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Preparation and characterization of starch/poly(L-lactic acid) hybrid foams

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Abstract

Starch/poly(L-lactic acid) (PLA) hybrid foams were prepared by baking a mixture of starch, PLA, and other ingredients in a hot mold. The effects of relative humidity, storage time, PLA 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 of the conditions investigated, the ultimate tensile strength was shown to exhibit 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 PLA helped improve the ultimate tensile strength and the percentage of elongation at break of the hybrid foams. Resistance to water absorption of the starch/PLA hybrid foams was superior to that of pure starch foams. Lastly, enzymatic degradation tests in an α-amylase solution showed that addition of PLA improved the resistance to enzymatic degradability of the hybrid foams.

Keywords: Starch foam; Starch-based hybrid foam; Poly(L-lactic acid); Moisture and water absorption; Mechanical properties; Degradability

1. Introduction

There has been a growing interest in the development of starch-based products, because starch is completely biodegradable, naturally abundant, and cheap. Starch foam products made by extrusion and solvent exchange processes have been explored as possible replacements for polystyrene-based foam products (Glenn & Irving, 1995; Lacourse & Altieri, 1989). Starch foams made by these processes have useful mechanical and thermal properties, but are difficult to form complex-shaped articles. It has been shown that a baking process can be used to prepare starch foam products, with thickness being as thin as 1.5 mm (Haas, Haas, & Tiefenbacher, 1996; Tiefenbacher, 1993). 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 preheated mold cavity. As the dough is heated, the starch component gelatinizes, while the water component vaporizes to serve as the blowing agent. The properties of baked starch foams depend very much on moisture content, type of starch, and type and amount of additives used (Andersen & Hodson, 1996; Lawton, Shogren, & Tiefenbacher, 1999; Shogren, Lawton, Tiefenbacher, & Chen, 1998). 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 studied and reported (Fanta, Swanson, & Shogren, 1992; Lourdin, Coignard, Bizot, & Colonna, 1997). 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 (Lourdin, Bizot, & Colonna, 1997).

Various synthetic polymers have been blended with unmodified starch in order to lower the density and to

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increase resistance to water absorption of the foams. To retain the biodegradability of the foams, various biodegradable polymers have been explored (Fang & Hanna, 2001). Among the various biodegradable polymers, poly(lactic acid) (PLA) is an interesting polymer. PLA is a biodegradable polymer commonly used in medical applications and has potential use as environmentally friendly packaging materials. PLA is a thermoplastic polyester that possesses high strength and high modulus. For poly(L-lactic acid) (PLLA), the tensile strength at yield, tensile strength at break, flexural strength, and notched Izod impact strength are ca. 70, 66, 119 MPa, and 66 J m^{-1} (Kaplan, 1998), respectively, while, for poly(D-lactic acid) (PDLA), these values are ca. 70, 59, 106 MPa, and 26 J m^{-1} (Kaplan, 1998), respectively.

The objectives for the present contribution were to improve physical and mechanical properties and resistance to moisture and water absorption of starch-based foam materials by adding poly(L-lactic acid) (PLA) 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). Poly(L-lactic acid) (PLA) was supplied as a courtesy by Daiseru Chemical Co., Ltd (Japan) in a granular form. Glycerol, urea, and ammonium chloride, used as plasticizers, were purchased from Carlo Erba (Italy). Guar gum was purchased from Sigma-Aldrich (USA) and magnesium stearate was supplied as a courtesy by Coin Chemical (Thailand) Co., Ltd. Guar gum was used as the thickening agent, while magnesium stearate was used as the mold-releasing agent. 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/PLA foams

Tapioca starch (pre-dried at 110 °C for 24 h), guar gum (1 wt% of starch), and magnesium stearate (2 wt% 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, PLA or a plasticizer (i.e. glycerol, urea, or ammonium chloride) was also added to the batter. Starch and starch/PLA foams were then prepared by first applying 25 g of the as-prepared batter in a mold cavity having a rectangular shape and then placing the mold in a Wabash V50H compression press (the temperature of the platens was pre-set at 220 °C). Slight pressure was applied just to close the mold. After 2 min of baking period, 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.

2.3. Characterization

Morphology of starch and starch/PLA 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/PLA 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, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $CuCl_2$, or NaCl, above which foam specimens were placed on a wire grid which was placed above the solution.

The percentage of moisture content in a foam specimen (pre-dried at 50 °C for 24 h) was taken as the percentage of weight increase after the specimen was conditioned in the atmosphere of a specified relative humidity for a specified storage time. The percentage of water absorption in a foam specimen (pre-equilibrated at 52% RH for 7 days) was taken as the percentage of weight increase after the specimen was completely submerged in 100 ml of distilled water at 25 °C for 10 min. It should be noted that the dimension of the specimens used in both of the moisture and water absorption tests were of equal size (i.e. cut into square pieces of 4×4 cm^2, with the thickness being fixed at 3.1 mm).

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 3-point flexural tests, the crosshead speed of 1.3 mm/min and the span of 50 mm were applied. Since starch-based forms are weak materials, a piece of adhesive tape was used to strengthen both ends of the specimens prior to clamping (for tensile test specimens). It should be noted the tensile test specimens were cut according to ASTM D 1623 (type I), while the flexural test specimens were cut according to ASTM D 790-92 (type I).

Selected starch and starch/PLA foams were also tested for their enzymatic degradability (Allenza, Schollmeyer, & Rohrbach, 1990). 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 warmed at 60 °C, while mechanically shaken, in a shaking 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. It should be noted that the specimens used in the enzymatic degradation tests were of equal size (i.e. cut into rectangular pieces of $1 \times 2\ cm^2$, with the thickness being fixed at 3.1 mm).

3. Results and discussion

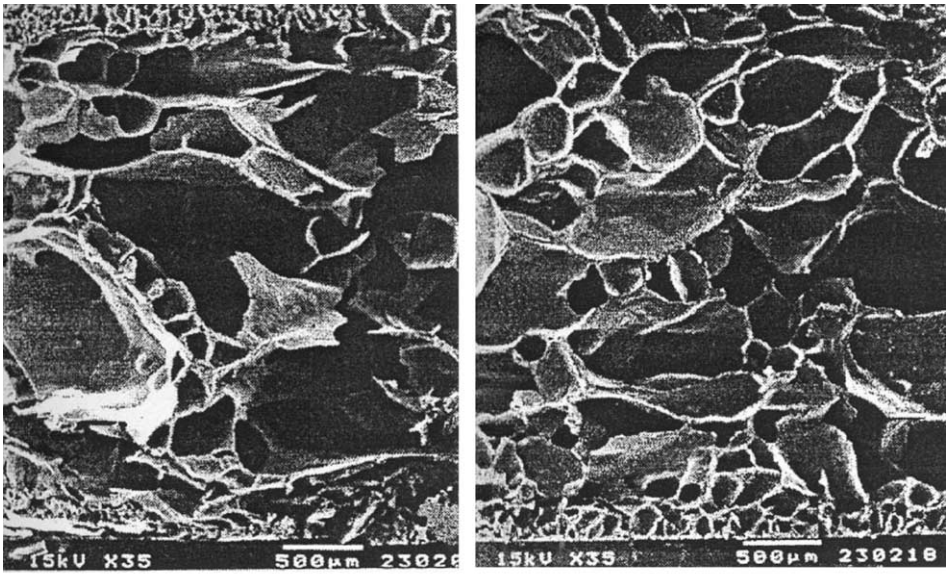
3.1. Morphology

Selected scanning electron micrographs of starch and starch/30 wt% PLA 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 around the opening edge of the mold as the batter was drying, causing extensive cell expansion and cell walls to rupture (Shogren, Lawton, Doane, & Tiefenbacher, 1998). Even though the skin layer of starch/30 wt% PLA foam was similar to that of the pure starch foam, the interior structure was apparently 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. $0.217 \pm 0.006\ g\ cm^{-3}$ versus $0.138 \pm 0.004\ g\ cm^{-3}$, respectively).

3.2. Moisture and water absorption

A number of factors (e.g. relative humidity, storage time, PLA content, and plasticizer content) affect moisture content of starch and starch/PLA foams. The effects of relative humidity, storage time, and PLA content on moisture content of various starch-based foams are illustrated in Fig. 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 PLA 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 PLA content. The decrease in the moisture absorption with increasing PLA content is due to the fact that PLA is less hygroscopic than starch (Averous, Fauconnier, Moro, & Fringant, 2000). It is interesting to note however, that the addition of PLA affected on the moisture absorption level, but not appreciably the kinetics of the absorption (see Fig. 2b for the almost identical gradient of the curves between 1 and 4 days).

Water absorption of starch and starch/PLA foams with varying PLA content has been investigated and it was found



(a) (b)

Fig. 1. Scanning electron micrograph of cross sections of (a) pure starch foam and (b) starch/30 wt% PLA hybrid foam.

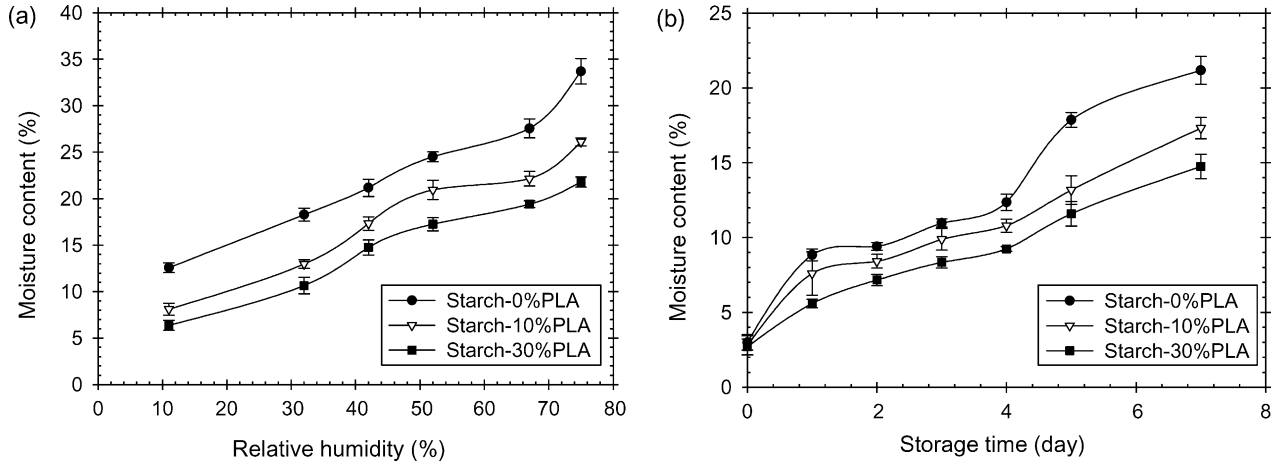


Fig. 2. Moisture content of pure starch and starch/PLA foams as a function of (a) relative humidity (the storage condition was 7 days and 25 °C) and (b) storage time (the storage condition was 42% RH and 25 °C).

to decrease with increasing PLA content (i.e. from 127±4% for pure starch foam down to 96±2% and to 77±3% for starch/PLA foams having the PLA content of 10 and 30 wt%, respectively). This finding is in general accordance with our earlier reports on starch-based hybrid forms having poly(vinyl alcohol) (PVA) and poly(ε-caprol actone) (PCL) as the blending components (Preechawong, Peesan, Rujiravanit, & Supaphol, 2004; Preechawong, Peesan, Supaphol, & Rujiravanit, 2004) in which water absorption of these hybrid foams was also a decreasing function of the content of the blended polymers (i.e. from 127±4% for pure starch foam down to 93±2% and to 77±2% for the hybrid foams having the PCL content of 10 and 30 wt%, respectively, and to 88±2% and to 74±3% for the hybrid foams having the PVA content of 10 and 30 wt%, respectively). The decrease in the water absorption of starch/PLA foams with increasing PLA content could, again, be explained as a result of the less hygroscopicity of PLA in comparison with starch (Averous et al., 2000).

Due to its hygroscopic nature, starch is prone to moisture and water absorption. In part, water molecules act as a natural plasticizer for starch, which helps render starch from being a hard and rigid plastic in its completely dry state to becoming 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 causes some problems, especially when it absorbs too much water. An alternative approach is to use other chemicals as a plasticizer for starch.

In this present 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. The presence of three hydroxyl groups in a glycerol molecule should be responsible to the highest tendency for moisture absorption of glycerol-plasticized starch foams observed.

3.3. Mechanical properties

3.3.1. Effect of relative humidity

Mechanical properties of starch and starch/PLA 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 Fig. 4. The values of both the tensile and flexural strength for all of the foam specimens investigated were found to increase initially with increasing relative humidity, reach

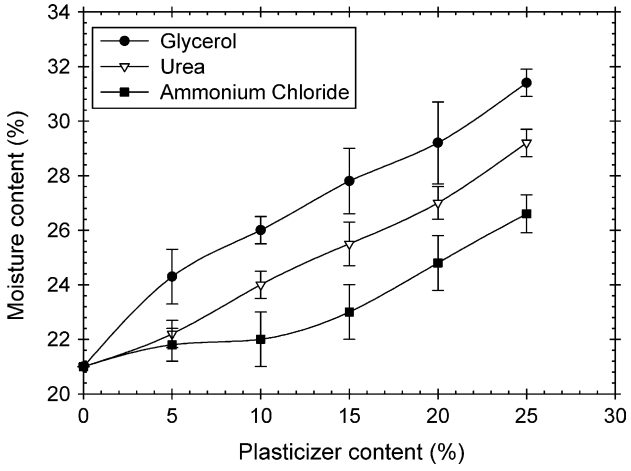


Fig. 3. Moisture content of pure starch foams as a function of plasticizer content. The storage condition was 42% RH and 25 °C for 7 days.

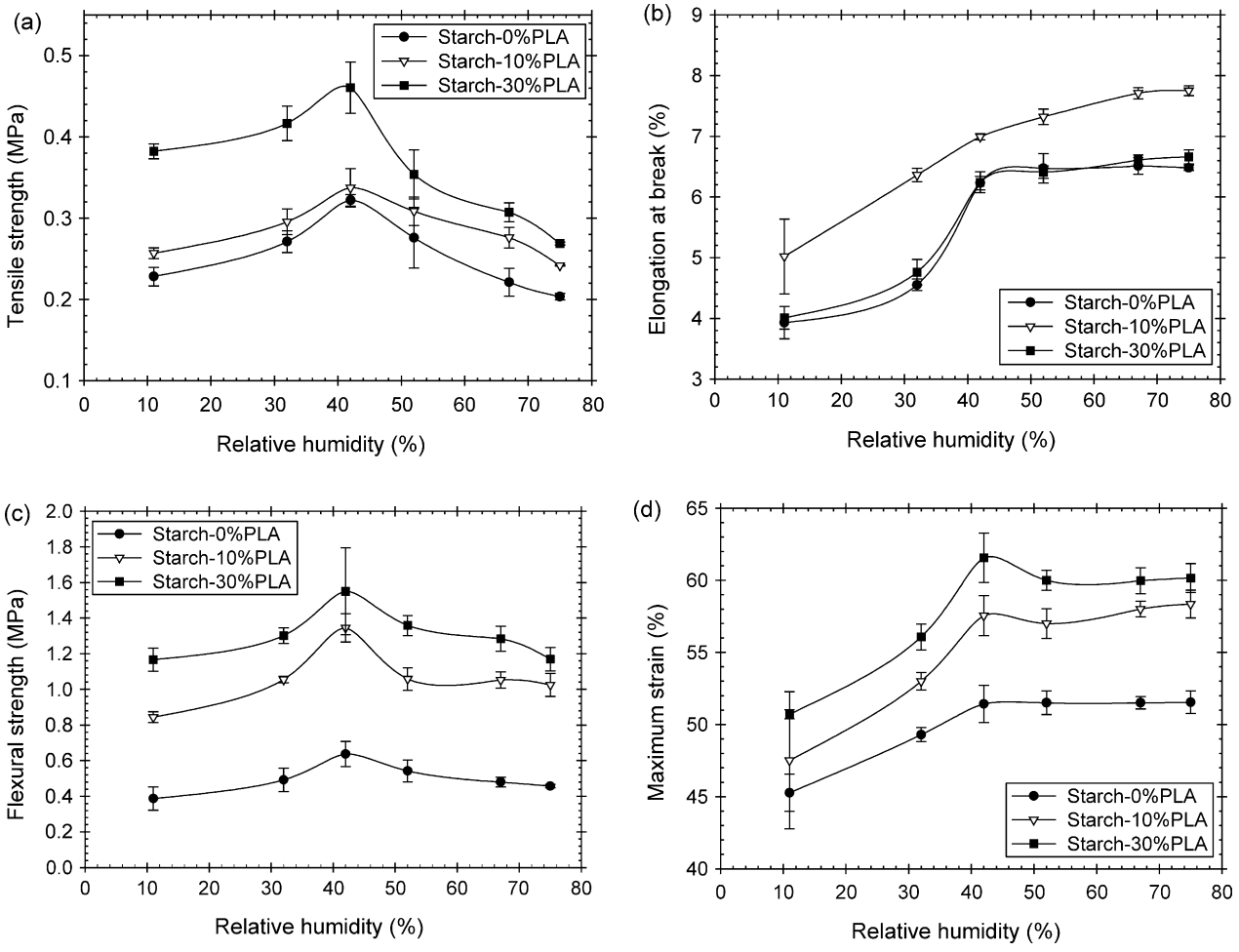


Fig. 4. Mechanical properties [i.e. (a) tensile strength, (b) percentage of elongation at break, (c) flexural strength, and (d) maximum flexural strain] of pure starch and starch/PLA foams as a function of relative humidity. The storage condition was 25 °C for 7 days.

a maximum at the relative humidity of 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 (Shogren, Lawton, Doane, & Tiefenbacher, 1998). For a given value of relative humidity, addition of PLA 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 initially increase with increasing relative humidity level (up to ca. 42% RH) and then became practically constant at relative humidity levels greater than ca. 42% RH (with an exception to the starch/10 wt% PLA foams which were found to increase slightly). The increased mobility of starch molecules due to the plasticizing effect of absorbed moisture should be responsible for the observed increase in both the percentage of elongation at break and maximum flexural strain with increasing relative humidity (Shogren, Lawton, Tiefenbacher, & Chen, 1998). The results observed were in general agreement with the results of starch/PVA and starch/PCL hybrid foams earlier reported (Preechawong, Peesan, Rujiravanit, & Supaphol, 2004; Preechawong, Peesan, Supaphol, & Rujiravanit, 2004).

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 the storage time of 2 days, and decrease with further increase in the storage time. The amount of absorbed moisture at the 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 8.4 ± 0.5 and $7.2 \pm 0.4\%$ for starch/PLA foams having the PLA 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 level of relative humidity, the presence of PLA was responsible for an appreciable increase in both the tensile and flexural

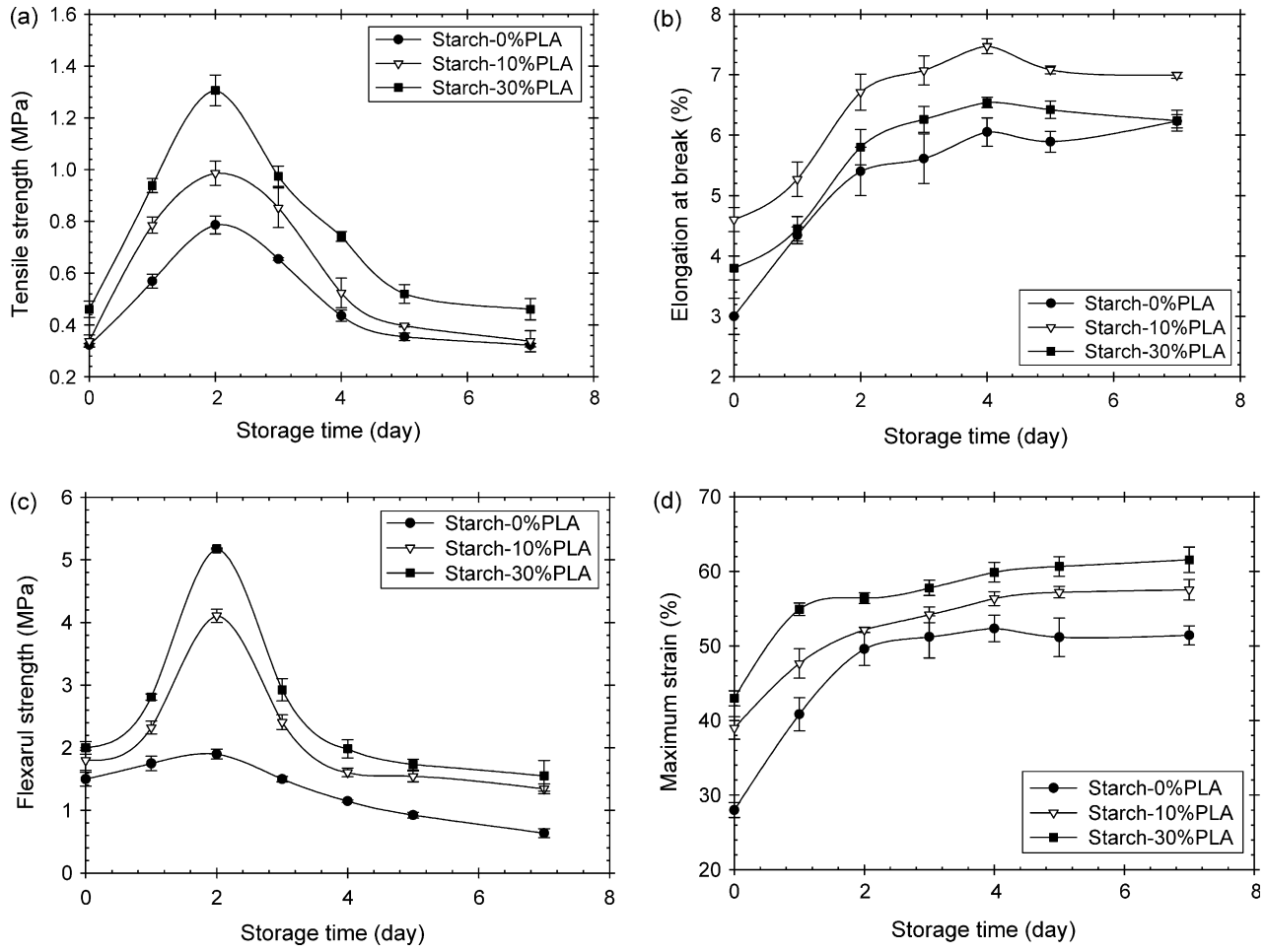


Fig. 5. Mechanical properties [i.e. (a) tensile strength, (b) percentage of elongation at break, (c) flexural strength, and (d) maximum flexural strain] of pure starch and starch/PLA foams as a function of storage time at 42% RH and 25 °C.

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 an increase in the storage time (up to 2–4 days) and then became practically unchanged with further increase in the storage time. The findings were, again, in general congruence with the results of starch/PVA and starch/PCL hybrid foams earlier reported (Preechawong, Peesan, Rujiravanit, & Supaphol, 2004; Preechawong, Peesan, Supaphol, & Rujiravanit, 2004).

3.3.3. Effect of moisture content

Since Fig. 2 shows relationship between the moisture content and the relative humidity (for a fixed storage time of 7 days) as well as the storage time (for a fixed relative humidity of 42% RH), the mechanical properties which were reported as a function of relative humidity in Fig. 4 and as a function of storage time in Fig. 5 can be also reported as a function of moisture content instead. Fig. 6 illustrates the effect of moisture content on mechanical properties of all of the starch-based foams investigated. Clearly, all of the mechanical properties investigated exhibited a finite relationship with the moisture content in the foam specimens.

Apparently, the values of both the tensile and flexural strength for all the foam specimens investigated were found to increase initially with increasing moisture content, reach a maximum (i.e. at $9.4 \pm 0.3\%$ for pure starch foam and 8.4 ± 0.5 and $7.2 \pm 0.4\%$ for starch/PLA foams having the PLA content of 10 and 30 wt%, respectively), and decrease with further increase in the moisture content. Both percentage of elongation at break and maximum flexural strain of all the foam specimens investigated were found to increase initially with an increase in the moisture content of up to ca. 9–12%, after which they became practically unchanged with further increase in the moisture content.

In the food literature, it is known that a brittle-to-ductile transition or the loss of crispness for starch-based materials occurs at the moisture content of about 9% (Li, Kloeppel, & Hsieh, 1998), thus the observed maxima in the tensile and flexural strength of these foam specimens at ca. 7–9% moisture content and the loss of stiffness at ca. 9 to 12% moisture content should correspond to the loss of crispness of the starch-based foams and, interestingly, the results

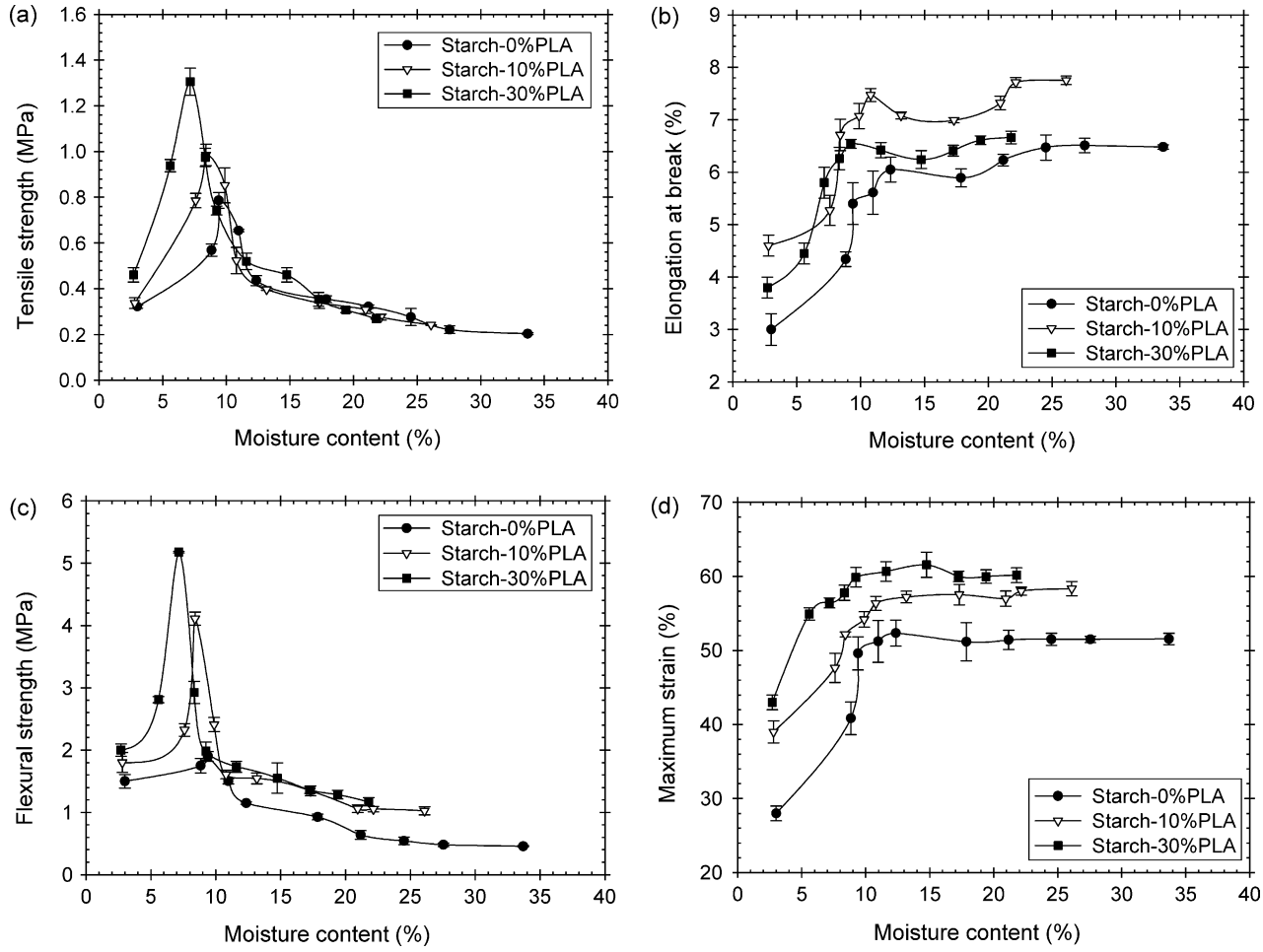


Fig. 6. Mechanical properties [i.e. (a) tensile strength, (b) percentage of elongation at break, (c) flexural strength, and (d) maximum flexural strain] of pure starch and starch/PLA foams as a function of moisture content.

suggested that the loss of crispness of the starch-based foams was found to occur at a bit lower moisture content with increasing PLA content. Interestingly, the addition of PLA made the forms more tolerable to low moisture level, while remaining flexible.

3.3.4. Effect of PLA content

The effects of PLA 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 strength of pure starch foam and starch/PLA foams having the PLA content of 10 and 30 wt% was found to be 0.79 ± 0.03, 0.99 ± 0.05, and 1.31 ± 0.06 MPa, respectively, and the percentage of elongation at break was found to be 5.4 ± 0.4, 6.7 ± 0.3, and 5.8 ± 0.3%, respectively; while, the flexural strength was found to be 2.9 ± 0.1, 4.1 ± 0.1, and 5.2 ± 0.0 MPa, respectively, and the maximum flexural strain was found to be 49.6 ± 2.2, 52.2 ± 0.3, and 56.4 ± 0.7%, respectively.

According to the values reported above, both tensile strength and flexural strength of these starch-based foams were found to increase with increasing PLA content. Basically, PLA has greater tensile strength than starch (i.e. 66 versus 22 MPa, respectively). As a result, addition of PLA in 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 PLA added (i.e. 10 wt%) and then decrease with further increase in the PLA content (i.e. 30 wt%) (see Fig. 5b). The initial increase in the percentage of elongation at break for starch/PLA foam containing the PLA content of 10 wt% might be explained based on the higher flexibility of PLA versus starch molecules (Shogren, Lawton, Doane,& Tiefenbacher, 1998) and on the ease for crack formation at the interface between PLA and starch phases. Upon further increase in the PLA content, the rigidity of the foams increased appreciably (a direct result of the higher tensile strength of PLA versus starch) (Liu, Feng, & Yi, 1999), leading to a reduction in the percentage of elongation at break for starch/30 wt% PLA foams. The maximum flexural strain of the foams was found to increase significantly with addition of small amount to PLA (i.e. 10 wt%) and then increase very

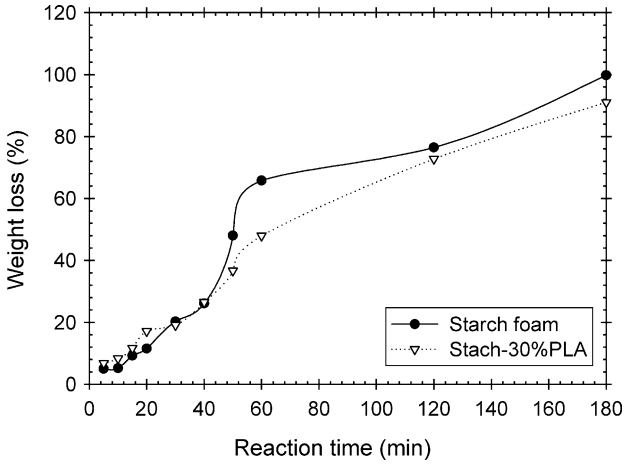


Fig. 7. Enzymatic degradation by α-amylase at 60 °C for (●) pure starch foams and (○) starch/30 wt% PLA hybrid foams.

slightly with further increase in the PLA content (i.e. 30 wt%). The most likely explanation for such improvement in the maximum flexural strain may be due to the inherent flexibility of PLA molecules in comparison with that of starch molecules (Shogren, Lawton, Tiefenbacher, & Chen, 1998).

3.4. Enzymatic degradation

Enzymatic degradation of starch and starch/PLA foams was tested by an in vitro hydrolysis with α-amylase at 60 °C and the results are expressed as a function of reaction time in Fig. 7. All of 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 for pure starch foams was observed at the onset reaction time of around 40 min, but no abrupt increase in the percentage of weight loss was observed for starch/30 wt% PLA hybrid foams. For pure starch foams, within the 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 with this time interval. Comparison between the percentage of weight loss curves of pure starch and starch/PLA foams suggests that starch/PLA foams was, in general, less subservient to enzymatic hydrolysis by α-amylase than pure starch foams at 'long' reaction times (i.e. greater than 40 min). This is in contrast to starch/PCL foams which was shown to be more subservient to enzymatic degradation by α-amylase than pure starch foams (Preechawong, Peesan, Supaphol, & Rujiravanit, 2004).

4. Conclusions

In the present contribution, starch/poly(L-lactic acid) (PLA) hybrid foams were prepared by baking a mixture of starch, PLA, and other ingredients in a hot mold. The effects of conditioning relative humidity, conditioning storage time, and PLA 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/PLA 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 PLA helped promote the resistance to water absorption of the hybrid foams. In all of 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). The loss of crispness of the starch-based foams was found to occur at the moisture content of around 7–9%. Addition of PLA improved the ultimate tensile strength and the elongation at break of the composite foams. Lastly, the enzymatic degradability of both starch and starch/PLA foams by α-amylase was found to increase with increasing reaction time and addition of PLA resulted in the hybrid foams being less subservient to enzymatic degradation by α-amylase than pure starch foams, especially for 'long' reaction times.

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