



Material Characterisation

Characterization of starch/poly(ϵ -caprolactone) hybrid foams

Dujdao Preechawong, Manisara Peesan, Pitt Supaphol*, Ratana Rujiravanit*

The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phythai Road, Pathumwan, Bangkok 10330, Thailand

Received 25 December 2003; accepted 29 January 2004

Abstract

Starch/poly(ϵ -caprolactone) (PCL) hybrid foams were prepared by baking a mixture of starch, PCL, and other ingredients in a hot mold. The effects of relative humidity, storage time, PCL content, and type and content of added plasticizer (e.g. glycerol, urea, or ammonium chloride) on moisture and water absorption, mechanical properties, and enzymatic degradability of the as-prepared foams were investigated. In all the conditions investigated, the ultimate tensile strength was a maximum when the relative humidity was 42% RH (for a fixed storage time of 7 days) and when the storage time was 2 days (for a fixed relative humidity of 42% RH). Addition of PCL helped improve the ultimate tensile strength and the percentage of elongation at break of the hybrid foams. Resistance to water absorption of the starch/PCL hybrid foams was superior to that of pure starch foams. Lastly, enzymatic degradation tests in an α -amylase solution showed that addition of PCL improved enzymatic degradability of the hybrid foams.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Starch foam; Starch-based hybrid foam; Poly(ϵ -caprolactone); Moisture and water absorption; Mechanical properties; Degradability

1. Introduction

There has been a growing interest in developing starch-based products, because starch is a totally biodegradable, cheap, natural biopolymer obtained from renewable resources. Starch foam products made by extrusion and solvent exchange processes have been investigated as possible replacements for commonly used polystyrene-based foam products [1,2]. Starch foams made by these processes have useful mechanical and thermal properties, but are difficult to form into complex-shaped articles. It has been shown that a baking process can be used to prepare starch foam products, with thickness as thin as 1.5 mm [3,4]. The process is essentially similar to the process used to make waffles and wafer cookies, which involves placing

a specified amount of starch/water mixed dough into a pre-heated mold cavity. As the dough is heated, the starch component gelatinizes, while the water component vaporizes to serve as the foaming agent. The properties of baked starch foams depend very much on the moisture content, the type of starch, and the type and amount of additives used [5–7]. Due to the hydrophilicity of the starch, baked starch foams are subservient to moisture and water absorption, which restrict actual utilization of these products.

Choice of a plasticizer used to impart flexibility to a plastic product depends on whether the base polymer is hydrophilic or hydrophobic. Hydrophobic plasticizers are used extensively with petroleum-based polymers. Hydrophobic plasticizers can also be used in starch-based plastics, but the molecules must be polar to allow partial compatibility with the starch molecules. Use of various plasticizers with starch has been investigated [8,9]. Under shearing and elevated temperature and pressure conditions, water and glycerol act as a good

* Corresponding author. Fax: +66-2215-4459.

E-mail addresses: pitt.s@chula.ac.th (P. Supaphol); ratana.r@chula.ac.th (R. Rujiravanit).

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 [10].

Various synthetic polymers have been blended with unmodified starch in order to lower the density and to increase resistance to water absorption of the foams. To retain the biodegradability of the foams, various biodegradable polymers have been used [11]. Among the various biodegradable polymers, poly(ϵ -caprolactone) (PCL) is an interesting material. PCL is a semi-crystalline polymer and its molecules are flexible and rather hydrophobic, thus PCL can be slowly utilized by microbes in buried environment. Additionally, its physical properties and commercial availability make it very attractive, not only as a substitute for non-biodegradable polymers for commodity applications, but also for specific applications in medicinal and agricultural areas. The ultimate tensile strength and the percentage of elongation at break of PCL films have been reported to be around 33 MPa and 1100%, respectively [12].

The objectives of this contribution were to improve physical and mechanical properties and resistance to water absorption of starch-based foam materials by adding PCL and/or a plasticizer (e.g. glycerol, urea, or ammonium chloride) with tapioca starch. Starch-based hybrid foams were then prepared by a baking process and were analyzed for their moisture and water absorption characteristics, mechanical properties, and enzymatic degradability. The results were compared with those obtained for pure starch foams.

2. Experimental details

2.1. Materials

Tapioca starch was supplied as a courtesy by Siam Modified Starch Co., Ltd. (Thailand). PCL was supplied as a courtesy by Daiseru Chemical Co., Ltd. (Japan). 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 by Coin Chemical (Thailand) Co., Ltd., with both of these chemicals being used as additives. Termamyl 120 α -amylase (120 KNU/g) was supplied as a courtesy by East Asiatic Co., Ltd. (Thailand).

2.2. Preparation of starch and starch/PCL foams

Tapioca starch (pre-dried at 110 °C for 24 h), 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, PCL or a plastici-

zer (i.e. glycerol, urea, or ammonium chloride) was also added to the batter. Starch and starch/PCL 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 well fitted by an exponential function with a time constant of around 3 min.

2.3. Characterization

Morphology of starch and starch/PCL foams was examined using a JEOL JSM 5200 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/PCL 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 times up to 7 days. The conditioning jars were partially filled with a saturated, aqueous solution of LiCl, MgCl₂, K₂CO₃, Mg(NO₃)₂, CuCl₂, or NaCl, above which foam specimens were placed on a wire grid.

The percentage of moisture content in a foam specimen (dried at 50 °C for 24 h) was taken as the percentage weight increase after the specimen was conditioned in a specified relative humidity atmosphere for a specified storage time. 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 time, 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, a crosshead speed of 1.3 mm/min and span of 50 mm were applied.

Selected starch and starch/PCL 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 CaCl₂·2H₂O was added to the vial, which was then held at 60 °C whilst being

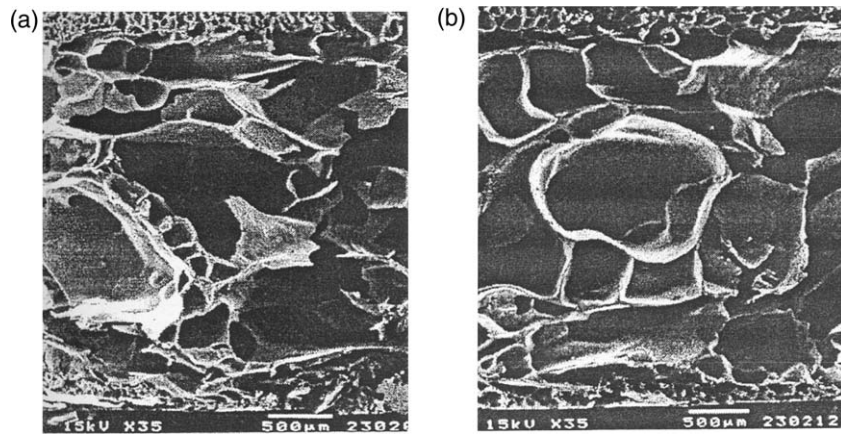


Fig. 1. Scanning electron micrograph of cross sections of (a) pure starch foam and (b) starch/PCL hybrid foam having a PCL content of 30% by weight.

mechanically shaken in a water bath for 3 h. Specimens were collected after different reaction time periods, ranging from 5 to 180 min, prior to being washed with distilled water and dried at 60 °C for 5 h. Their weights were then recorded and used to determine the percentage of weight loss.

3. Results and discussion

3.1. Morphology

Selected scanning electron micrographs of starch and starch/PCL foams are shown in Fig. 1. Both micrographs show that the skin layers for both types of foam exhibited small, dense, and closed cell structure, while the interior showed large, loose, and opened cell structure. The dense outer skin layer was likely caused by abrupt evaporation of the water molecules in the batter layer adjacent to the hot surface of the mold. The batter layer, therefore, dried very rapidly, leaving less time for cell expansion. The large, loose, and

opened cell structure of the interior was a result of the venting of large amount of water molecules from the molding as the batter was drying, causing extensive cell expansion and cell wall rupture [13]. Even though the skin layer of starch/PCL foam having the PCL content of 30 wt% was similar to that of the pure starch foam, the interior structure was a bit denser. This can be verified based on the fact that the density of this hybrid foam was greater than that of the pure starch foam (i.e. 0.204 versus 0.138 g/cm³, respectively).

3.2. Moisture and water absorption

A number of factors (e.g. relative humidity, storage time, PCL content, and plasticizer content) affect moisture content of starch and starch/PCL foams. The effects of relative humidity, storage time, and PCL content on moisture content of various starch-based foams are illustrated in Fig. 2. The moisture content in all the foams studied (after being conditioned in a specified relative humidity atmosphere for 7 days at 25 °C) was

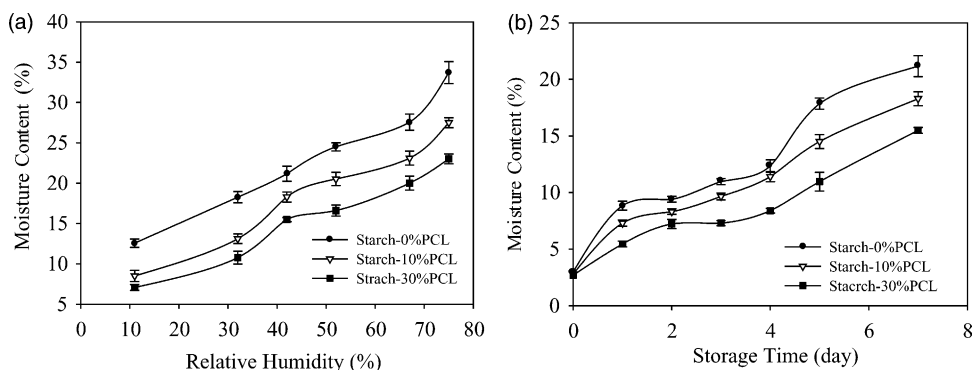


Fig. 2. Moisture content of pure starch and starch/PCL foams as a function of (a) relative humidity and (b) storage time.

found to increase with increasing relative humidity and, for a given relative humidity level, it was found to decrease with increasing PCL 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 time, and, for a given storage time, the moisture content was, again, found to decrease with increasing PCL content. The decrease in the tendency to absorb moisture with increasing PCL content is due to the fact that PCL is less hygroscopic than starch [14].

Water absorption of starch and starch/PCL foams with varying PCL content has been investigated and it was found to decrease with increasing PCL content (i.e. from $127 \pm 4\%$ for pure starch foam down to $93 \pm 2\%$ and to $77 \pm 2\%$ for starch/PCL foams having the PCL content of 10 and 30 wt%, respectively). The decrease in water absorption for starch/PCL foams with increasing PCL content can be explained based on the fact that PCL is less hygroscopic than starch [14]. In a recent report [15], we have found that water absorption of starch/poly(vinyl alcohol) (PVA) foams was also a decreasing function of the PVA content (i.e. from $127 \pm 4\%$ for pure starch foam down to $88 \pm 2\%$ and to $74 \pm 3\%$ for starch/PVA foams having PVA content of 10 and 30 wt%, respectively).

Due to its hygroscopic nature, starch is prone to moisture and water absorption. Water molecules act, in part, as a natural plasticizer for starch, which helps render starch from being a hard and rigid plastic in its completely dry state into a more flexible plastic. Since it has been shown that the amount of absorbed moisture depended very strongly on the relative humidity level of the service environment (which, in some cases, is not easy to control), use of water as the plasticizer for starch may cause problems, especially when it absorbs too much water. An alternative approach is to use other chemicals as a plasticizer for starch.

In this contribution, three chemicals (i.e. glycerol, urea, and ammonium chloride) were used to plasticize pure starch foams. Fig. 3 shows moisture content of pure starch foams containing glycerol, urea, or ammonium chloride after being conditioned at 42% RH and 25 °C for 7 days as a function of plasticizer content. Obviously, starch foams containing glycerol as the plasticizer 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 monotonically increase with an increase in its content.

3.3. Mechanical properties

3.3.1. Effect of relative humidity

Mechanical properties of starch and starch/PCL foams (after being conditioned in a specified relative

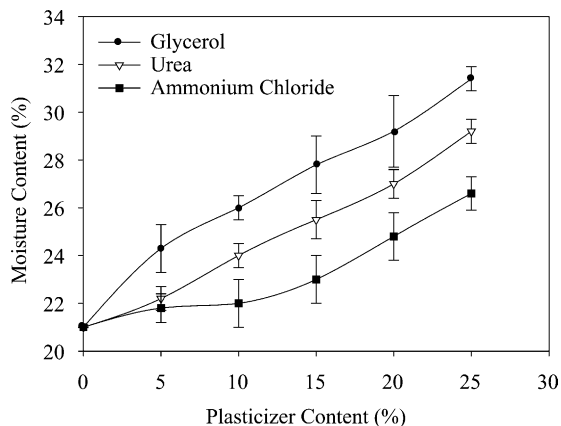


Fig. 3. Moisture content of pure starch foams as a function of plasticizer content. The storage condition was 42% RH and 25 °C for 7 days.

humidity atmosphere for 7 days at 25 °C) were measured and the results are shown as a function of relative humidity in Fig. 4. Very clearly, the values of both the tensile and flexural strength for all of the foam specimens investigated were found to initially increase with increasing relative humidity, reach a maximum at 42% RH, and decrease with further increase in the relative humidity. At “low” relative humidity levels (i.e. less than 42% RH), the cell structure of starch-based foams was so brittle that cracks could form and propagate, whereas at “high” relative humidity levels (i.e. greater than 42% RH), the high amount of absorbed moisture weakened the cell structure appreciably [13]. For a given value of relative humidity, addition of PCL was responsible for a significant increase in both the tensile and flexural strength of the hybrid foams over those of the pure starch 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 either 42 or 52% RH) and then became practically constant at relative humidity levels greater than either 42 or 52% RH. The increased mobility of starch molecules due to the plasticizing effect of absorbed moisture could be responsible for the observed increase in both the percentage of elongation at break and maximum flexural strain with increasing relative humidity [6].

3.3.2. Effect of storage time

The effect of storage time on mechanical properties of starch-based foams is illustrated in Fig. 5. Apparently, the values of both the tensile and flexural strength for all of the foam specimens investigated were found to initially increase with increasing storage time, reach a maximum at a storage time of 2 days, and decrease with further increase in the storage time. The

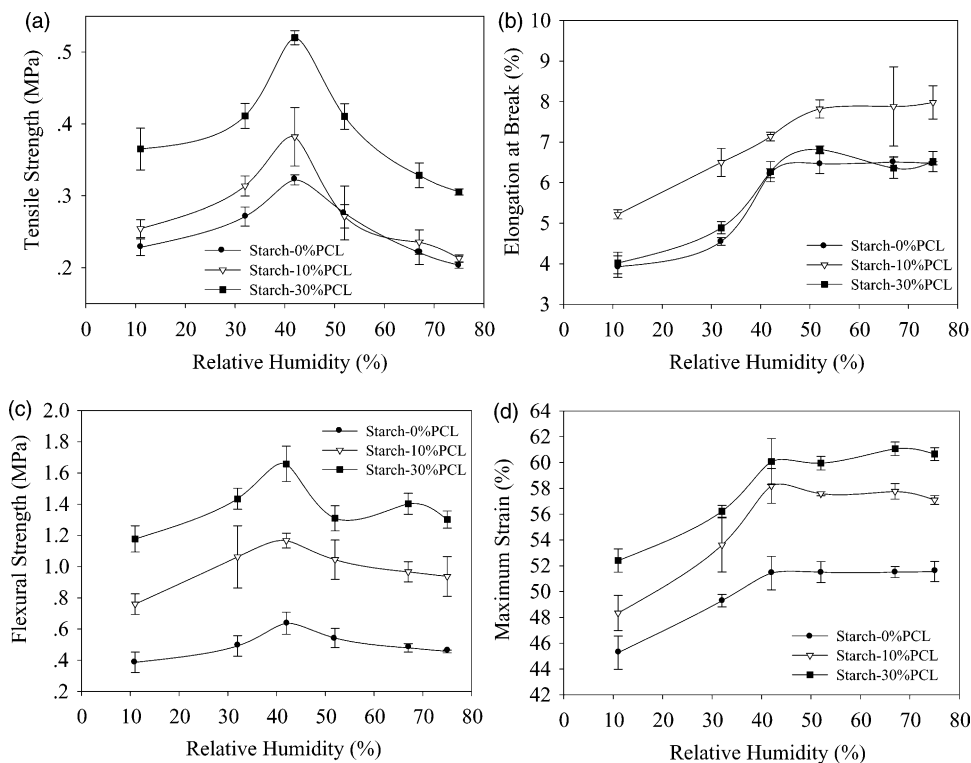


Fig. 4. Mechanical properties (i.e. (a) tensile strength, (b) percentage of elongation at break, (c) flexural strength, and (d) maximum flexural strain) of pure starch and starch/PCL foams as a function of relative humidity. The storage condition was 25 °C for 7 days.

amount of absorbed moisture at a storage time of 2 days in all of the starch-based foams studied (i.e. $9.4 \pm 0.3\%$ for pure starch foam and $8.3 \pm 0.2\%$ and $7.2 \pm 0.4\%$ for starch/PCL foams having PCL content of 10 and 30 wt%, respectively) may be just the optimal amount where the rigidity and the flexibility of the starch molecules are balanced. For a given value of relative humidity, the presence of PCL was responsible for an appreciable increase in both the tensile and flexural strength of the hybrid foams in comparison with those of the pure starch foams. Both percentage of elongation at break and maximum flexural strain of the foam specimens were found to initially increase with increase in the storage time (up to either 3 or 4 days) and then became practically unchanged with further increase in the storage time.

3.3.3. Effect of PCL content

The effects of PCL addition and content on mechanical properties of starch-based foams after conditioning at 42% RH and 25 °C for 2 days have been investigated and the results can be read directly from Fig. 5. The tensile strengths of pure starch foam and starch/PCL foams having PCL contents of 10 and 30 wt%

were found to be 0.79 ± 0.03 , 0.91 ± 0.05 , and 1.31 ± 0.14 MPa, respectively; the percentage of elongation at break was found to be $5.4 \pm 0.4\%$, $6.2 \pm 0.3\%$, and $5.6 \pm 0.1\%$, respectively; the flexural strength was found to be 2.9 ± 0.1 , 3.3 ± 0.1 , and 5.7 ± 0.1 MPa, respectively, and the maximum flexural strain was found to be $49.6 \pm 2.2\%$, $52.8 \pm 0.6\%$, and $54.4 \pm 1.1\%$, respectively.

According to the values reported above, both tensile strength and flexural strength of these starch-based foams were found to increase with increasing PCL content. Basically, PCL has greater tensile strength than starch (i.e. 33 versus 22 MPa, respectively). As a result, addition of PCL to the foam structure should help improve the tensile property as well as the rigidity of the resulting hybrid foams. The percentage of elongation at break of the foams was found to increase with small amount of PCL added (i.e. 10 wt%) and then decrease with further increase in the PCL content (i.e. 30 wt%). The initial increase in the percentage of elongation at break for starch/PCL foam containing PCL content of 10 wt% can be explained based on the higher flexibility of PCL versus starch molecules [13] and on the ease of crack formation at the interface

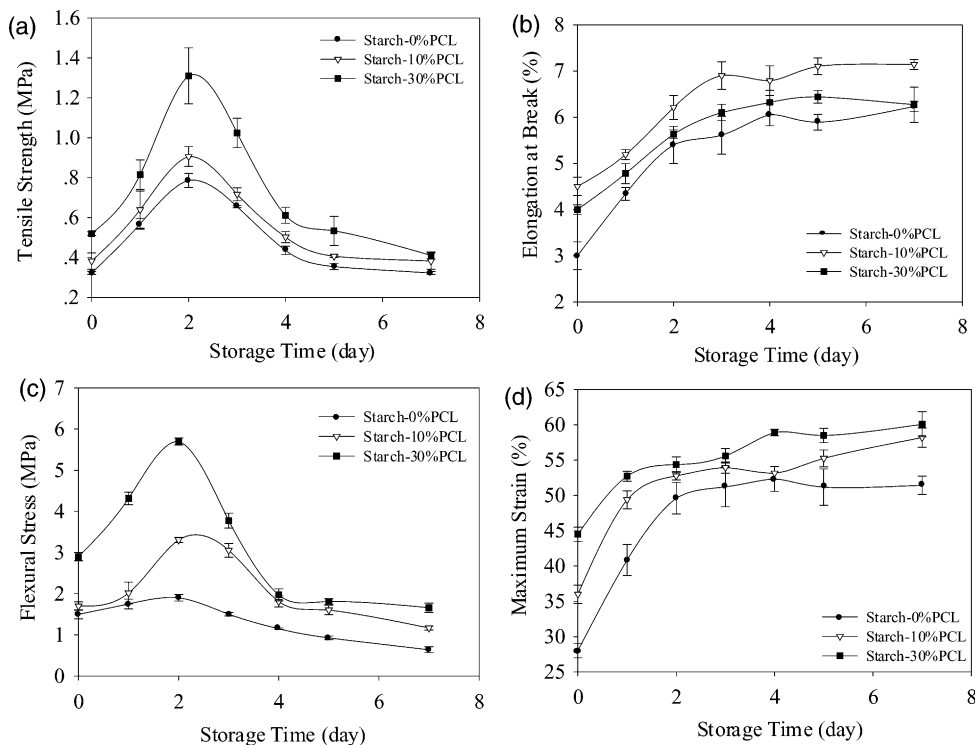


Fig. 5. Mechanical properties (i.e. (a) tensile strength, (b) percentage of elongation at break, (c) flexural strength, and (d) maximum flexural strain) of pure starch and starch/PCL foams as a function of storage time at 42% RH and 25 °C.

between PCL and starch phases. Upon further increase in the PCL content, the rigidity of the foams increased appreciably (a direct result of the higher tensile strength of PCL versus starch) [16], leading to a reduction in the percentage of elongation at break for starch/PCL foam containing PCL content of 30 wt%. The maximum flexural strain of the foams was found to increase significantly with addition of small amounts of PCL (i.e. 10 wt%) and then increase very slightly with further increase in the PCL content (i.e. 30 wt%). The explanation for such improvement in the maximum flexural strain is the inherent flexibility of PCL molecules in comparison with that of starch molecules [6].

3.4. Enzymatic degradation

Enzymatic degradation of starch and starch/PCL foams was tested by α -amylase in vitro at 60 °C and the results are expressed as a function of reaction time in Fig. 6. All the foam specimens 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 onset reaction time of 40 min for pure starch foams and 50 min for starch/PCL foams, respectively. For reaction

times of less than 40 min, water molecules were being absorbed into the foam structure, thus only limited parts of the foams were accessible to the enzyme, and this could be the reason for the slow enzymatic degradation observed during this time interval. Comparison between the percentage of weight loss curves of pure starch and starch/PCL foams suggests that starch/PCL

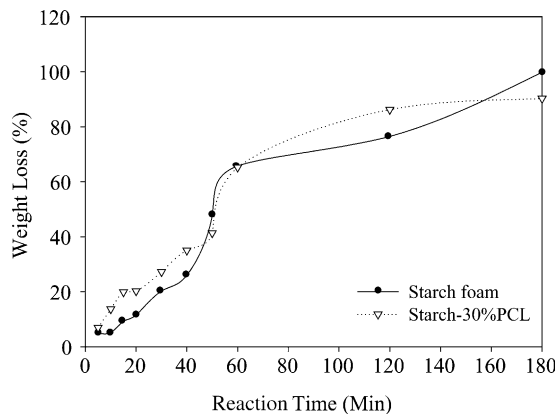


Fig. 6. Enzymatic degradation by α -amylase at 60 °C for (●) pure starch foams and (○) starch/PCL hybrid foams having a PCL content of 30% by weight.

foams are, in general, more subservient to enzymatic hydrolysis by α -amylase than pure starch foams. This may be due to the ease of enzymatic degradation of PCL molecules.

4. Conclusions

In the present contribution, starch/poly(ϵ -caprolactone) (PCL) hybrid foams were prepared by baking a mixture of starch, PCL, and other ingredients in a hot mold. The effects of conditioning relative humidity, conditioning storage time, and PCL content on moisture and water absorption, mechanical properties, and biodegradability of the as-prepared hybrid foams were investigated and the results were compared with those of the pure starch foams. Moisture absorption for both starch and starch/PCL foams was found to increase with increasing conditioning relative humidity level (the storage condition was 25 °C for 7 days) and conditioning storage time (the storage condition was 42% RH and 25 °C). Addition of PCL helped promote the resistance to water absorption of the hybrid foams. In all the testing conditions investigated, the ultimate tensile strength was found 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 PCL improved the ultimate tensile strength and the percentage of elongation at break of the composite foams. Lastly, the enzymatic degradability of both starch and starch/PCL foams by α -amylase was found to increase with increasing reaction time and addition of PCL helped increase slightly the enzymatic degradability of the hybrid foams.

Acknowledgements

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 owe 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.

References

- [1] N.L. Lacourse, P.A. Altieri, US Patent No. 4,863,655 (1989).
- [2] G.M. Glenn, D.W. Irving, *Cereal Chemistry* 72 (1995) 155.
- [3] K.F. Tiefenbacher, *Journal of Macromolecular Science—Pure and Applied Chemistry* A30 (1993) 727.
- [4] F. Hass, J. Hass, K.F. Tiefenbacher, US Patent No. 5,576,049 (1996).
- [5] P.J. Andersen, S.K. Hodson, US Patent No. 5,545,450 (1996).
- [6] R.L. Shogren, J.W. Lawton, L. Chen, K.F. Tiefenbacher, *Journal of Applied Polymer Science* 68 (1998) 2129.
- [7] J.W. Lawton, R.L. Shogren, K.F. Tiefenbacher, *Cereal Chemistry* 76 (1999) 682.
- [8] C.L. Swanson, R.L. Shogren, G.F. Fanta, S.H. Imam, *Journal of Environment and Polymer Degradation* 1 (1993) 155.
- [9] D. Lourdin, L. Coignard, H. Bizot, P. Colonna, *Polymer* 38 (1997) 5401.
- [10] D. Lourdin, H. Bizot, P. Colonna, *Journal of Applied Polymer Science* 63 (1997) 1047.
- [11] Q. Fang, M.A. Hanna, *Industrial Crops and Products* 13 (2001) 219.
- [12] M.F. Koenig, S.J. Huang, *Polymer* 36 (1995) 1877.
- [13] R.L. Shogren, J.W. Lawton, W.M. Doane, K.F. Tiefenbacher, *Polymer* 39 (1998) 6649.
- [14] L. Averous, N. Fauconier, L. Moro, C. Fringant, *Journal of Applied Polymer Science* 76 (2000) 1117.
- [15] D. Preechawong, M. Peesan, R. Rujiravanit, P. Supaphol, *Macromolecular Symposia*, accepted for publication.
- [16] L. Zhiqiang, F. Yi, Y. Xiao-Su, *Journal of Applied Polymer Science* 74 (1999) 2667.