibility first underwent respective decrease or increase and then began increasing or decreasing with further increases in RER. However, SI of those extruded with ethanol exhibited simple increase while compressibility showed a decrease as RER increased.

X-ray Diffraction

The x-ray diffraction patterns of starch acetates with different DS values and extruded with water are shown in Fig. 9. The diffractographs of all samples showed a partial crystalline pattern with peaks at 2θ = 9.2, 19.75, and 28.15°, which originated from formation of the well-ordered structure during extrusion. The intensities of these peaks first increased with increases in DS to 1.68, and then became weak when DS was increased further to 2.23. This can be explained by high DS limiting amylose molecules to form hydrogen bonds. X-ray patterns of starch acetates extruded with ethanol (not shown) were similar.

CONCLUSION

Starch acetates with the DS values of 0.57, 1.11, 1.68, and 2.23 were extruded with either water or ethanol. The microstructure and physical and mechanical properties of starch acetate foams having different DS values depended on the type of blowing agent. High DS increased the hydrophobicity of starch acetate, and this increase resulted in a low compatibility with water, but a high compatibility with ethanol. Therefore, starch acetates with high DS extruded with water gave dense foams with thick cell walls, low radial expansion ratios (RER), low spring indices (SI), high unit density, and high

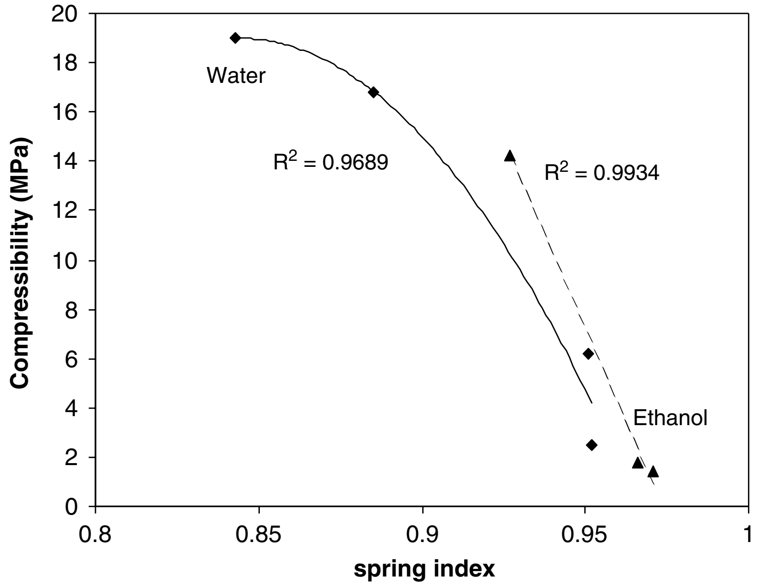

Fig. 7. Relationship between spring index and compressibility.

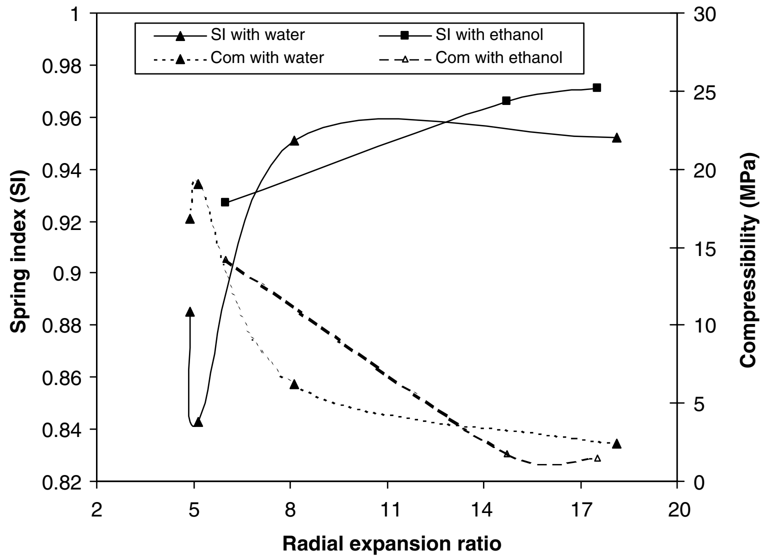

Fig. 8. Relationship between mechanical properties (spring index and compressibility) and RER.

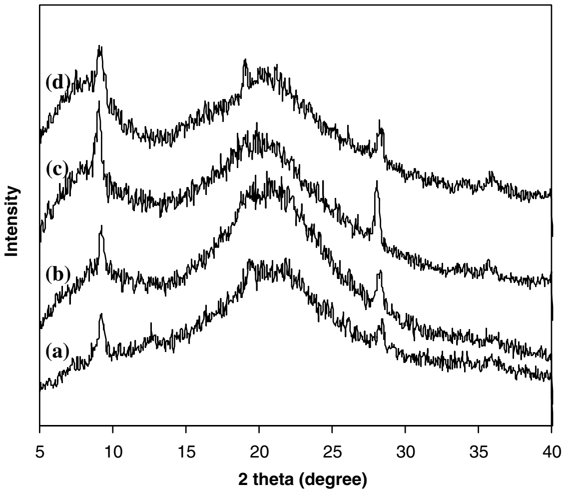

Fig. 9. X-ray patterns of starch acetates (a) DS0.57, (b) DS1.11, (c) DS1.68, and (d) DS2.23 extruded with water.

compressibility. When extruded with ethanol, high DS resulted in uniform cells with thin and smooth cell walls, high RER, high SI, low unit density, and compressibility. Partial crystalline structures were found in these foams because of formation of well-ordered structures during extrusion.

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