Macromol. Symp. **2004**, *216*, 217-227

Preparation and Properties of Starch/Poly(vinyl alcohol) Composite Foams

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Summary: Starch/poly(vinyl alcohol) (PVA) composite foams were prepared by baking a mixture of starch, PVA, and other ingredients in a hot mold. The effects of relative humidity, storage period, PVA content, and type and content of plasticizer (e.g. glycerol, urea, or ammonium chloride) on moisture content, water absorption, mechanical properties, and biodegradability of the as-prepared foams were investigated. In all of the testing conditions investigated, the ultimate tensile strength was shown to be a maximum when the relative humidity was 42%RH (for a fixed storage period of 7 days) and when the storage period was 2 days (for a fixed relative humidity of 42%RH). Addition of PVA improved the ultimate strength and the elongation at break of the composite foams. An increase in the amount of added plasticizer was responsible in an increase in the percentage of elongation at break at the expense of the tensile strength of the composite foams. Resistance to water absorption of starch/PVA composites foams was found to be superior to that of pure starch foams. Lastly, enzymatic degradation tests with α-amylase showed that addition of PVA affected a little to the enzymatic degradability of the composite foams.

Keywords: biodegradability; mechanical properties; moisture and water absorption; poly(vinyl alcohol); starch-based composite foam; starch foam

Introduction

Starch is a potentially useful material for making biodegradable plastics due mainly to its natural abundance, low cost, and thermoplastic properties.[1] Pure starch plastics, however, have some drawbacks, which include poor dimensional stability (a direct result of the high water absorption), poor mechanical properties, and poor processability.[2] To solve some of these problems, modification of starch molecules through various physical[3,4] or chemical[5] means have been considered.

Blending of starch or its derivatives, either in granular or destructurized form, with various polymers has been investigated. Starch has been added to a thermoplastic polymer, such as polyethylene (PE) and poly(vinyl chloride) (PVC), in order to impart biodegradable characteristics to the resulting blends. It has also been added to various expensive,

DOI: 10.1002/masy.200451221

biodegradable polyesters in order just to reduce the unit cost of the finished products. Some of the well-known examples are starch/polycarprolactone (PCL),[6,7] starch/poly(3-hydroxybutyrate-*co*-hydroxyvalerate),[6,8] and starch/poly(vinyl alcohol) (PVA) blends.[9-11]

It has been observed that addition of PVA helped improve moisture resistance to the baked foams.[9-11] Effects of added plasticizers have also been studied.[12-13] Under shearing and elevated temperature and pressure conditions, water and glycerol act as a good destructuring–plasticizing agent. Normally, plasticizers are added to adjust the properties of starch from being a soft (i.e. at high contents) to a brittle (i.e. at low contents) material.[14]

In the present contribution, biodegradable starch-based foams with good mechanical integrity have been prepared by blending tapioca starch with poly(vinyl alcohol) (PVA), along with other ingredients. Composite foams of various formulations have been prepared and analyzed for their mechanical properties, water absorption, and biodegradability.

Experimental Details

Materials

Tapioca starch was supplied as a courtesy from Siam Modified Starch Co., Ltd. (Thailand). Poly(vinyl alcohol) (PVA) having the degree of hydrolysis of around 97.5 to 99.5% was purchased from Fluka. Glycerol, urea, and ammonium chloride, used as plasticizers, were purchased from Carlo Erba. Guar gum was purchased from Sigma-Aldrich and magnesium stearate was supplied as a courtesy from Coin Chemical (Thailand) Co., Ltd. Both chemicals were used as additives. Termamyl 120 α-amylase (120 KNU/g) was supplied as a courtesy from East Asiatic Co., Ltd. (Thailand).

Preparation of Starch and Starch/PVA Foams

Tapioca starch (pre-dried at 110°C for 24 hours), guar gum (1% by weight of starch), and magnesium stearate (2% by weight of starch) were first dry-mixed using a Moulinex kitchen-aid mixer. Distilled water was then added to the mixture and the batter was further mixed for 20 min. For certain formulations, PVA or a plasticizer (i.e. glycerol, urea, or ammonium chloride) was also added to the batter. Starch and starch/PVA foams were then prepared by first applying 25 g of as-prepared batter in a picture-frame mold and then placing the mold in a Wabash V50H compression press (the temperature of the platens was pre-set at 220°C). After 2 min, the mold was cooled down to room temperature at a cooling rate that was fitted well by an exponential decay with a time constant of around 3 min.

Characterization

Morphology of starch and starch/PVA foams was examined using a JEOL JSM 520-2AE scanning electron microscope (SEM). The operating voltage used was 10 kV. Some fractured specimens obtained after mechanical property measurement were selected and were cut about 2 mm below the fractured surface and mounted on aluminum stubs, after which they were coated with a thin layer of gold.

Before moisture content determination and mechanical property measurement, starch and starch/PVA foams were conditioned in a conditioning jar having a specific relative humidity level of 11, 32, 42, 52, 67, or 75%RH at 25°C for various storage periods up to 7 days. The conditioning jars were prepared by filling the jars with saturate, aqueous solutions of LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $CuCl_2$, and NaCl, respectively.

The percentage of moisture content in a foam specimen (dried at 50°C for 24 hours) was taken as the percentage of weight increase after the specimen was conditioned in a specified relative humidity atmosphere for a specified storage period. The percentage of water absorption in a foam specimen (equilibrated at 50%RH for 7 days) was taken as the percentage of weight increase after the specimen was soaked in 100 ml of distilled water at 25°C for 10 min.

After the foam specimens were conditioned in a specified relative humidity atmosphere for a specified storage period, they were tested for various mechanical properties, e.g. tensile strength, percentage of elongation at break, flexural strength, and maximum flexural strain. These measurements were carried out using a Lloyd LRX mechanical testing machine, with the maximum load of 2500 N. For tensile tests, a crosshead speed of 5.2 mm/min and gauge length of 118 mm were used, while, for flexural tests, the crosshead speed of 1.3 mm/min and the span of 50 mm were applied.

Selected starch and starch/PVA foams were also tested for their enzymatic degradability. Each foam specimen was weighed before being placed in a test vial. A reaction mixture containing 25 ml of 0.05 M acetate buffer (pH 6.0), 1 ml of Termamyl α-amylase (120 KNU/g), and 54 mM of $CaCl_2{\cdot}2H_2O$ was added to the vial, which was then heated in a shaking water bath at 60°C for 3 hours. Specimens were collected after different reaction time periods, ranging from 5 to 180 min, were reached prior to being washed with distilled water and dried at 60°C for 5 hours. Their weights were then recorded and used to determine the percentage of weight loss.

Results and Discussion

Morphology

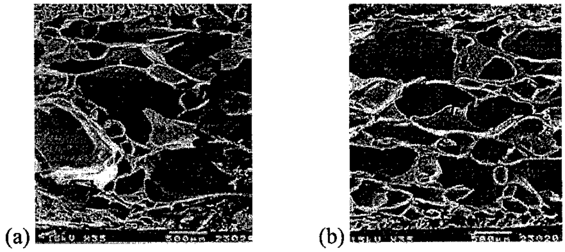
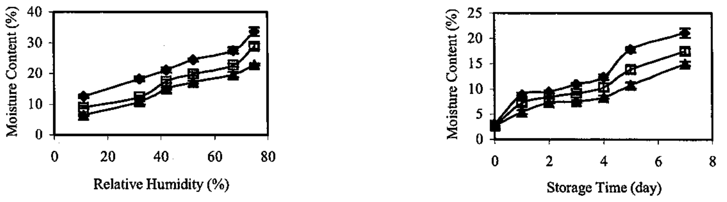


Figure 1. Scanning electron micrograph of cross sections of (a) starch and (b) starch/PVA (30 wt.%) composite foams.

Selected scanning electron micrographs of starch and starch/PVA foams are shown in Figure 1. Both micrographs show that the skin layers for both types of foam exhibited small, dense, and closed cell structure, whereas the interior showed large, loose, and opened cell structure. The densified outer skin layer was caused by abrupt evaporation of the batter layer close to the hot surface of the mold, causing the batter to dry very rapidly. The large, loose, and opened cell structure of the interior was a result of the large amount of steam venting out of the mold, causing cell walls to rupture.[10] Even though the skin layer of starch/PVA foam was similar to that of the starch foam, the interior structure was a bit denser. This is verified by the fact that the density of this starch/PVA foam (i.e. 0.225 g/cm^3) was higher than that of the pure starch foam (i.e. 0.138 g/cm^3).

Moisture and Water Absorption



(a) (storage condition: 25°C for 7 days)

(b) (storage condition: 25°C and 42%RH)

Figure 2. Moisture content of starch and starch/PVA foams as a function of (a) relative humidity and (b) storage period. Keys: (◆) 0, (□) 10, and (▲) 30 wt.% PVA.

A number of factors (e.g. relative humidity, storage period, PVA content, and plasticizer content) affect moisture content of starch and starch/PVA foams. The effects of relative humidity, storage period, and PVA content on moisture content of various starch-based foams are illustrated in Figure 2. The moisture content in all of the foams studied (after being conditioned in a specified relative humidity atmosphere for 7 days at 25°C) was found to increase with increasing relative humidity and, for a given relative humidity level, it was found to decrease with increasing PVA content. For a fixed relative humidity level of 42%RH at 25°C, the moisture content in all of the foams investigated was found to increase monotonically with increasing storage period, and, for a given storage period, the moisture content was, again, found to decrease with increasing PVA content. The decrease in the tendency to absorb moisture with increasing PVA content is due to the fact that PVA is less hygroscopic than starch is.

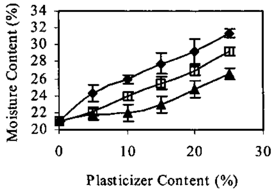


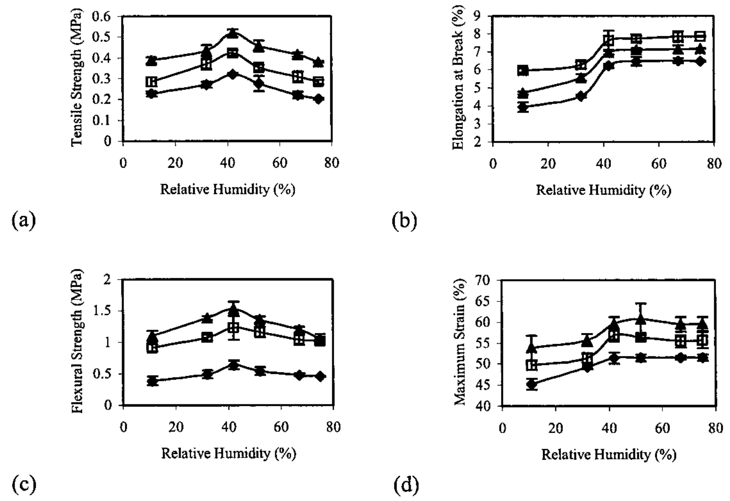
Figure 3. Moisture content of pure starch foams as a function of plasticizer content. The storage condition was at 42%RH and 25°C for 7 days. Keys: (◆) glycerol, (□) urea, and (▲) ammonium chloride.

The moisture content of pure starch foams containing glycerol, urea, or ammonium chloride after being conditioned at 42%RH and 25°C for 7 days is shown in Figure 3. Apparently, starch foams containing glycerol had a higher tendency to absorb moisture than those containing urea or ammonium chloride and, for a given type of added plasticizer, the moisture content was found to increase with an increase in its content.

Water absorption of starch and starch/PVA foams with varying PVA content has been investigated and it was found to decrease with increasing PVA content (i.e. from 127 ± 4% for pure starch foam down to 88 ± 2% and to 74 ± 3% for starch/PVA foams having the PVA content of 10 and 30 wt.%, respectively). It was postulated that a decrease in the water absorption for starch/PVA foams with increasing PVA content is due to the fact that a highly hydrolyzed PVA (for the particular PVA resin, the degree of hydrolysis was around 97.5 to 99.5%) is highly crystalline and insoluble in cold water.

Mechanical Properties

Effect of Relative Humidity



(a) (b)

(c) (d)

Figure 4. Mechanical properties [i.e. (a) tensile strength, (b) percentage of elongation at break, (c) flexural strength, and (d) maximum flexural strain] of starch and starch/PVA foams as a function of relative humidity. The storage condition was at 25°C for 7 days. Keys: (◆) 0, (□) 10, and (▲) 30 wt.% PVA.

Mechanical properties of starch-based foams (after being conditioned in a specified relative humidity atmosphere for 7 days at 25°C) were measured and the results are shown as a function of relative humidity in Figure 4. Apparently, all of the starch-based foams investigated exhibited a maximum in both tensile and flexural strength at the relative humidity level of 42%RH. At "low" relative humidity levels, the cell structure of starch-based foams was so brittle that cracks could form and propagate, whereas, at "high" relative humidity levels, the high amount of absorbed moisture weakened their cell structure.[11] It was also obvious that, for a given value of relative humidity, addition of PVA was responsible for a significant increase in both the tensile and flexural strength of the foams. Both percentage of elongation at break and maximum flexural strain of the foams were found to increase initially with increasing relative humidity level (up to 42%RH) and then became constant at relative humidity levels higher than 42%RH. An increase in the mobility of the starch molecules as a result of the absorbed moisture should be the reason for the observed increase in both the percentage of elongation at break and maximum flexural strain with increasing relative humidity level.[11]

Effect of Storage Period

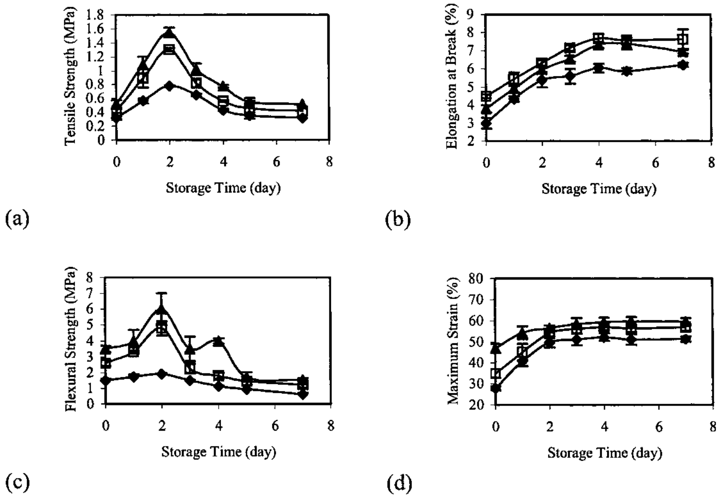
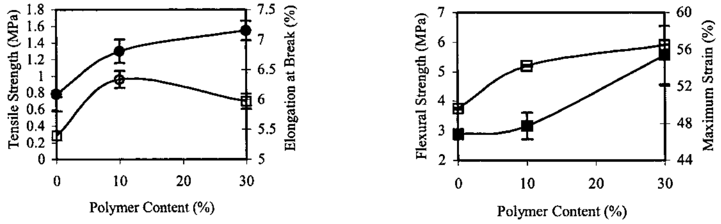


Figure 5. Mechanical properties [i.e. (a) tensile strength, (b) percentage of elongation at break, (c) flexural strength, and (d) maximum flexural strain] of starch and starch/PVA foams as a function of storage period at 42%RH and 25°C. Keys: (◆) 0, (□) 10, and (▲) 30 wt.% PVA.

The effect of storage period on mechanical properties of starch-based foams is illustrated in Figure 5. Obviously, all of the starch-based foams studied attained a maximum in both tensile and flexural strength after conditioning at 42%RH and 25°C for 2 days and the balance between the rigidity of the unplasticized or lightly-plasticized starch molecules and the mobility of the plasticized starch molecules may be responsible for the observed maximum in both of the strength values. It was also apparent that, for a given storage period, addition of PVA was responsible for an increase in both the tensile and flexural strength of the foams. Figure 5b shows that the percentage of elongation at break of the foams increased steadily with increasing storage period during the first four days of conditioning, after which it was found to vary very slightly. The rapid uptake of moisture during the first four days of conditioning may be responsible for the observed steady increase in the percentage of elongation at break of the foams.[15] The maximum flexural strain of the foams was also found to increase steadily with increasing storage period during around the first three to four days of conditioning, after which it was found to be practically unchanged.

Effect of PVA Content



(a) (b)

Figure 6. Mechanical properties [i.e. (●) tensile strength, (○) percentage of elongation at break, (■) flexural strength, and (□) maximum flexural strain] of starch and starch/PVA foams as a function of PVA content. The storage condition was 42%RH and 25°C for 2 days.

The effects of PVA addition and content on mechanical properties of starch-based foams after conditioning at 42%RH and 25°C for 2 days are shown graphically in Figure 6. Both tensile strength and flexural strength of the starch-based foams investigated were found to increase with increasing PVA content. Basically, PVA has higher tensile strength than starch (i.e. 95 versus 22 MPa); therefore, addition of PVA in the foam structure should help improve the tensile property as well as the rigidity of the resulting composite foams. The percentage of elongation at break of the foams was first found to increase with addition of 10 wt.% PVA and then decrease with further addition of PVA (up to 30 wt.%). The initial increase in the percentage of elongation at break for starch/PVA (10 wt.%) foam might be explained based on the higher flexibility of PVA versus starch molecules[10] and on the ease for crack formation at the interface between PVA and starch phases. Upon further increase in the PVA content, the rigidity of the foams increased appreciably (a direct result of the higher tensile strength of PVA versus starch),[16] leading to a reduction in the percentage of elongation at break for starch/PVA (30 wt.%). The maximum flexural strain of the foams was found to increase appreciably with addition of 10 wt.% PVA and then increase very slightly with further increase in the PVA content (up to 30 wt.%). The most likely explanation for such improvement in the maximum flexural strain may be due to the inherent flexibility of PVA molecules in comparison with starch molecules.

Effect of Plasticizer

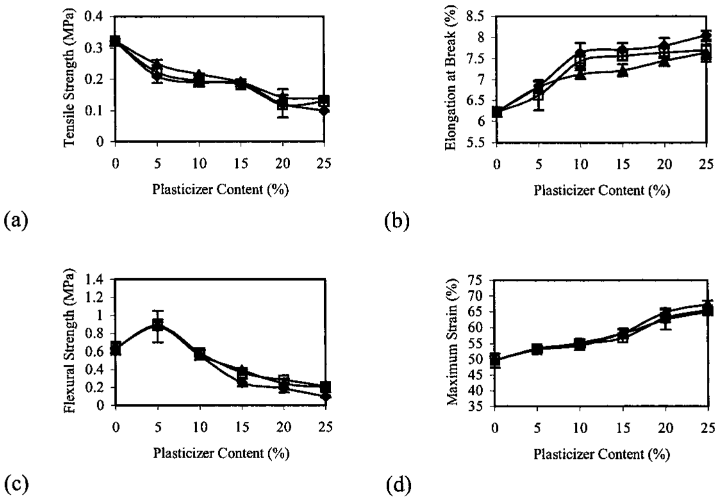


Figure 7. Mechanical properties [i.e. (a) tensile strength, (b) percentage of elongation at break, (c) flexural strength, and (d) maximum flexural strain] of pure starch foams as a function of plasticizer content. The storage condition was 42%RH and 25°C for 7 days. Keys: (◆) glycerol, (□) urea, and (▲) ammonium chloride.

The general purpose for incorporating a plasticizer into a plastic is to convert an otherwise hard and rigid plastic into a flexible or semi-flexible one. Since starch molecules are inherently rigid, addition of a plasticizer should make a starch-based article more pliable. In addition to moisture, three plasticizers (i.e. glycerol, urea, and ammonium chloride) are individually added into pure starch foams in order to study their effect on mechanical properties of the foams.

The effect of added plasticizer on mechanical properties of pure starch foams, after conditioning at 42%RH and 25°C for 7 days, is illustrated in Figure 7. As we normally expected, the tensile strength of the foams investigated was found to decrease, while the resulting percentage of elongation at break was found to increase, with addition and increasing amount of added plasticizer. This is probably because plasticizer molecules soften starch molecules by penetrating into starch granules and basically destroying the inter-molecular hydrogen bonds of starch molecules.[17] This, in turn, helps increase mobility of the starch molecules, resulting in decreased tensile strength and increased percentage of elongation at break. In case of flexural properties, the flexural strength of the foams was initially found to increase with increasing plasticizer content of up to 5 wt.%. Further increase in the plasticizer content greater than 5 wt.% resulted in the reduction of the flexural strength of the plasticized foams. The maximum flexural strain of the foams, however, was found to increase gradually with addition and increasing amount of added plasticizer. It is obvious that the type of plasticizer added did not, at all, affect the mechanical properties of the foams.

Enzymatic Degradation

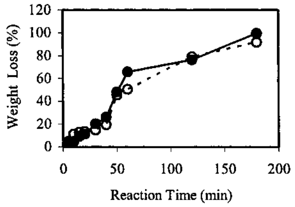


Figure 8. Enzymatic degradation by α-amylase at 60°C for (●) pure starch foams and (○) starch/PVA (30 wt.%) composite foams.

Enzymatic degradation of starch and starch/PVA foams was tested by α-amylase in vitro at 60°C and the results are plotted as a function of reaction time in Figure 8. All of the foams investigated exhibited a monotonic increase in the percentage of weight loss with increasing reaction time. An abrupt increase in the percentage of weight loss was observed at the reaction time of around 40 min. During "small" reaction times (i.e. less than 40 min), water molecules are being absorbed into the foam structure and this could be an explanation for the slow enzymatic degradability observed within this region. It is also apparent from Figure 8 that addition of PVA had little effect on the enzymatic degradability of the foams.

Conclusions

In the present contribution, starch/poly(vinyl alcohol) (PVA) composite foams were prepared by baking a mixture of starch, PVA, and other ingredients in a hot mold. The effects of conditioning relative humidity, conditioning storage period, PVA content, and type and content of added plasticizer (e.g. glycerol, urea, or ammonium chloride) on moisture and water absorption, mechanical properties, and biodegradability of the as-prepared composite foams were investigated and the results were compared with those of the pure starch foams.

Moisture absorption for both starch and starch/PVA foams was found to increase with increasing conditioning relative humidity level (the storage condition was 25°C for 7 days) and conditioning storage period (the storage condition was 42%RH and 25°C). Addition of PVA helped promote the resistance to water of the composite foams. In all of the testing conditions investigated, the ultimate tensile strength was shown to be a maximum when the relative humidity was 42%RH (for a fixed storage period of 7 days) and when the storage period was 2 days (for a fixed relative humidity of 42%RH). Addition of PVA improved the ultimate strength and the elongation at break of the composite foams. An increase in the amount of added plasticizer was responsible in an increase in the percentage of elongation at break at the expense of the tensile strength of pure starch foams. Lastly, the enzymatic degradability of both starch and starch/PVA foams by α-amylase was found to increase with increasing reaction time and addition of PVA affected a little to the enzymatic degradability of the composite foams.

Acknowledgments

This work is financially supported by Chulalongkorn University through a grant provided by the Rachadapisek Somphot Endowment Fund. The authors wish to thank Siam Modified Starch Co., Ltd. (Thailand), Coin Chemical (Thailand) Co., Ltd., and East Asiatic Co., Ltd. (Thailand) for supplying materials and essential chemicals for this work. They also due their gratitude to David C. Martin of the University of Michigan, USA, and John W. Ellis of LabTech Engineering Co., Ltd. (Thailand) for their technical knowledge and helpful suggestions.

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