

# Shrinkage and Re-expansion of Extruded Starch Acetate Foams

Jiahua Zhou,<sup>1</sup> Milford Hanna<sup>2</sup>

<sup>1</sup>Faculty of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510090, China

<sup>2</sup>Industrial Agricultural Products Center and Department of Biological Systems Engineering, University of Nebraska-Lincoln, Lincoln, Nevada 68583-0730

Received 9 November 2005; accepted 1 April 2006

DOI 10.1002/app.24781

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The effects of concentration of steam, heating time, pretreatment, and cooling conditions on the shrinkage and re-expansion of extruded starch acetate foam were investigated. The re-expansion ratio was determined from the degree by which the foam cells were moistened under the condition tested. The higher the concentration of steam used, the faster and greater the foam re-expanded. Shrinkage was a result of the negative pressure resulting from cooling and condensation of steam or ethanol inside the foam and the unbalanced osmosis of steam transported out of the foam and air transported into the foam and the resistance of

foam cell walls. Quenching re-expanded foams led to significant shrinkage, especially for foams re-expanded with highly concentrated steam. Shrinkage cannot be avoided even if the foam is kept at the same temperature it was expanded at the nozzle. Gradually reducing the degree of concentration of steam could reduce the shrinking tendency of the re-expanded foam. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4264–4268, 2006

**Key words:** expansion; starch acetate foam; shrinkage; steam

## INTRODUCTION

Expandable polystyrene is used widely in the packaging industry for its excellent mechanical strength, water resistance, and low density, but it causes serious environmental problems.<sup>1–6</sup> Foamed polystyrene occupies a large volume in a landfill and is very hard to degrade. It is also very expensive to recycle. Native starch has been thought to be a good substitute of petroleum-based plastics. However, the low mechanical strength, low water resistance, and low compatibility with hydrophobic polymers limit the application of starch-based biodegradable plastics.<sup>7,8</sup> Starch acetate is potentially a good substitute for polystyrene as it is made from biodegradable and renewable starch. Considerable research has been done on the preparation and extrusion foam of starch acetate.<sup>9–19</sup> However, starch acetate cannot be expanded like expandable bead polystyrene. It must be prefoamed. The low density of such prefoamed starch acetate makes it very costly to deliver. From that point of view, preparing a high density foam from shrinkage for transportation and then re-expanding it on-site would have some advantages over conventionally prepared foamed products.

Unfortunately, very little research has been done on the re-expansion of shrunken/collapsed starch acetate foam. Guan and Hanna<sup>20</sup> studied the re-expansion of starch acetate foam with saturated steam (100%) and found that the processing time must be controlled to achieve a suitable degree of re-expansion while minimizing shrinkage. They attributed the re-expansion of shrunken starch acetate foam to the residual ethanol inside the foam because the outer skin expanded less than did the center. However, there are no other reports on the mechanism involved in the expansion and shrinkage of starch acetate foam. The aim of this research was to study the mechanism of re-expansion and re-shrinkage of prefoamed starch acetate foam.

## MATERIALS AND EQUIPMENT

### Preparation of starch acetate

Starch acetate (DS 2.24) was prepared according to Zhou and Hanna.<sup>14</sup>

### Extrusion of starch acetate foam

Starch acetate was extrusion-foamed with a twin-screw extruder using 20% ethanol as the blowing agent and 5% talc as the nucleating agent. The temperature profile of the extruder barrel was 80°C–120°C–160°C–160°C. The screw speed was 120 rpm and the diameter of the nozzle was 4 mm. The extrudate

Correspondence to: M. Hanna (mhanna1@unl.edu).  
Contract grant sponsor: China Scholarship Council.

was cut with rotating knife into lengths of about 5 cm. Foamed starch acetate was allowed to cool naturally and then dried in a convection oven at 105°C for 6 h to remove residual ethanol and water. The dry foams were stored in polyethylene bags tightly before steam-re-expansion treatments were applied.

### Presoaking of starch acetate foam

Predried starch acetate foams were immersed in absolute ethanol or distilled water for 2 min before the re-expansion experiment.

The re-expansion of collapsed starch acetate foam: The partially shrunken/collapsed starch acetate foams were heated in a steam cooker. Steam and air were mixed before entering the cooker. The flow rates of air and steam were adjusted separately. The temperature of steam and hot air were 100°C and the percentage of steam to the total volume of steam-air mixture was denoted as the concentration of steam. The sample was put on a sheet of paper inside the cooker. The diameters of the samples were measured at preselected time intervals from photographs. At least five pieces were used for each run and five measurements were taken on each piece. The mean values of diameters of the treated samples and the original (partially collapsed) foam were recorded.

The re-expanded starch acetate foams were handled in one of the following three ways. In method one, the steam and hot air were shut off and the cover removed immediately at the end of re-expansion process. In method two, the steam was shut off with only hot air on after treatment until the expansion and collapsing stabilized. In method three, the concentration of steam was reduced gradually by 20% each time after keeping at that point for 5 min until steam stream was completely shut off.

### The determination of glass transition of starch acetate

The glass transition temperature of starch acetate was determined according to the procedure described in Xu et al.<sup>21</sup> The heating rate was 5°C/min and the onset temperature was reported as glass transition temperature.

## RESULTS AND DISCUSSIONS

### Re-expansion of dry starch acetate foams

The dried, partially collapsed extruded starch acetate foams were exposed to steam of different concentration. The results were shown in Figure 1. When foam was exposed to 100% steam, it started expanding within a few seconds and reached equilibrium in

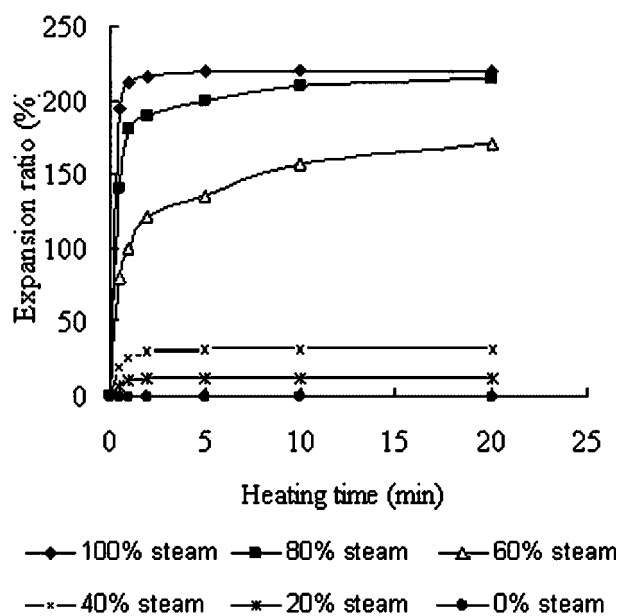


Figure 1 The effect of heating time on the re-expansion of dried starch acetate foam exposed to steam of different concentrations.

less than 1 min. The maximum expansion was close to the maximum expansion of foam upon exiting the extruder die. Prolonged exposure did not expand the foam further. When foam was exposed to 80% steam, it expanded a little bit slower but the maximum expansion was about the same as that treated with 100% steam. When the steam concentration was lowered to 60%, the expansion speed was significantly slower and the final expansion ratio was much lower than those treated with 80 and 100% steam. When the concentration of steam was 40% and lower, the foam re-expanded very little.

Steam played an important role in the re-expansion of partially collapsed foam. Before being re-expanded, the starch acetate foam must first be moistened and softened. It was observed in current research that, the higher the concentration of steam, the faster the starch acetate foam softened (data not shown) and hence, the faster the foam re-expanded. After the foam reached its maximum expansion ratio, no shrinkage was observed when the temperature and the concentration of steam were kept constant. Steam of low concentration did not soften the starch acetate foam adequately and did not expand the foam completely. The re-expansion of starch acetate is quite different from the expansion of polymer from molten state. Starch acetate does not melt under the re-expansion process; its flexibility could be characterized by its glass transition temperature and the environment temperature. It was reported that foam stopped shrinking or expanding when the temperature of the foam was less than 30°C, above

TABLE I  
Glass-Transition Temperature ( $T_g$ ) of Starch Acetate  
as a Function of Moisture Content

Moisture content (%)	Glass-transition ( $^{\circ}\text{C}$ )
6.5	142.9
9.6	108.8
13.8	99
21.4	82
26.2	74

the glass transition temperature of a matrix polymer.<sup>22</sup> Table I shows the relationship between glass transition temperature and moisture content of starch acetate. However, the exact relationship between the amount of water and ethanol inside the cell wall and steam concentration was difficult to determine.

The driving force for re-expansion of starch acetate should be steam, but it is not clear how steam expands the foam. One possible explanation for this is that steam penetrates the cell wall, condenses, and then is reheated by subsequent steam and reevaporized. The (vaporized) steam inside the cell wall expands the softened cell wall. The residual air inside cell may play some role in the expansion but it does not appear to dominate the process, as the specific volume of partially collapsed foam expanded more than four times that of the original one upon heating. For a given amount of air under the same pressure, the change of volume with temperature from 25 to 100 $^{\circ}\text{C}$  is only about 25% calculated from the ideal universal gas equation.

In the foaming of polystyrene, expandable bead steam acts as heating media only. As PS is highly hydrophobic, the amount of steam entering the foam is insignificant. The vaporization of solvent in polystyrene bead should be the major driving force in expansion.<sup>6</sup> Guan and Hanna<sup>20</sup> studied the re-expansion of starch acetate foam with saturated steam. They attributed the re-expansion to the residual blowing agent (ethanol) inside the foam as they found that the outer skin re-expanded less than the core. It was explained that the outer layer foamed less because it contained less residual ethanol. However, there could be other reasons for the lower degree of expansion of the outer layer of starch acetate foam. All samples in the current research were completely dried but they could be expanded. Other reasons might account for the denser outer layer as well. The outer layers may stick together during the shrinkage process after leaving the extruder die. The breakage of some cell structure also may attribute to their failure to re-expand. Another explanation is that the outer layers reshrink after re-expansion. During the cooling process, the outer layers cool down first and, therefore, shrink first. As the outer layers shrink upon cooling, they form a thick layer,

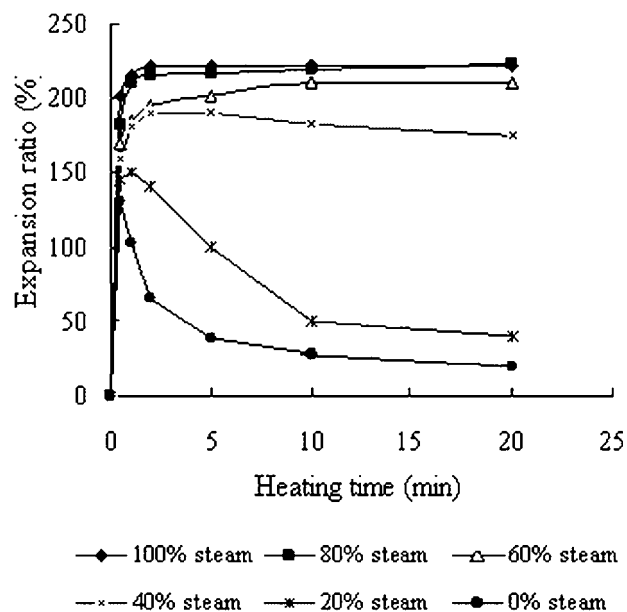


Figure 2 The effect of heating time on the re-expansion of collapsed starch acetate foam presoaked in ethanol and exposed to steam of different concentrations.

which inhibits the foam from shrinking further. To support this argument, starch acetate foam was presoaked in ethanol and water for 2 min and then heated with steam of different concentrations at 100 $^{\circ}\text{C}$  for different lengths of time. The results are shown in Figures 2 and 3.

There was no great difference between dry foam and wet foam when treated with steam of high concentration. However, the difference became greater

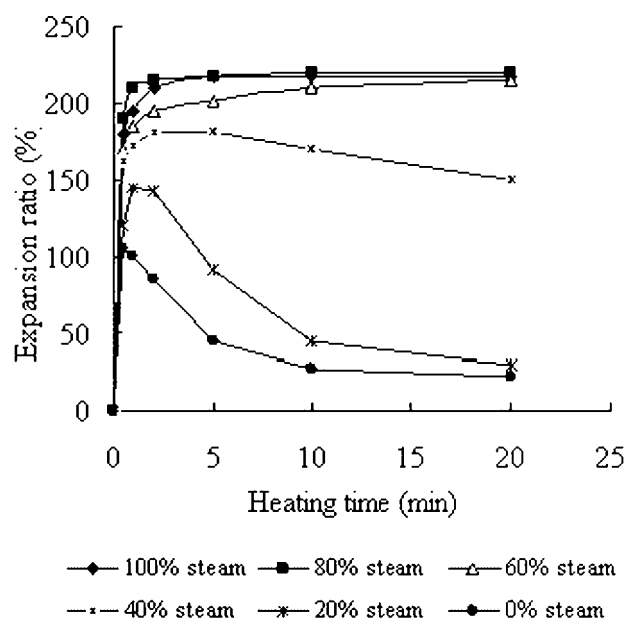
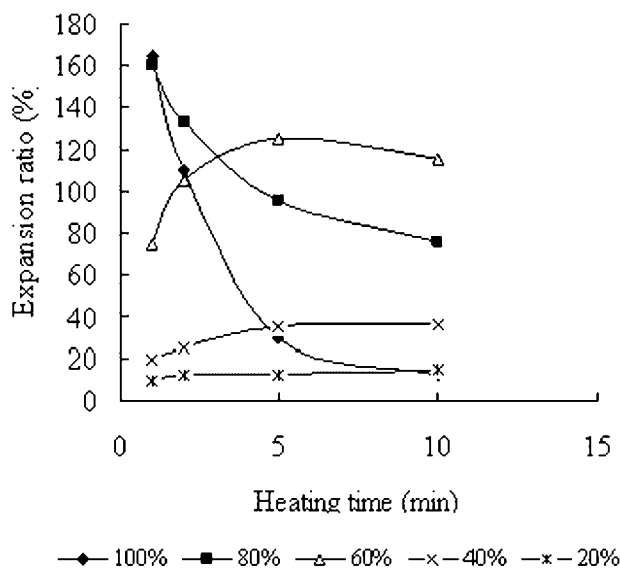


Figure 3 The effect of heating time on the re-expansion of collapsed starch acetate foam presoaked in water and exposed to steam of different concentrations.



**Figure 4** The effect of heating time on the re-shrinkage of starch acetate foam re-expanded with steam of different concentrations and then held at ambient conditions.

as the steam concentration was reduced. The prewetted foams re-expanded with a concentration of 60% or greater did not show much difference. When the concentration of steam dropped below 60%, there was a maximum expansion during the heating process. Upon heating the presoaked starch acetate foam, the water inside the foam softened the foam cell walls. The vaporized steam then expanded the foam quickly. The expansion reached a maximum level and then the foam collapsed even when the heating temperature was kept constant. The mechanism behind this phenomenon could be a result of the imbalance in the osmosis between steam moving out through the cell walls and air moving in through the cell walls. With starch acetate being hydrophilic, the osmosis of water moving out of the foam could be faster than the air moving into the foam. So, as the heating progressed, a negative pressure was created and the foam collapsed until the foam cell was dry enough to resist the shrinkage even when the temperature was kept constant. There was not much difference between the results for water and ethanol.

### The shrinkage of starch acetate foam

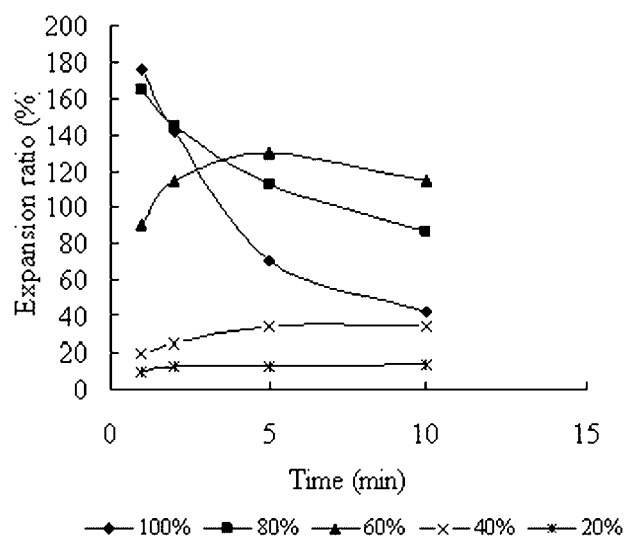
The extent of shrinkage is determined by two factors.<sup>14,15,23-25</sup> One factor is negative pressure, which is the driving force of shrinkage. The second one is the strength of the foam cell walls. The first factor is controlled by two elements. One element is the cooling and condensation of steam inside the cell wall. The other element is the imbalance between osmosis of gases into and out of the foam cells. The expanded foam must be dried out or cooled down to stabilize

its shape after re-expansion with steam and heat. Three processes were employed to study the shrinkage of re-expanded starch acetate foam.

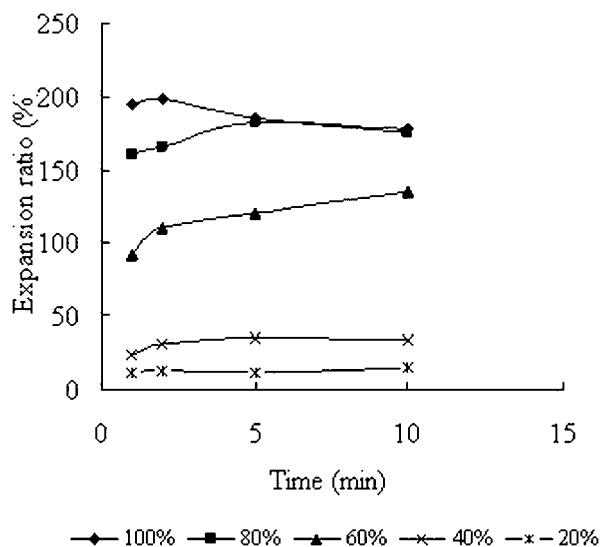
In the first process, the expanded foam was allowed to cool down under ambient condition, i.e., roughly 25°C and atmospheric pressure. The results are shown in Figure 4. The heating time had great influence on the shrinkage of foam treated with steam of high concentration. It is very likely that the structure of the starch acetate was altered on prolong heating. The heating time did not have much influence on the shrinkage of starch acetate treated with steam of low concentration. To achieve a high final expansion ratio, steam of relatively low concentration should be used. The relatively large shrinkage of foam treated with steam of high concentration was a result of relatively weak cell walls and relatively low concentration of air inside the foam cell. As air is a noncondensable gas, the cooling produced less pressure change with air.

The second process was to hold the re-expanded foam at 100°C with hot air (not steam) until the shrinkage stabilized. The results are shown in Figure 5. As there was no temperature change in the expansion and shrinking processes, the shrinkage of the foam was controlled only by the unbalanced osmosis of steam moving in and out of the foam. The removal of water from the foam, on the one hand, produced negative pressure, which promoted the shrinking of foam. On the other hand, it reduced the moisture content of foam cell wall, which increased the cell strength and inhibited the shrinkage of foam cell. The overall effect of the drying (process) produced less shrinkage than those exposed to ambient condition.

The third process involved controlled cooling. The concentration of steam was reduced by 20% after



**Figure 5** Shrinkage of re-expanded starch acetate foam held in 100°C hot air atmosphere.



**Figure 6** Shrinkage of re-expanded starch acetate foam under controlled cooling.

kept at that level for 5 min each until the steam stream was shut off; the expansion ratio was measured after the foam was completely dried. The results are shown in Figure 6. The gradual reductions in steam concentration produced only a small negative pressure, which the foam cells could stand, avoiding significant shrinkage.

### CONCLUSIONS

Partially collapsed/shrunken foams formed by extrusion were re-expanded with steam. Softening of the cell walls was a prerequisite of re-expansion of the starch acetate foams. Steam had a great impact on the re-expansion process. Starch acetate foam expanded faster and further when heated with steam of higher concentrations. Dry air did not expand the predried starch acetate foam even with prolonged heating. Wetted starch acetate foam expanded minimally with dry hot air. Re-shrinkage of the foams resulted not only from the cooling and condensation of steam but also from the unbalanced osmosis of

gases in and out of the foam cells. To avoid re-shrinkage, the negative pressure produced from the cooling and drying processes must be within the range, which the foam cell walls can withstand.

### References

- Kitch, D. Global Overview—Biodegradable Polymers and Organics Recycling, *Biocycle, Journal of Composting and Organics Recycling (Magazine)*, The JG Press, February 2001.
- Park, C. P.; Bushitol, C.; Waltham, M. A. *J Cell Plast* 2005, 41, 389.
- Naway, A.; Victoria, H.; Paul, Y. *Cell Polym* 2003, 22, 260.
- Nawaby, V.; Yamamoto, Y.; Handa, P. *Soc Plast Eng Annu Tech Conf* 2002, 60, 1902.
- Onteniente, J.; Laurent, H.; Abbes, B. *Starch/Staerke* 2000, 52, 267.
- Wall, K. F.; Bhavnani, S. H.; Overfelt, R. A.; Sheldon, D. S.; Williams, K. *Metall Mater Trans B* 2003, 34, 843.
- Alavi, S. H.; Rizvi, S. H.; Harriott, P. *Food Res Int* 2003, 36, 321.
- Lourdin, D.; Della, V. G.; Colonna, P. In *Biopolymer Science: Food and Non Food Applications*; Institut National de la Recherche Agronomique: France, 1999, 291.
- Shogren, R. L. *Carbohydr Polym* 1996, 29, 57.
- Mark, A. M.; Mehlretter, C. L. *Starch* 1970, 22, 108.
- Miladinov, V. D.; Hanna, M. A. *Ind Eng Chem Res* 1999, 38, 3892.
- Miladinov, V. D.; Hanna, M. A. *Ind Crops Prod* 2001, 13, 21.
- De Graaf, R. A.; Broekroelofs, A.; Janssen, L. P. B. M. *Starch/Staerke* 1998, 50, 198.
- Zhou, J. H.; Hanna, M. A. *Starch/Stärke* 2004, 56, 484.
- Zhou, J. H.; Hanna, M. A. *J Appl Polym Sci* 2005, 97, 1880.
- Wang, Y.; Wang, L. *Starch/Stärke* 2002, 54, 25.
- Zurima, G.; Elevina, P. *Starch/Stärke* 2002, 54, 148.
- Fringanta, C.; Rinaudo, M.; Foray, M. F.; Bardet, M. *Carbohydr Polym* 1998, 35, 97.
- Tarvainen, M.; Sutinen, R.; Peltonen, S.; Tiihonen, P.; Paronen, P. *J Pharm Sci* 2002, 91, 282.
- Guan, J.; Hanna, M. A. *Trans ASAE* 2004, 46, 1613.
- Xu, Y. X.; Zhou, J. H.; Hanna, M. A. *Cereal Chem* 2005, 82, 105.
- Brummer, T.; Meuser, F.; Van Lengerich, B.; Niemann, C. *Starch/Staerke* 2002, 54, 9.
- Turner, D.; Dlugogorski, B.; Palmer, T. *Colloids Surf A* 1999, 150, 171.
- Advani, S. G.; Arefmanesh, A. *Adv Transp Process* 1993, 9, 445.
- Della, V. G.; Lourdin, D.; Bergnes, V. *Recents Progres en Genie des Procedes* 1999, 13, 393.