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Preparation and properties of biodegradable foams from starch acetate and poly(tetramethylene adipate-*co*-terephthalate)☆

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Abstract

Biodegradable composite foams were prepared by extruding starch acetate, with degree of substitution (DS) 1.78, with poly(tetramethylene adipate-*co*-terephthalate) (EBC). The foams' chemical structures, thermal behaviors, and microstructures were investigated by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). By measuring these properties, it was found that low EBC contents in the blends favored the miscibility of the two polymers, as characterized by (1) disappearance of EBC carbonyl peak and appearance of hydrogen-bonded EBC carbonyl groups in FTIR spectra; (2) an increase in T_g of starch acetate and the decreases in T_m values of starch acetate and EBC in DSC thermograms; and (3) formation of a homogeneous morphology in SEM. However, large amounts of EBC decreased the miscibility of these two polymers, as reflected by the foams' physical and mechanical properties. With a small amount of EBC, the foams had high radial expansion ratios (RER) and spring indices (SI) and low unit densities and compressibilities. Biodegradation rates of the composite foams decreased with the addition of EBC to starch acetate.

Keywords: Composite foam; Miscibility; Functional properties; Biodegradation

1. Introduction

Loose-fill packaging materials offer effective protection for fragile products by absorbing or isolating impact energy during transportation and handling (Fang & Hanna, 2000a). Generally, expanded polystyrene (ESP) 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 the potential products of its eventual degradation are environmental concerns. As a result, in recent years, researchers have focused their efforts on biodegradable polymers. Arvanitoyannis (1999) discussed, in detail, the preparation and potential properties of totally and partially biodegradable polymer blends based on natural and synthetic macromolecules. Recent advances in chemical syntheses of biodegradable polymers were presented by Okada (2002). Green polymers provide ecological benefits and are environmentally acceptable (Scott, 2000).

Unlike synthetic biopolymers, plant-based biopolymers are of interest because they are not only inexpensive and totally degradable but they also use surplus farm production (Pavlath & Robertson, 1999). Of the natural biopolymers, starch has received most of the attention with respect to the production of starch-based foams (Altieri & Lacourse, 1990; Wang & Shogren, 1997). However, starch's hydrophilicity, poor mechanical properties, and dimensional instability make the products very sensitive to the relative humidity at which they are stored and used (Simmons & Thomas, 1995).

One possible approach to improve the mechanical properties of starch foam is to blend starch with other

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biopolymers (Fang & Hanna, 2000b; Simmons & Thomas, 1995). However, adding high amounts of starch to a biopolymer matrix decreased its mechanical and physical properties, mainly because the immiscibility of hydrophilic starch and hydrophobic polymers, at the molecular level, led to phase separation (Bhattacharya, Vaidya, Zhang, & Narayan, 1995). Therefore, it becomes important to increase the miscibility of starch and other polymers. A popular method is to graft some reactive functional groups such as carboxylic acid and anhydride onto the hydrophobic polymers. These functional groups react with the OH groups on starch to form intermolecular hydrogen bonds, resulting in a stable blend (Jang, Huh, Jang, & Bae, 2001; Shogren, Thompson, Greene, Gordon, & Cote, 1991; Wu, 2003).

Moreover, starch's water-resistance can be improved by chemically modifying the hydroxyl groups of starch with a hydrophobic compound (Demirgoz et al., 2000; Kiatkamjornwong, Thakeow, & Sonsuk, 2001; Pavlath & Robertson, 1999; Sagar & Merrill, 1995; Thiebaud et al., 1997). Of chemically modified starches, starch acetate with high degree of substitution (DS) is one of the most important starch esters for engineering materials (Mullen & Pacsu, 1942; Whistler & Hilbert, 1944; Wolff, Olds, & Hilbert, 1951). However, similar to starch, pure starch acetate foam cannot provide satisfactory mechanical properties (Xu & Hanna, accepted). Again, it is necessary to mix them with other biopolymers to broaden the range of application. Zhang, Deng, Zhao, and Huang (1997) prepared biodegradable polymer blends of starch acetate and poly(3-hydroxybutyrate) (PHB) and evaluated the miscibility of the two biopolymers by measuring thermal behavior and phase morphology.

Poly(tetramethylene adipate-*co*-terephthalate) (EBC), developed by Eastman Chemical Co. (Kingsport, TN), is a synthetic biodegradable polymer with a molecular structure shown in Fig. 1. EBC has been reported to be compatible with other natural polymers and to offer superior adhesion because of the carbonyl group. Therefore, the objective of this study was to prepare composite foams containing different proportions of starch acetate and EBC and to investigate selected properties for potential as biodegradable loose-fill and other packaging materials.

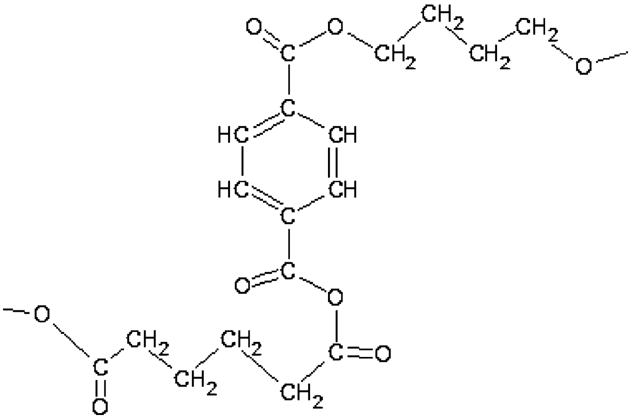


Fig. 1. Chemical structure of poly(tetramethylene adipate-*co*-terephthalate).

2. Materials and methods

2.1. Materials

EBC, in the form of 3–5 mm spherical granules, was purchased from Eastman Chemical Co. (Kingsport, TN) under the trade name of Eastar Bio (TM) GP Copolyester. Starch acetate with DS 1.78 was prepared in our lab by reacting high-amylose (∼70%) corn starch (American Maize Products Co., Hammond, IN) with acetic anhydride (Aldrich Chemical Co., Milwaukee, WI). Talc (magnesium silicate) was purchased from Barret Minerals, Inc. (Dillon, MT).

2.2. Preparation of the blends

Starch acetate and EBC were dried at 80 °C for 24 h, and then physically premixed at the weight ratios of 100/0, 95/5, 90/10, 85/15, 80/20, 75/25, 70/30, and 60/40 in a Hobart mixer (Model C-100, Hobart Corp., Troy, OH). During mixing, talc was added to all samples as a nucleating agent at the level of 5 wt% based on total dry weight. Ethanol was added at 15% by weight. The mixtures were allowed to equilibrate for 12 h at 25 °C before extrusion. The extrusion was performed in a laboratory twin screw with co-roating mixing screws (Model CTSE-V, C.W. Brabender, Inc., S. Hackensack, NJ). 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 die nozzle was used to produce cylindrical foam extrudates. The screw speed was maintained at 100 rpm. The extrudates were cut into finite lengths with a rotary cutter operating at the speed of 20 rpm at the die exit.

2.3. Fourier transform infrared spectroscopy (FTIR)

IR spectra of starch acetate/EBC blends were measured using an FTIR spectrometer (Nicolet Avatar 360, Madison, WI) with an Analect FXA-530B diffuse/specular reflectance accessory for DRIFTS. Ground samples were diluted 1:20 with KBr before acquisition. A background of pure KBr was acquired before the sample was scanned. For each spectrum, the DRIFTS were set with an angle of 5° and 128 scans were acquired. FTIR spectrum of pure EBC was recorded using an attenuated total reflection (ATR) method. Sample was first dissolved in 2% dichloromethane solution, and cast directly onto the ZnSe ATR cell. For each spectrum, 128 consecutive scans with 4 cm^{-1} resolution were averaged.

2.4. Differential scanning calorimetry (DSC)

DSC measurement was performed with a Perkin–Elmer DSC1 (Norwalk, CT). About 10 mg of the dried, ground samples (<2% moisture) were placed in the stainless steel DSC pans (Perkin–Elmer). The samples were heated from 20 to 250 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The glass transition temperature (T_g) and melting point temperature (T_m) were taken as the inflection point of the increment of specific heat capacity and as the peak value of the endothermal process in the DSC curves, respectively.

2.5. Scanning electron microscopy (SEM)

The morphologies of the blended foams were observed under a SEM (Hitachi S-3000N, Tokyo, Japan). Before testing, the samples were sliced and 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.

2.6. Physical properties

2.6.1. Radial expansion ratio (RER)

RER of the foams were calculated according to the method of Bhatnagar and Hanna (1996) by dividing the mean cross-sectional area of the extrudates by the cross-sectional area of the extruder die nozzles. Each mean value was the average of 20 observations.

2.6.2. Unit density

Unit density of the foams was determined by using a glass bead displacement method (Bhatnagar & Hanna, 1995). 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 extrudates. Five replications were used to obtain mean values.

2.7. Mechanical properties

2.7.1. Spring index (SI)

SI measurements were carried out using an Instron universal testing machine (Model 5566, Instron Engineering Corp., Canton, MA). A 6-cm cylindrical probe was used to compress an extrudate sample to 80% of its original dimension at a loading rate of 30 mm/min (Altieri & Lacourse, 1990). The sample was recompressed after 1 min releasing the first compression load. SI was calculated by dividing the recompression force by the initial compression force and has an ideal value of nearly 1. The mean value was obtained by averaging five replications.

2.7.2. Compressibility

Compressibility was calculated using the same data collected in SI test. It was calculated by dividing the peak force required to achieve a deformation of 80% of the original dimension by the axial initial cross-section area of the extrudate (Fang & Hanna, 2000a).

2.8. Biodegradability

Biodegradability of the starch acetate/EBC foams was measured according to the method of Ghorpade, Gennadios, and Hanna (2001). Briefly, extrudates (50 g) were placed in the laboratory composting system for 12 weeks. Humidified air and external heat were applied to the system. The exhaust gases were directed to a gas chromatograph (GC) (Perkin–Elmer, Norwalk, CT) to measure each eluted gas concentration three times each week. Biodegradability was expressed as CO_2 percentage in eluted gas and the mean value per week was obtained by averaging the measurements within one week.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR was used to examine the possible interaction between starch acetate and EBC (Guan, Liu, Zhang, & Yao, 1998; Yin, Yao, Cheng, & Ma, 1999). This interaction was expected to increase their miscibility. The FTIR spectra of EBC, starch acetate, and some of their blends are presented in Fig. 2. In spectrum for starch acetate, the peak at 1742 cm^{-1} was attributed to the stretching of ester carbonyl C=O, while the absorption peak at 3466 cm^{-1} was assigned to the stretching of the non-substituted OH groups in starch molecules (Xu, Miladinov, & Hanna, 2004). However, no adsorption peak was found between 3000 and 3600 cm^{-1} in EBC spectrum, implying no OH group existed, as observed from its chemical structure. The adsorption peaks at 2962 and 1704 cm^{-1} corresponded to the stretchings of CH groups and C=O groups, respectively.

When starch acetate was mixed with EBC, some changes in the spectra of the blends were found compared to those for starch acetate and EBC. First, in the carbonyl C=O stretching region, the carbonyl peak (1742 cm^{-1}) for net starch acetate decreased as EBC content increased from 10 to 40 wt%. The absorption peak (1704 cm^{-1}) of net EBC almost disappeared in all blends. Instead, the bands centered at 1711–1730 cm^{-1} were assigned to the hydrogen-bonded carbonyl groups, indicating the intermolecular hydrogen bonds (O–H···O=C) formed between starch acetate and EBC (Wu & Zhang, 2001). The OH groups of starch acetate acted as proton donors and the carbonyl groups of EBC were proton acceptors (Zhang et al., 1997). On the other hand, in the OH stretching region, the intensity of absorption peak for starch acetate

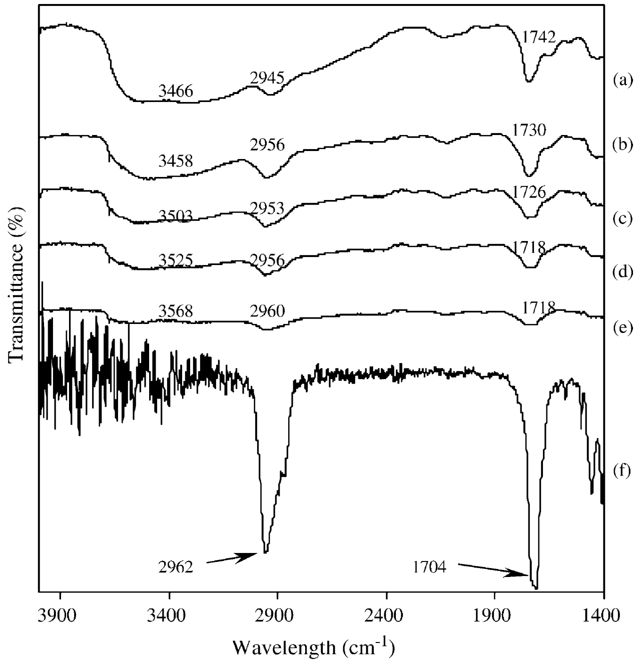


Fig. 2. FTIR spectra of (a) starch acetate; (b) starch acetate–EBC (90–10 wt%) foam; (c) starch acetate–EBC (80–20 wt%) foam; (d) starch acetate–EBC (70–30 wt%) foam; (e) starch acetate–EBC (60–40 wt%) foam; and (f) EBC.

decreased as EBC content increased from 10 to 40 wt%. This was because the absence of hydroxyl groups in EBC molecules decreased the OH concentration in the blends. Moreover, this peak in the blends with EBC above 20 wt% shifted to a higher wave number. This increase in the wave number suggested that the intermolecular interaction between the two polymers decreased, suggesting a phase separation (Zeng, Zhang, Wang, & Zhu, 2003).

3.2. *Differential scanning calorimetry (DSC)*

The thermal characterization of the polymer blends is a well-known method for determination of the miscibility of polymer blends (Peng et al., 2003). Table 1 presents the DSC results for EBC, starch acetate, and foam blends thereof. Typical curves for EBC, starch acetate, and a blend with 10 wt% EBC are shown in Fig. 3. As can be seen, EBC had a T_m of 112.7 °C and a melting enthalpy (ΔH_m) of 8.71 J/g. No T_g was observed for it, indicating high crystallinity (Yoshie, Azuma, Sakurai, & Inoue, 1995). On the other hand, starch acetate foam had a T_g of 162.9 °C, a T_m of 219.9 °C and an ΔH_m of 0.91 J/g.

When a low amount of EBC was added to starch acetate, T_g values of the foams were composition dependent. T_g first increased to a maximum value of 166.2 °C with the addition of 5 wt% EBC, then decreased to 165.5 and 164.9 °C with EBC contents of 10 and 15 wt%, respectively. However, when EBC content in the blend was greater than 20 wt%, T_g values of corresponding foams decreased to a value close to that of starch acetate foam, and remained almost constant, irrespective of EBC fraction. The increase in T_g, at low EBC content, indicted a high miscibility in the blend, which probably was caused by an interaction between starch acetate and EBC molecules (Cao, Zhang, Huang, Yang, & Wang, 2003). This interaction prohibited the mobility of starch acetate molecules. The independence of T_g on composition at high EBC content suggested poor miscibility and a phase separation between starch acetate and EBC (Braganca & Rosa, 2003; Zhang et al., 1997).

Table 1
DSC results of starch acetate (SA), EBC, and their blend foams

Composition	T_g (°C)	$T_{m\ EBC}$ (°C)	$\Delta H_{m\ EB-EBC}$ (J/g)	$T_{m\ SA}$ (°C)	ΔH_{SA} (J/g)
Starch acetate	162.6	–	–	219.9	0.91
Starch acetate + 5%EBC	166.2	–	–	206.3	0.55
Starch acetate + 10%EBC	165.5	96.3	0.13	189.4	0.54
Starch acetate + 15%EBC	164.9	94.9	0.28	180.1	0.57
Starch acetate + 20%EBC	162.0	96.8	0.57	–	–
Starch acetate + 25%EBC	162.5	96.2	0.71	–	–
Starch acetate + 30%EBC	163.4	96.6	0.88	–	–
Starch acetate + 40%EBC	163.6	96.8	1.10	–	–
EBC	–	112.7	8.71	–	–

T_m can also be used to examine the miscibility of polymer blends. In the foam with 5 wt% EBC, T_m of starch acetate decreased by 16 °C compared to that of starch acetate foam, whereas a melting peak for EBC was not detected, probably because of low content. When EBC content was greater than 10 wt%, two melting peaks, 96.3 °C for EBC and 189.4 °C for starch acetate, were observed. With further increase in EBC content, T_m of EBC in the blend remained approximately the same,

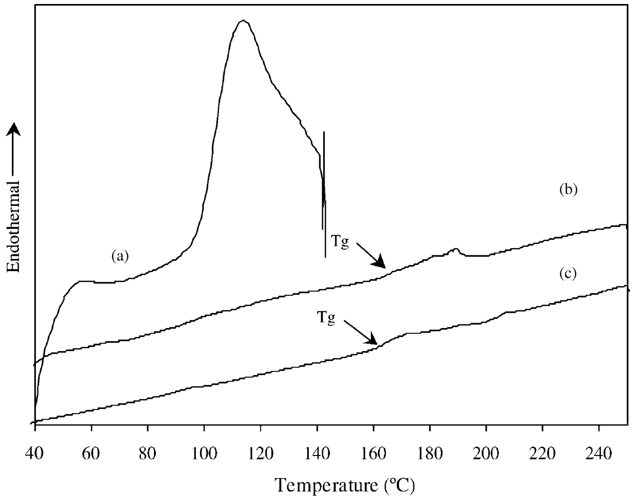


Fig. 3. DSC curves of (a) EBC; (b) starch acetate–EBC (90–10 wt%) foam; and (c) starch acetate foam.

even with an increase in ΔH_m. T_m value for starch acetate, on the other hand, decreased continuously up to 15 wt% EBC content. No melting peak was found for starch acetate when EBC content was above 20 wt%. These changes in T_m values suggested an interaction between starch acetate and EBC at low EBC content (Stenhouse, Ratto, & Schneider, 1997).

3.3. Morphology study

The morphology of a foam is an important parameter since most of its properties, especially its mechanical properties, depend on it (Bikiaris & Panayiotou, 1998). Morphologies of the starch acetate foam and several blended foams were observed by SEM and are presented in Fig. 4. Uniform cell sizes accompanied by smooth thin cell walls were observed for starch acetate foam. In the blended foams, starch acetate was the major component and acted as a continuous phase matrix, whereas EBC, as the minor component, formed the dispersed phase. When 5 wt% EBC was added, the dispersion of EBC in the starch acetate matrix was uniform. The foam had a homogeneous morphology with smooth thin cell walls. The light EBC filaments, attached on the edge of the cell walls, increased the strength of the cell walls. All of these indicated good miscibility between starch acetate and EBC. However, as EBC content increased to 10 wt%, the cell walls of the foam were still thin, but small EBC particles were distributed visibly on the cell walls. This implied decreased dispersion of EBC in starch acetate matrix. When EBC amount increased further to 20 wt%, EBC particles became more obvious and clustered together, suggesting poor adhesion and low miscibility of starch acetate and EBC. Moreover, the cell walls were found to be thicker. This was due to the fact that when high amounts of EBC were added, EBC gradually played an important role in the foam-forming components. EBC itself is difficult to expand, thereby hindering the foam expansion and resulting in thicker cell walls.

3.4. Radial expansion ratio (RER) and unit density

RER and unit density are important physical properties of the extruded foams. High RER and low unit density are ideal for foams because of the reduced cost. Fig. 5 shows the changes in RER and unit density of the foams with increasing EBC contents. As observed, starch acetate foam had a RER value of 25.1. When EBC was added to

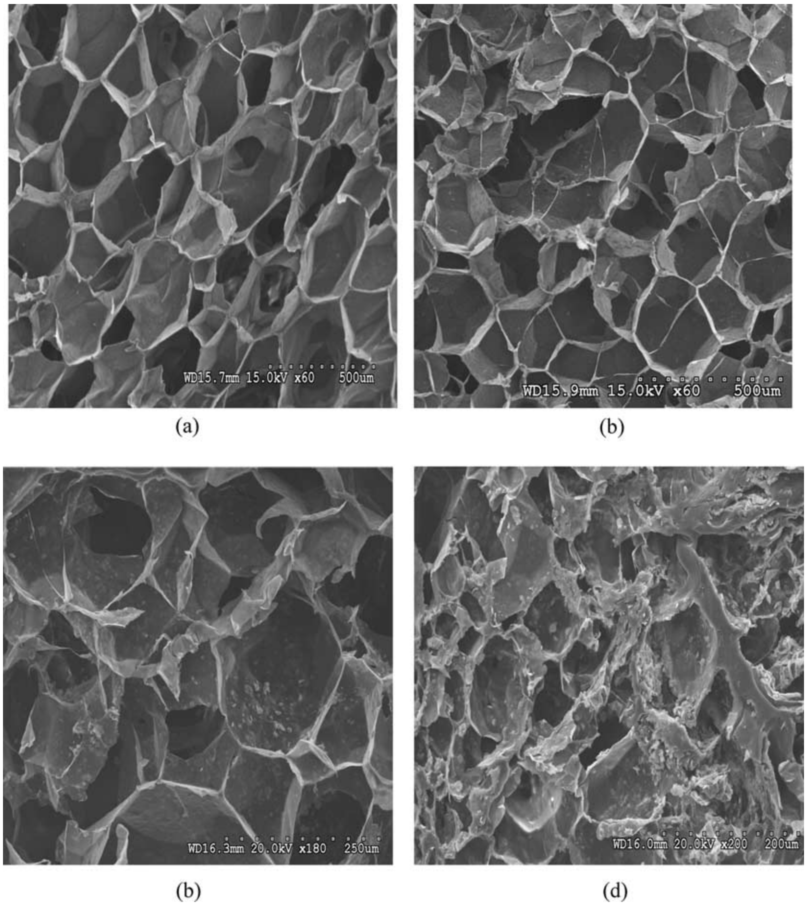


Fig. 4. Scanning electron micrographs of (a) starch acetate foam (60× magnification); (b) starch acetate–EBC (90–5 wt%) foam (60× magnification); (c) starch acetate–EBC (90–10 wt%) foam (100× magnification); and (d) starch acetate–EBC (80–20 wt%) foam (200× magnification).

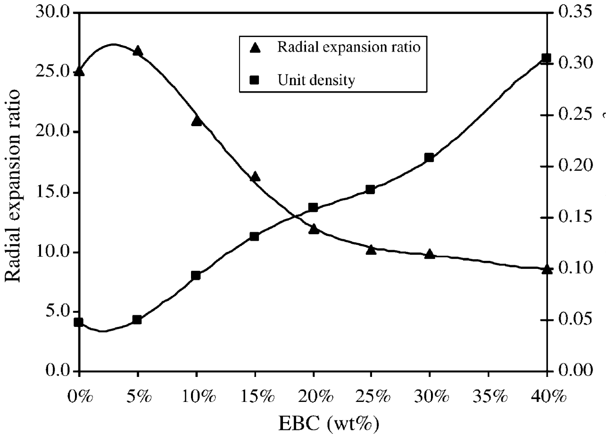


Fig. 5. Unit densities and radial expansion ratios of starch acetate–EBC foams as a function of EBC content.

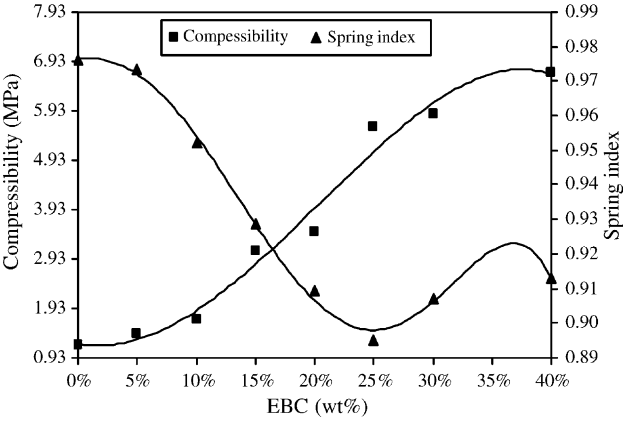


Fig. 6. Changes in compressibilities and spring indeces of starch acetate–EBC foams as the function of EBC content.

starch acetate, RER of the foams first increased to 26.9 with the addition of 5 wt% EBC, then decreased continuously to 8.6 as EBC content was increased to 40 wt%. The RER value was acceptable up to 10 wt% EBC content because at this point RER value still remained more than 20. Furthermore, the rate at which RER decreased slowed down when the EBC content increased above 20 wt%. It was found that RER of the foam with 20 wt% EBC was 11.9, while the foam with 40 wt% EBC had a RER of 8.6. The starch acetate foam, in spite of having high expansion ratio, shrank significantly after exiting the extruder.

The foam containing 5 wt% EBC had a unit density of 0.050 g/cm^3, slightly higher than that of starch acetate (0.047 g/cm^3). However, increasing EBC further led to a significant increase in unit density of the blended foams.

Based on above data set, it was concluded that addition of a small amount of EBC had favorable effects on RER and unit density of the foam, whereas greater amounts of EBC had a negative effect on them. These changes in RER and unit density of the foams were related to the morphology of the foams. The foams with a small amount of EBC displayed a homogeneous morphology. The good miscibility of starch acetate and EBC increased the elasticity of cell walls of the foams and prevented the cells from collapsing, thus making the foams trap more vaporized solvent and having a high RER and a low unit density (Fang & Hanna, 2000b). With addition of high amounts of EBC in the blend, the dispersion of EBC in starch acetate matrix decreased. Meanwhile, higher amounts of EBC made the cell walls thicker, restricting the expansion of the foams and increasing the unit density. Foam with low RER and high unit density is unsuitable for loose-fill and other packaging materials.

3.5. Spring index (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 in loose-fill packaging material (Bhatnagar & Hanna, 1996). The changes of SI and compressibility of the foams with increasing EBC content are presented in Fig. 6. It was found that with the addition of EBC, SI of the foams first decreased from 0.977 (for starch acetate foam) to a minimum value of 0.897 when the EBC content was 25 wt%, then began to increase with further addition of EBC to 40 wt% (0.91). However, a small amount of EBC did not affect significantly ($P > 0.05$) the SI values of the foams because SI of the foam with 5 wt% EBC was 0.973, which was not different than that of starch acetate foam.

The compressibility of the foams increased nonlinearly with increasing EBC content. The addition of a small amount of EBC did not increase compressibility of the foam significantly ($P > 0.05$). The foams with 5 wt% EBC and 10 wt% EBC had compressibility values of 1.42 and 1.69 MPa, respectively, while the compressibility of starch acetate foam was 1.18 MPa. At EBC content greater than 15 wt%, further increase in EBC resulted in significant ($P < 0.05$) increases in the compressibilities of the foams.

The changes in mechanical properties of the foams could also be explained by their morphology. At low EBC content, the increase in the strength of the cell walls, due to good miscibility of EBC and starch acetate, made the foam more elastic, which resulted in a high SI and low compressibility. This elasticity decreased with the addition of more EBC and was a result of low miscibility of starch acetate and EBC.

3.6. Biodegradability

Biodegradability of composite foams is a critical functionality issue with respect to their application. Polymer blends are usually exposed to activated sludge or buried in soil for a fixed period to characterize their biodegradability. Weight loss or change in molecular weight has been used to assess a polymer's biodegradability (Nakayama et al., 1998; Thiebaud et al., 1997). In our experiment, a laboratory-composting system connected with a gas chromatograph was employed and percentage of CO_2 in the eluted gas was used to express the extent of biodegradation. The aerobic bioconversion of starch acetate foams and several starch acetate and EBC composite foams are presented in Fig. 7. Starch acetate foam had an initial percentage of CO_2 of 10.04% after one week and showed the rapid degradation after 9 weeks. When 5 wt% EBC was added to starch acetate, the biodegradation rate of the composite foam was lower within the time period studied and the percentage of CO_2 in the eluted gas was only 6.75% after 4 weeks. The decrease in the degradation rate, with the addition of EBC, was attributed to the steric hindrance caused by the intermolecular hydrogen bonds between starch acetate and EBC, which inhibited microbial attack. When the amount of EBC increased to 10 wt%, large size cells of the foams, with a lower dispersion of EBC in starch acetate matrix, increased the sites accessibility to microbial attack, thus

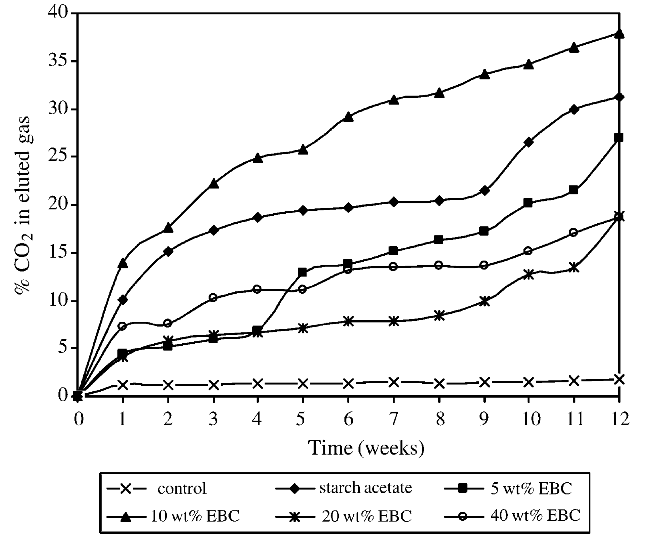
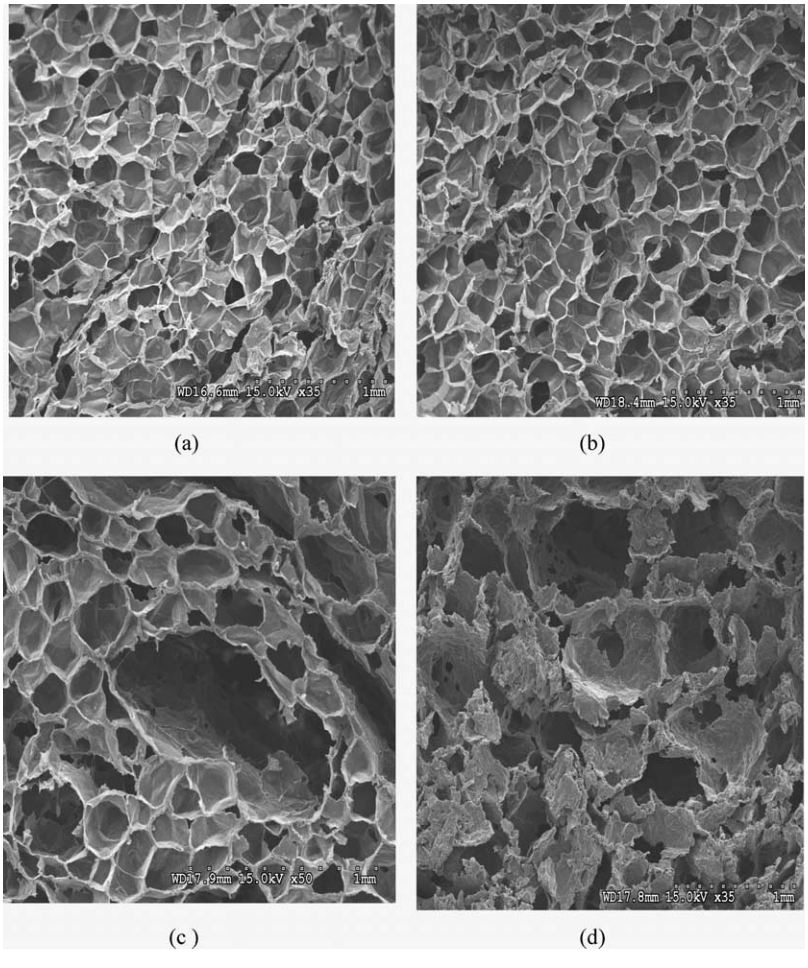


Fig. 7. Aerobic biodegradation of starch acetate foam and several starch acetate–EBC foams.



(a) (b)

(c) (d)

Fig. 8. Scanning electron micrographs of (a) starch acetate foam (35× magnification); (b) starch acetate–EBC (95–5 wt%) foam (35× magnification); (c) starch acetate–EBC (90–10 wt%) foam (50× magnification); and (d) starch acetate–EBC (80–20 wt%) foam (magnification 35×) after 3 months of composting.

increasing rate of degradation. Further increasing the amounts of EBC to 20 and 40 wt% decreased the biodegradation rate of the composite foams since EBC was highly crystalline. The organization of chains made the foams less susceptible to biodegradation (Rosa, Rodrigues, Guedes, & Calil, 2003). The morphologies of foams after 3 months of composting are shown in Fig. 8. The blend foam with 5 wt% had a low biodegradation rate. Increasing the amount of EBC in the blend increased the biodegradation rate. The findings are in good agreement with biodegradability test.

4. Conclusions

Good compatibility and functional properties of the starch acetate/poly(tetramethylene adipate-*co*-terephthalate) (EBC) composite foams were observed when a small amount of EBC was added to starch acetate. In Fourier transform infrared spectroscopy spectra, the peak for carbonyl groups of EBC disappeared and the bands for hydrogen-bonded carbonyl groups were found. T_g of starch acetate increased, while its T_m values decreased. A homogeneous morphology was observed in scanning electron micrograph. In addition, the foams had high radial expansion ratios and spring indices, together with low unit densities and compressibilities. Higher amounts of EBC in the blends decreased the miscibility of these two polymers, which reduced the physical and mechanical properties of the foams. Biodegradation rates of the composite foams decreased with the addition of EBC in the blends.

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References

Altieri, P. A., & Lacourse, N. L. (1990). Starch based protective loose fill material. In: *Corn utilization conference III Proceedings of the National corn growers association, June 20–21, St Louis, MO*.

Arvanitoyannis, I. S. (1999). Totally and partially biodegradable polymer blends based on natural and synthetic macromolecules: Preparation, physical properties, and potential as food packaging materials. *Journal of Macromolecular Science—Review in Macromolecular Chemistry and Physics*, *C3*(2), 205–271.

Bhatnagar, S., & Hanna, M. A. (1995). Physical, mechanical, and thermal properties of starch-based plastic foams. *Transactions of the ASAE*, *38*(2), 567–571.

Bhatnagar, S., & Hanna, M. A. (1996). Starch-based plastic foams from various starch sources. *Cereal Chemistry*, *73*(5), 601–604.

Bhattacharya, M., Vaidya, U. R., Zhang, D. M., & Narayan, R. (1995). Properties of blends of starch and synthetic polymers containing anhydride groups. II. Effect of amylopectin to amylose ratio in starch. *Journal of Applied Polymer Science*, *57*, 539–554.

Bikiaris, D., & Panayiotou, C. (1998). LDPE/starch blends compatibilized with PE-*g*-MA copolymers. *Journal of Applied Polymer Science*, *70*, 1503–1521.

Braganca, F. C., & Rosa, D. S. (2003). Thermal, mechanical and morphological analysis of poly(ε-caprolactone), cellulose acetate and their blend. *Polymers for Advanced Technologies*, *14*, 669–675.

Cao, X. D., Zhang, L. N., Huang, J., Yang, G., & Wang, Y. X. (2003). Structure–properties relationship of starch/waterborne polyurethane composite. *Journal of Applied Polymer Science*, *90*, 3325–3332.

Demirgoz, D., Elvira, C., Mano, J. F., Cunha, A. M., Piskin, E., & Reis, R. L. (2000). Chemical modification of starch based biodegradable polymeric blends: effects on water uptake, degradation behaviour and mechanical properties. *Polymer Degradation and Stability*, *70*, 161–170.

Fang, Q., & Hanna, M. A. (2000a). Mechanical properties of starch-based foams as affected by ingredient formulation and foam physical characteristics. *Transactions of the ASAE*, *43*(6), 1715–1723.

Fang, Q., & Hanna, M. A. (2000b). Functional properties of polylactic acid starch-based loose fill packaging foams. *Cereal Chemistry*, *77*(6), 779–783.

Ghorpade, V. M., Gennadios, A., & Hanna, M. A. (2001). Laboratory composting of extruded poly(lactic acid) sheets. *Bioresource Technology*, *76*, 57–61.

Guan, Y. L., Liu, X. F., Zhang, Y. P., & Yao, K. D. (1998). Study of phase behavior on chitosan/viscose rayon blend film. *Journal of Applied Polymer Science*, *67*, 1965–1972.

Jang, B. C., Huh, S. Y., Jang, J. G., & Bae, Y. C. (2001). Mechanical properties and morphology of the modified HDPE/starch reactive blend. *Journal of Applied Polymer Science*, *82*, 3313–3320.

Kiatkamjornwong, S., Thakeow, P., & Sonsuk, M. (2001). Chemical modification of cassava starch for degradable polyethylene sheets. *Polymer Degradation and Stability*, *7*, 363–375.

Mullen, J. W., & Pacsu, E. (1942). Preparation and properties of starch triesters. *Industrial and Engineering Chemistry*, *34*(10), 1209–1217.

Nakayama, A., Kawasaki, N., Aiba, S., Maeda, Y., Arvanitoyannis, I., & Yamamoto, N. (1998). Synthesis and biodegradability of novel copolyesters containing γ-butyrolactone units. *Polymer*, *39*(5), 1213–1222.

Okada, M. (2002). Chemical syntheses of biodegradable polymers. *Progress in Polymer Science*, *27*(1), 87–133.

Pavlath, A. E., & Robertson, G. H. (1999). Biodegradable polymers vs. recycling: What are the possibilities. *Critical Reviews in Analytical Chemistry*, *29*(3), 231–241.

Peng, S. W., An, Y. X., Chen, C., Fei, B., Zhuang, Y. G., & Dong, L. S. (2003). Miscibility and crystallization behavior of poly(3-hydroxyvalerate-*co*-3-hydroxyvalerate)/poly(propylene carbonate) blends. *Journal of Applied Polymer Science*, *90*, 4054–4060.

Rosa, D. S., Rodrigues, T. C., Guedes, C. G. F., & Calil, M. R. (2003). Effect of thermal aging on the biodegradation of PCL, PHB-V, and their blends with starch in soil compost. *Journal of Applied Polymer Science*, *89*, 3539–3546.

Sagar, A. D., & Merrill, E. W. (1995). Properties of fatty-acid esters of starch. *Journal of Applied Polymer Science*, *58*, 1647–1656.

Scott, G. (2000). Green polymers. *Polymer Degradation and Stability*, *68*(1), 1–7.

Shogren, R. L., Thompson, A. R., Greene, R. V., Gordon, S. H., & Cote, G. (1991). Complexes of starch polysacchrides and poly(ethylene *co*-acrylic acid): Structural characterization in the solid state. *Journal of Applied Polymer Science*, *47*, 2279–2286.

Simmons, S., & Thomas, E. L. (1995). Structural characteristics of biodegradable thermoplastic starch/poly(ethylene-vinyl alcohol) blends. *Journal of Applied Polymer Science*, *58*, 2259–2285.

Stenhouse, P. J., Ratto, J. A., & Schneider, N. S. (1997). Structure and properties of starch/poly(ethylene-*co*-vinyl alcohol) blown films. *Journal of Applied Polymer Science*, *64*, 2613–2622.

Thiebaud, S., Aburto, J., Alric, L., 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.

Wang, L., & Shogren, R. L. (1997). Preparation and properties of corn starch-based loose fill foams. In: *Proceedings of the sixth annual meeting of bioenvironment Degradability and polymer society, St Paul, MN*.

Whistler, R. L., & Hilbert, G. E. (1944). Mechanical properties of films from amylose, amylopextin, and whole starch triacetates. *Industrial and Engineering Chemistry*, *36*(9), 796–798.

Wolff, I. A., Olds, D. W., & Hilbert, G. E. (1951). Triesters of cornstarch, amylose, and amylopectin. *Industrial and Engineering Chemistry*, *43*, 911–914.

Wu, C. S. (2003). Physical properties and biodegradability of maleated-polycaprolactone/starch composite. *Polymer Degradation and Stability*, *80*, 127–134.

Wu, Q. X., & Zhang, L. N. (2001). Structure and properties of casting films blended with starch and waterborne polyurethane. *Journal of Applied Polymer Science*, *79*, 2006–2013.

Xu, Y. X., & Hanna, M. A. (2004). Physical, mechanical, and morphological characteristics of extruded starch acetate foam as affected by DS values and solvent type. *Journal of Polymers and the Environment*, accepted for publication.

Xu, Y. X., Miladinov, V., & Hanna, M. A. (2004). Synthesis and characterization of starch acetates with high degree of substitution. *Cereal Chemistry, 81*(6), 735–740.

Yin, Y. J., Yao, K. D., Cheng, G. X., & Ma, J. B. (1999). Properties of polyelectrolyte complex films of chitosan and gelatin. *Polymer International*, *48*, 429–433.

Yoshie, N., Azuma, Y., Sakurai, M., & Inoue, Y. (1995). Crystallization and compatibility of poly(vinyl alcohol)/poly(3-hydroxybutyrate) blends: Influence of blend composition and tacticity of poly(vinyl alcohol). *Journal of Applied Polymer Science*, *56*, 17–24.

Zeng, M., Zhang, L. N., Wang, N. G., & Zhu, Z. C. (2003). Miscibility and properties of blend membranes of waterborne polyurethane and carboxymethylchitin. *Journal of Applied Polymer Science*, *90*, 1233–1241.

Zhang, L. L., Deng, X. M., Zhao, S. J., & Huang, Z. T. (1997). Biodegradable polymer blends of poly(3-hydroxybutyrate) and starch acetate. *Polymer International*, *44*, 104–110.