

## CHAPTER IV

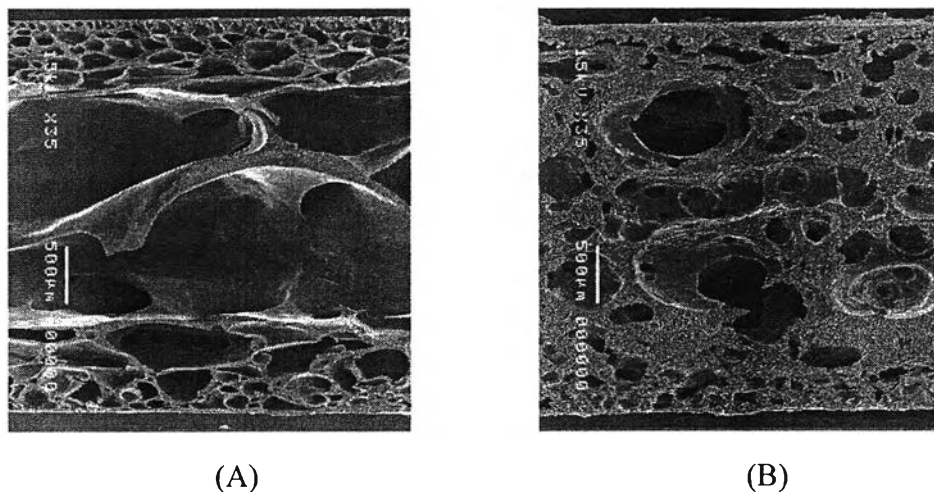
### RESULTS AND DISCUSSION

The foaming process of a starch batter inside a hot mold can be divided into several steps. First, the temperature of the batter increases above the gelatinization temperature or to the boiling point. Next, the starch gelatinizes and becomes a thick paste at which point the entrapped water rapidly evaporate into steam. The steam trapped in the paste expands causing the paste to fill the mould and begin to exit the vents around the edge of the mould. In the final and longest step of the baking process, the starch foam gradually dries to obtain the foam having the residual moisture content of ca. 2–4% (Soykeabkaew, Supaphol, & Rujiravanit, 2004).

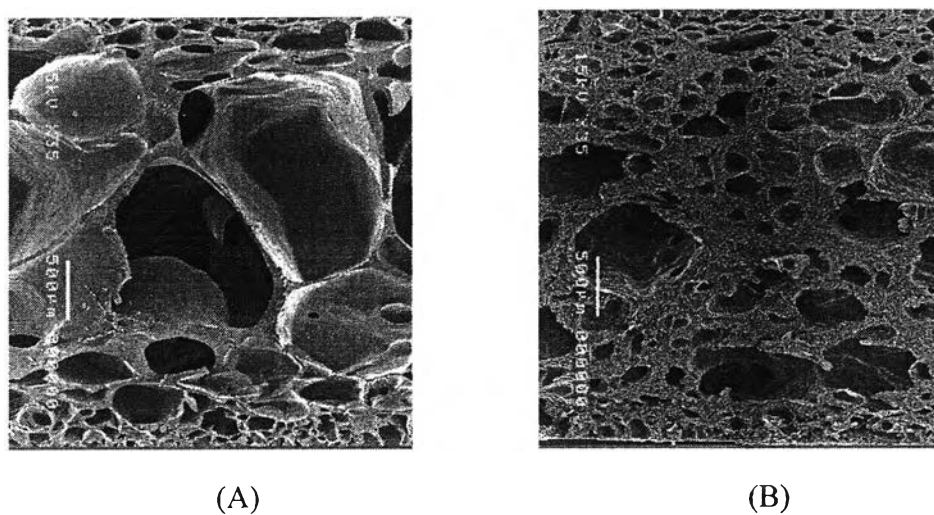
In order for foam formation to occur, starch pastes must have a certain rheological characteristics. First, the starch paste must have sufficient elastic strength so that expanding steam bubbles are trapped in the paste rather than breaking with the consequent collapse of the foam. It has been found, for example, that a corn starch-water dispersion that has been jet-cooked will only form a dried film rather than foam after baking. Jet-cooking completely disrupts starch granules giving a more fluid starch paste. This point, the starch paste must have sufficient elastic strength in order to withstand the force of the rapid expansion without a permanent, structural damage. Secondary, the viscosity of the starch paste must increase rapidly after expansion to stabilize the foam structure and prevent collapse as water evaporates. (Shogren, Lawton, Doane, & Tiefenbacher, 1998).

Selected scanning electron micrographs of pure native tapioca starch foam, 50 wt% natural rubber/native tapioca starch composite foam are shown in Fig. 4.1 and pure octyl tapioca starch foam and 50 wt% natural rubber/octyl tapioca starch composite foam are shown in Fig. 4.2 All 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 contact 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).



**Fig. 4.1** Scanning electron micrographs for cross-sections of pure native tapioca starch based foam (A.) and 50%wt of natural rubber/native tapioca starch composite foams (B).



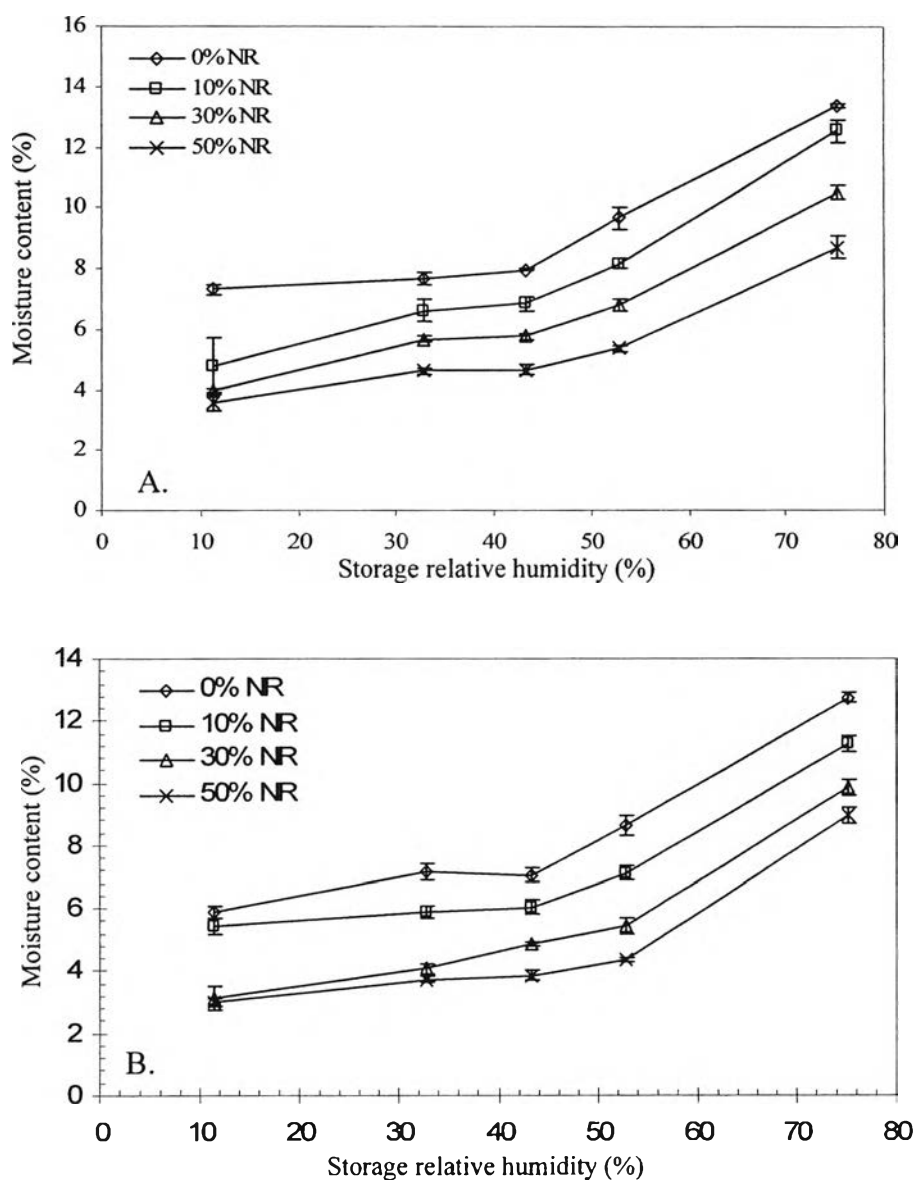
**Fig. 4.2** Scanning electron micrographs for cross-sections of pure octyl tapioca starch based foam (A.) and 50%wt of natural rubber/octyl tapioca starch composite foams (B).

Even though, the incorporating natural rubber into starch-based foam was made the interior structure was apparently denser. This can be verified based on the fact that the density of this composite foam was greater than that of the pure starch foam (i.e.  $0.17 \pm 0.0071 \text{ gcm}^{-3}$  for pure native tapioca starch foam and  $0.57 \pm 0.035 \text{ gcm}^{-3}$  for native tapioca starch foam with 50%wt natural rubber. These values measure after equilibrated at 52.9 %relative humidity for 7 days).

Because, the smallest repeating unit of starch is a glucose and each unit of glucose contains 3 hydroxyl groups so starch is naturally hydrophilic while natural rubber, contains 93-95% cis 1,4-poly-isoprene is naturally hydrophobic. Due to the difference in polarity between starch and natural rubber, phase separation was occurred. Shey *et al.*, (2006) prepared baked starch-based foam with natural rubber latex. In the mixing process, they found little white spots contained in starch-based batter. These spots are due to the coagulation of latex before baking. To stabilize and prevent the coagulation of natural rubber latex, Terix X10, a non ionic surfactant, was used. A suitable amount of Terix X10 was 0.17%wt of the added distilled water.

The effects of storage relative humidity and natural rubber content on moisture content of various starch-based foams are illustrated in Fig.4.3 For a fixed percent natural rubber content, the moisture content in all of the foams studied (after being equilibrated in various specified storage relative humidity for at least 7 days at 25 °C) was found to increase with increasing relative humidity. Specifically, the resulting moisture content of starch-based foam with 0, 10, 30 and 50 %wt natural rubber content which equilibrated at 52.9 % RH at least 7 days was found to be ca. 9.66, 8.16, 6.79 and 5.35% respectively. Shey, Imam, Glenn and Ort (2006) reported the moisture content for potato starch-based foam which incorporating with natural rubber latex at 0, 9, 18 and 27 wt% of added water after 7 days of conditioning at 50% RH to be ca. 9.6, 9.1, 7.9 and 7.7%, respectively. Obviously, our results seem to agree fairly well with those reported by these authors.

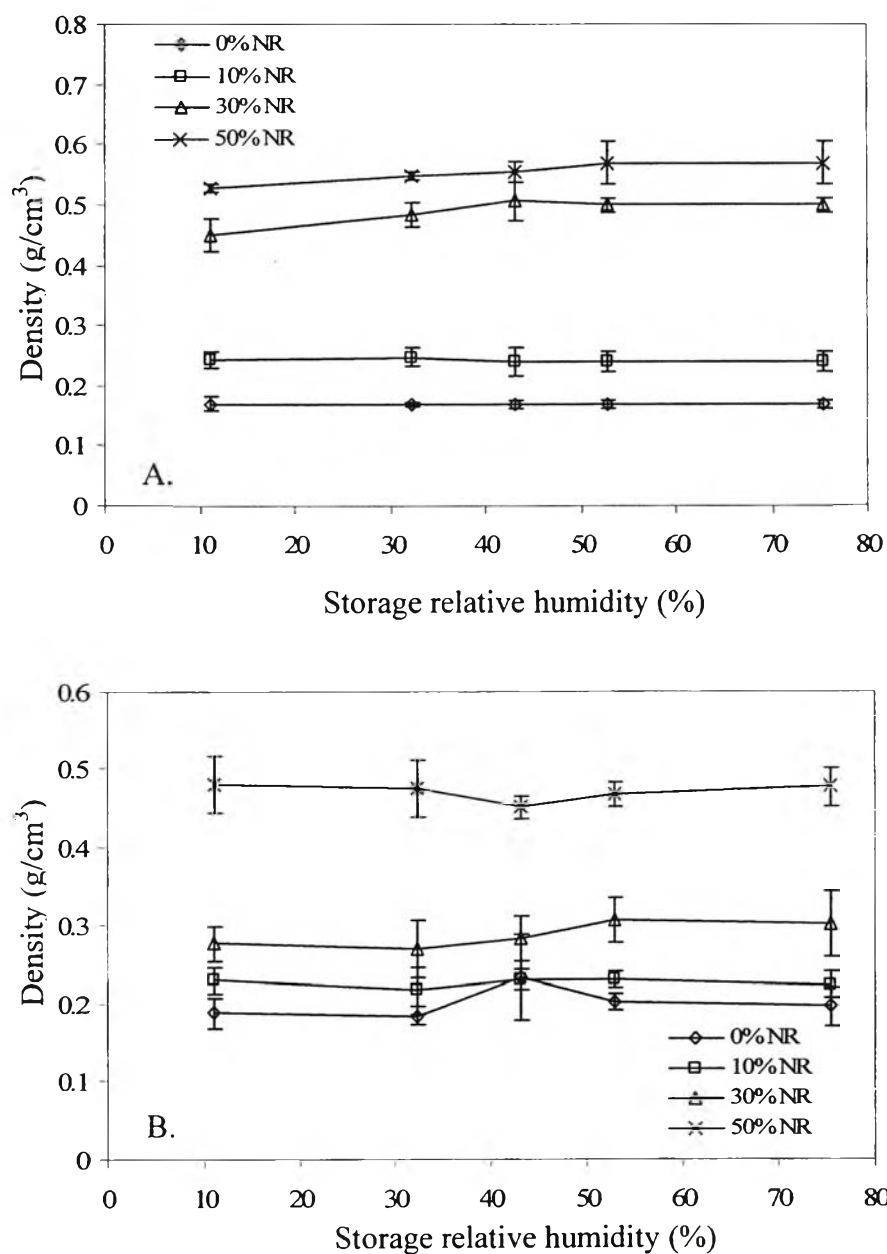
For a given relative humidity level, the moisture content was found to decrease with increasing natural rubber content. The decrease in the tendency to absorb moisture with increasing natural rubber content is due to the fact that natural rubber is a naturally hydrophobic polymer.



**Fig. 4.3** Effects of storage relative humidity and natural rubber content on moisture content for natural rubber/starch composite foams, native tapioca starch (A.) and octyl tapioca starch (B.).

Between native tapioca starch composite foams and octyl tapioca starch composite foams, the octyl tapioca starch composite foams showed lower moisture content than native tapioca starch is due to the less polarity of octyl tapioca starch

than native tapioca starch so native tapioca starch was more susceptible to absorb moisture than octyl tapioca starch.



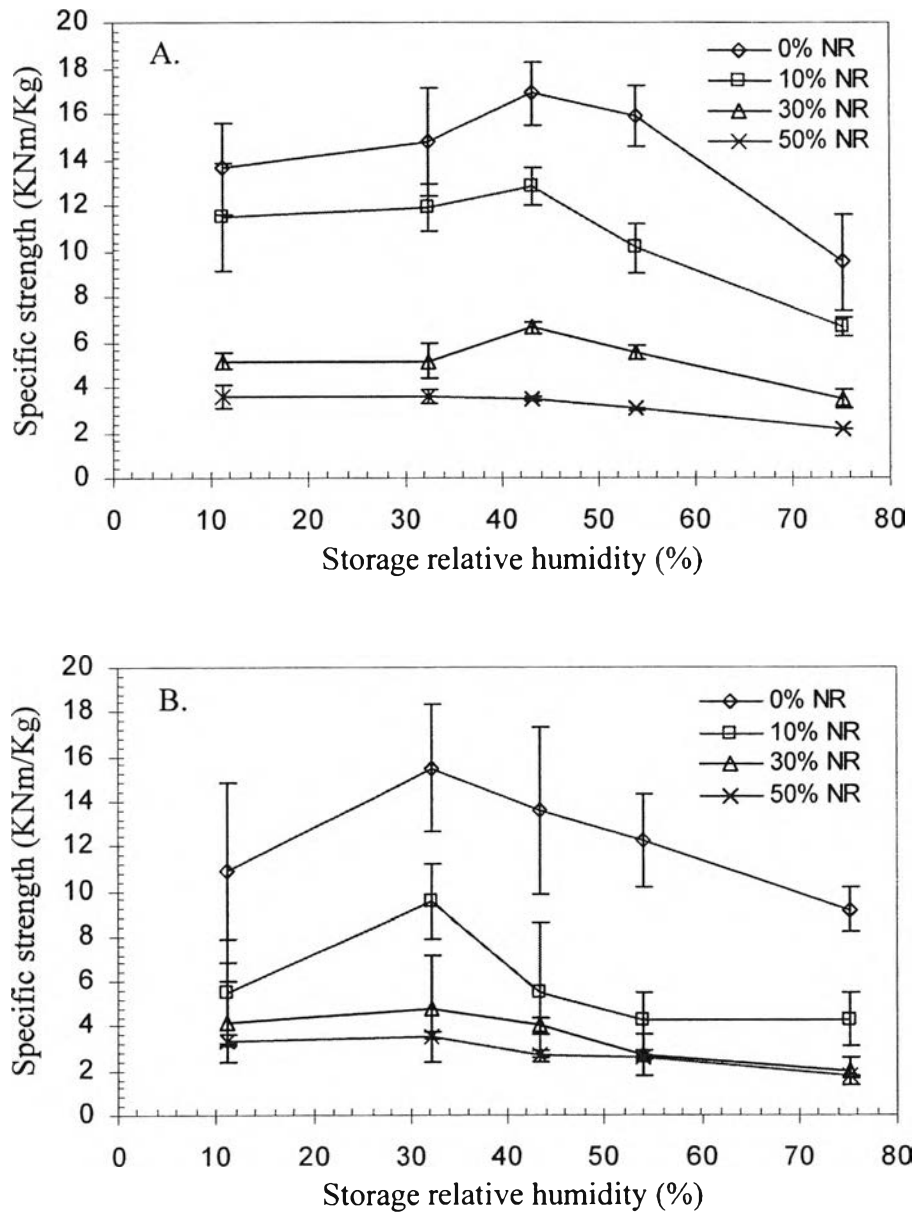
**Fig.4.4** Effects of storage relative humidity and natural rubber content on density of natural rubber/starch composite foams, native tapioca starch (A.) and octyl tapioca starch (B.).

Due to its hygroscopic nature, starch is prone to moisture 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 (Preechawong *et al.*, 2004). An alternative approach to modified starch-based foam into flexible plastic but less moisture absorption can be modified by using flexible hydrophobic polymer.

In this contribution, natural rubber was used as modifying agent in order to improve flexibility and moisture resistance of as prepared starch-based foam so we incorporated natural rubber latex in the batter formulation. The solids in natural rubber latex are comprised mainly of *cis*-1,4-polyisoprene. When this latex cures or dries, an elastic and hydrophobic material is produced. However, before the latex is cured, it is in an aqueous emulsion, which allows the rubber to be evenly distributed throughout the batter in the production of baked starch foams (Shey *et al.*, 2006). Fig. 4.3 shows moisture content of starch-based foams after being conditioned at 11.3, 32.8, 43.2, 52.9, 75.3% RH and 25 °C for 7 days as various natural rubber contents. Obviously, starch foams containing natural rubber had a lower tendency to absorb moisture.

In order to evaluate the effects of each parameter on mechanical properties such as natural rubber content and storage relative humidity. The reported properties were divided by its density to obtain the specific properties such as specific flexural strength and specific flexural modulus. Only maximum flexural strain was reported in the form of strain. Fig. 4.4 illustrates the effects of natural rubber content on the density of starch-based foam with various the storage relative humidity. The density of starch-based composite foams increased with increasing the natural rubber content which was not surprising, as latex does not foam upon baking whereas storage relative humidity do not have much effect on foam density. At higher density starch-based composite foams became smaller average cell size and thicker cell wall (Shogren *et al.*, 2002) Figs. 4.8-4.9 verify that the average cell size of starch-based composite foams was decreased with increasing natural rubber content. Due to the

density changing of starch-based composite foams were affected to the mechanical properties of starch-base foam (Soykeabkaew *et al.*, 2004). In order to eliminate this effect, the mechanical properties of starch-based composite foams were reported in term of specific properties.

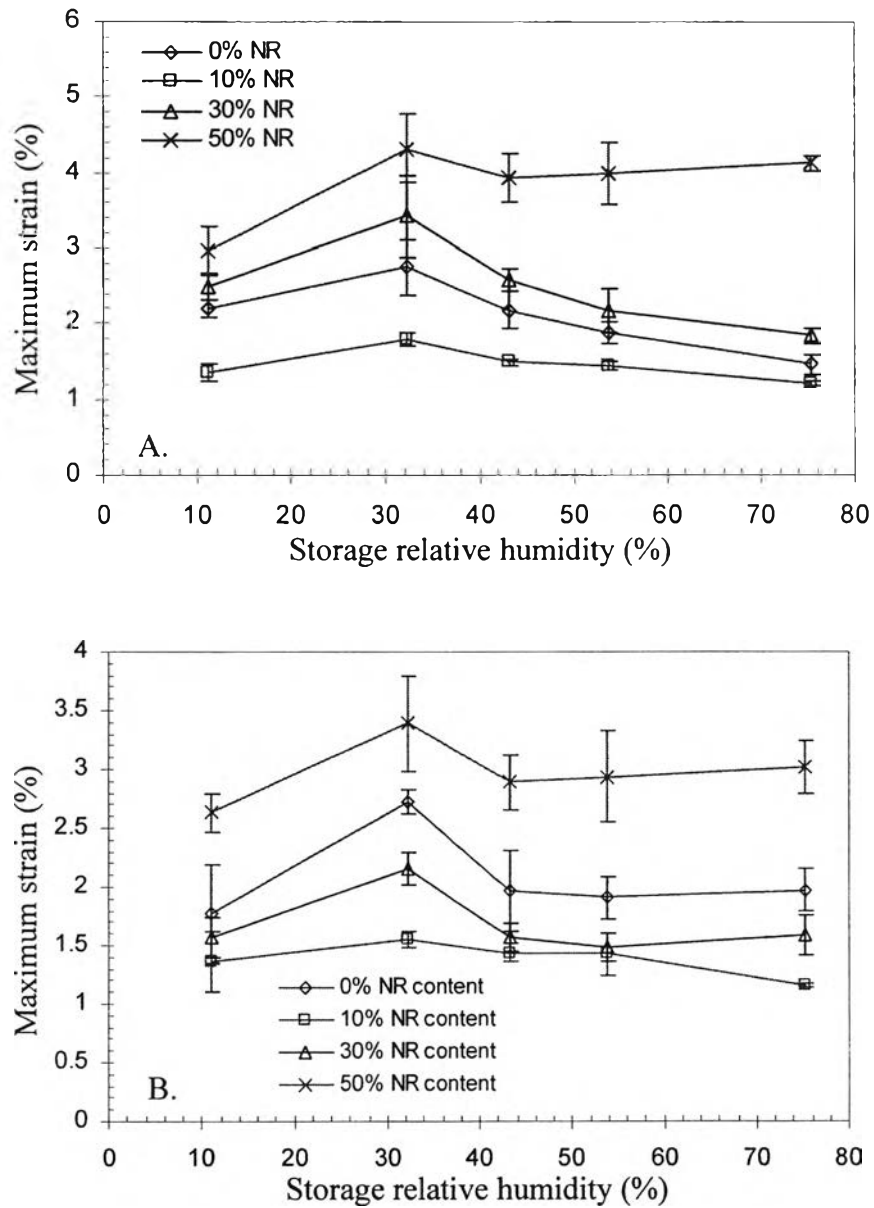


**Fig. 4.5** Effects of storage relative humidity and natural rubber content the specific flexural strength for (A) native tapioca starch and (B) Octyl tapioca starch composite foams.

The effects of natural rubber content and storage relative humidity on the specific flexural strength, specific flexural modulus and maximum flexural strain of starch-based foam are illustrated in Figs. 4.5 - 4.7 respectively. In Fig. 4.5, the specific flexural strength for all of the natural rubber/starch composite foams showed similar dependence on the storage relative humidity, in that it was exhibited lower than the pure starch foam. With an increase in the natural rubber content, the specific flexural strength was found to decrease monotonically. For a given natural rubber content, the flexural strength of the foam specimens exhibited dependence on the storage relative humidity, in that it increased initially with increasing relative humidity to reach a maximum at the relative humidity of 43.2 and 32.8% RH for native tapioca starch and octyl tapioca starch respectively, and then decrease with further increase in the relative humidity.

In Fig. 4.6, the maximum flexural strain for all of the prepared natural rubber/starch composite foams exhibited similar dependence on the storage relative humidity, in that it increased with increasing storage relative humidity up to 32.8 %RH where the maximum flexural strain reached a maximum and then decreased with further increase in the storage relative humidity. For a given storage relative humidity, native tapioca starch composite foam exhibited greater maximum flexural strain than did the pure native tapioca starch foam, with an exception on the 10 %wt of natural rubber content which exhibited lower maximum flexural strain than the native tapioca starch foams at all natural rubber contents. The maximum flexural strain for native tapioca starch composite foams was found to increase with increasing fiber content. In the case of octyl tapioca starch composite foams, only at 50 %wt of natural rubber content greater maximum flexural strain than did the pure octyl tapioca starch foam.





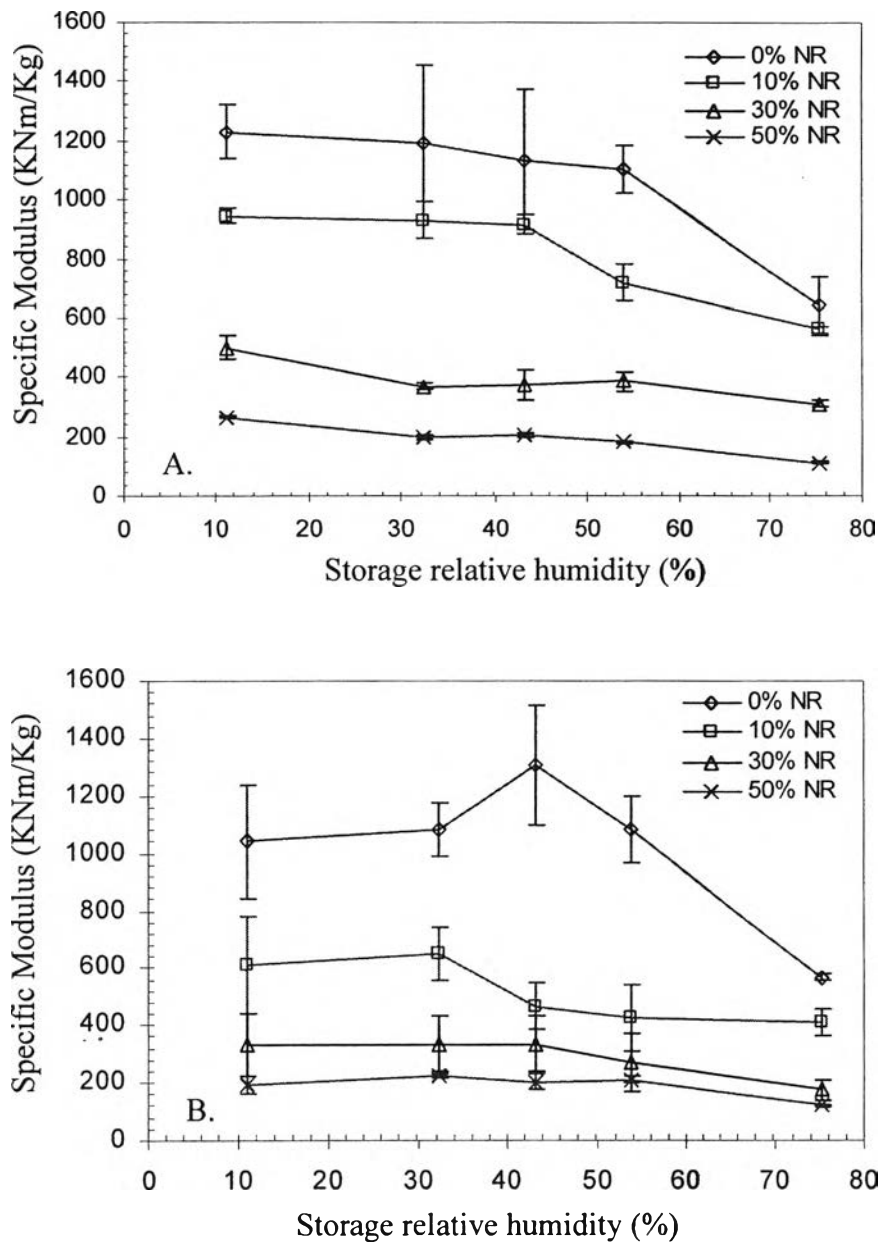
**Fig. 4.6** Effects of storage relative humidity and natural rubber content on the maximum flexural strain for (A) native tapioca starch and (B) octyl tapioca starch composite foams.

In Fig. 4.7, the specific flexural modulus for all of the prepared natural rubber/starch composite foams showed a similar dependence on the storage relative humidity, in that it decreased with increasing storage relative humidity. An exception to the observed trend was observed for the pure octyl tapioca starch foams in which specific flexural modulus initially increased, reached a maximum value at the storage

relative humidity of around 43.2 %RH, and then decreased with further increase in the storage relative humidity. For a fixed storage relative humidity, most of the natural rubber/starch composite foams showed lower specific flexural modulus than did the pure starch foam and the specific flexural modulus was found to decrease with increasing natural rubber content.

Similar results were also reported in the literature (Glenn, Orts, & Nobes, 2001b). Glenn, Orts, and Nobes (2001b) studied the effect of moisture content on mechanical properties of starch-based panels having the moisture contents of 3.4, 7.5, 11.1, and 14.5%. For flexural strength and flexural strain at maximum force, the starch-based panels behaved very similarly to what was observed in the present study in that these property values increased initially with increasing moisture content, reached a maximum at the moisture content of around 7.5%, and then decreased with further increase in the moisture content. For flexural modulus of elasticity, they reported that it decreased with increasing moisture content, which is in general accord with our results. In the food literature, it is known that a brittle-to-ductile transition or the loss of crispness for starch-based foams occurs at the moisture content of about 9% (Li, Kloeppel, & Hsieh, 1998). This could explain the observed maxima in both the specific flexural strength and the maximum flexural strain of pure starch foam and natural rubber/starch composite foams at the moisture content of around 8–9%.

Possible explanation for the low values of the observed specific flexural strength and maximum flexural strain for pure starch foam and natural rubber/starch composite foams at low and high moisture contents may be the brittleness of the materials at low moisture contents and the plasticizing effects due to the presence of large amount of absorbed moisture at high moisture contents (Dufresne et al., 1999; Lourdin et al., 1997; Shogren, Lawton, Tiefenbacher, & Chen, 1998b). In the food literature, it is known that a brittle-to-ductile transition or the loss of crispness for starch-based foams occurs at the moisture content of about 9% (Li, Kloeppel, & Hsieh, 1998). This could explain the observed maxima in both the specific flexural strength and the maximum flexural strain of pure starch foam and natural rubber/starch composite foams at the moisture content of around 8–9%.



**Fig. 4.7** Effects of storage relative humidity and natural rubber content on the specific flexural modulus for (A) native tapioca starch and (B) Octyl tapioca starch composite foams.

The observed monotonous decrease in the flexural modulus of elasticity with increasing moisture content may be explained mainly based on the plasticizing effect, in which the increasing amount of absorbed moisture caused the foams to be less stiff (Dufresne et al., 1999; Glenn, Orts, & Nobes, 2001b).

The results also showed that, generally, addition of natural rubber latex was responsible for the much improvement in flexibility of composite foams as evidenced by the increase of the maximum flexural strain. However, 10 %wt natural rubber of native tapioca starch composite foams and 10, 30 %wt natural rubber of octyl tapioca starch composite foams showed lower maximum flexural strain than the starch composite foams at all natural rubber contents. This may be because, at low natural rubber content, rubber phase added may act as defects which can promote crack propagation, hence reducing the maximum flexural strain.

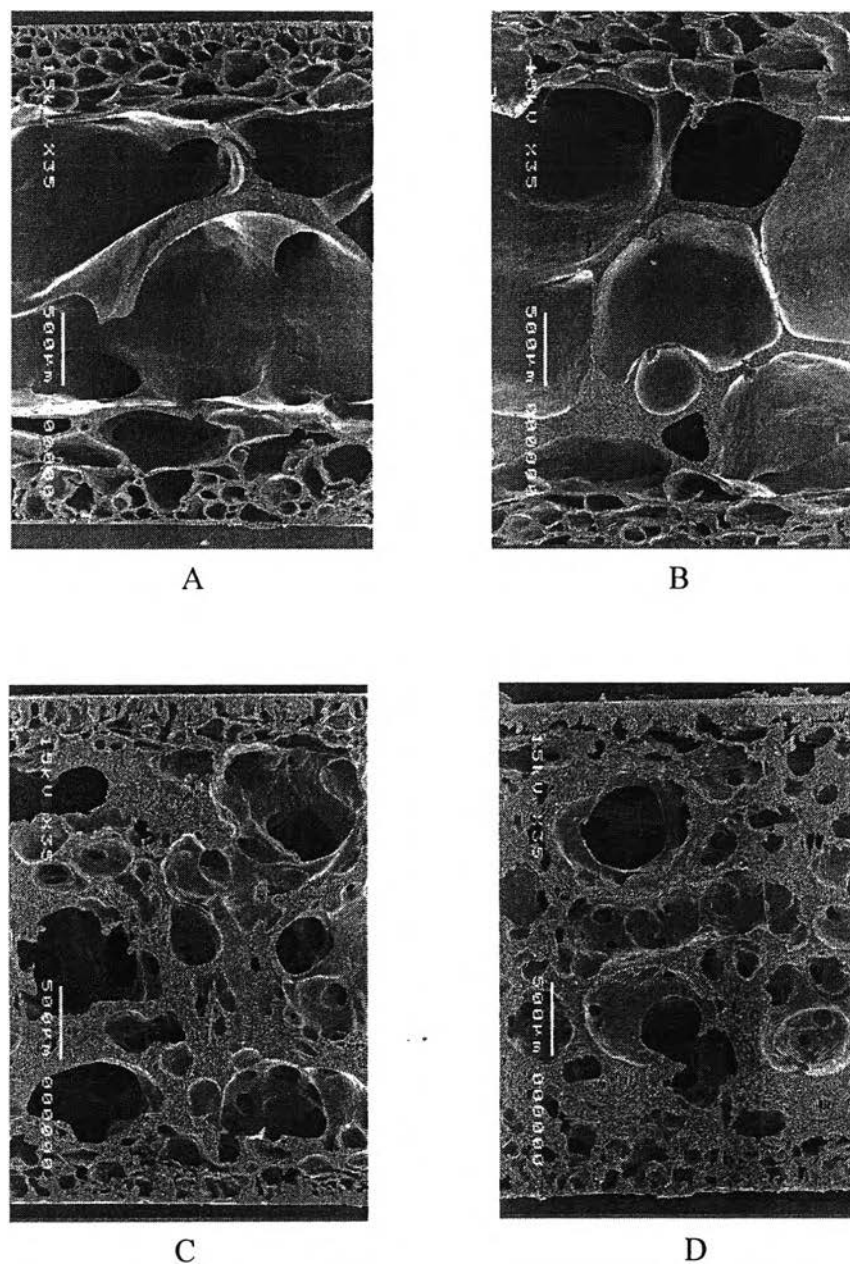
The advantage of the additional of latex into the batter is to reduce the effect of relative humidity on the flexural properties (Shey, Imam, Glenn, & Orts, 2006). As evidence by at high natural rubber content around 30 and 50 %wt natural rubber, the moisture resistance of prepared foam can be improve as shown in Fig.4.5 and 4.7, the specific flexural strength and the specific flexural modulus were changed not much when comparing with pure starch-based foam, it tended to be a constant value even low or high storage relative humidity.

In general, native starch commonly existed in granule structure with about 15–45% crystallinity (Zobel, 1998), and starch-based materials were susceptible to aging and starch recrystallization (retrogradation). Starch based-articles plasticized with glycerol, a conventional starch-based material, was thought to tend to retrogradation after being stored for a period of time, and this retrogradation embrittled starch based-materials (Van Soest & Knooren, 1997). The retrogradation of starch-based articles came from a lot of hydrogen interaction between hydroxyl groups of starch. Between native tapioca starch composite foams and octyl tapioca starch composite foams, native tapioca starch composite foams showed greater flexural properties than octyl tapioca starch ones did at all natural rubber content (see Fig. 4.5). The lower values of the flexural properties may result from the octyl group of octyl tapioca starch; the octyl group may disturb the retrogradation of octyl tapioca starch composite foams.

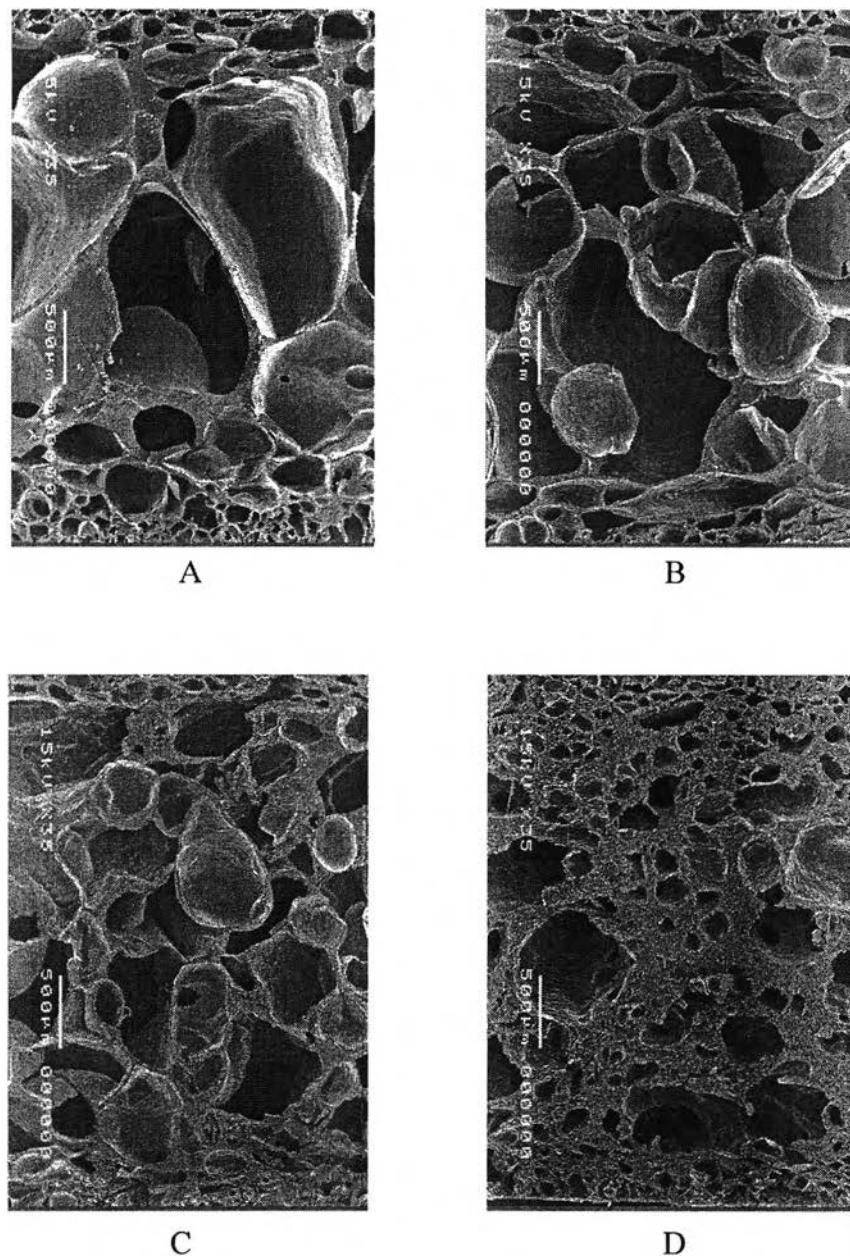
As it was pointed earlier, the natural rubber latex does not foam upon baking so the density of starch-based composite foams increased with increasing the natural rubber content. According to Fig. 3, higher natural rubber content resulted in higher density. At higher density, the natural rubber/starch composite foams became smaller

average cell size and thicker cell wall. Figs. 4.8 and 4.9 verify that the average cell size for all of natural rubber/starch composite foam was smaller than that for pure starch foam and the average cell size for natural rubber/starch composite foams decreased with increasing natural rubber content.

Since, the incorporated natural rubber was improving the flexibility as evidenced by increased in maximum flexural strain. Not surprisingly, the specific flexural strength as well as the specific flexural modulus also decreased with increased natural rubber content. In order to improve the specific flexural strength and specific flexural modulus, the cellulose pulp was selected as reinforcing filler.



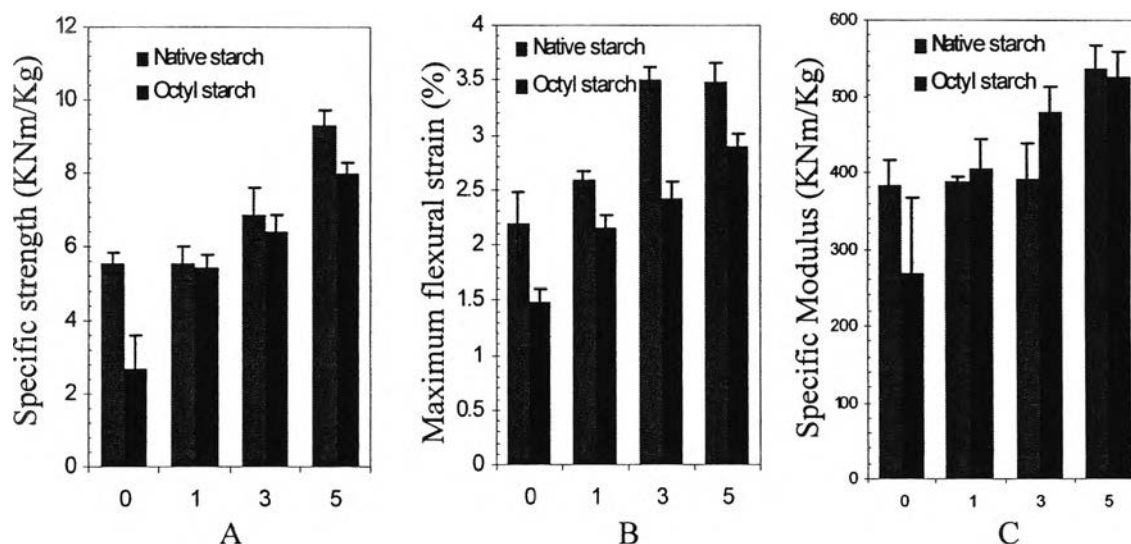
**Fig. 4.8** Scanning electron micrographs for cross-sections of (A) pure native tapioca starch foam and natural rubber/native tapioca starch composites foams at (B) 10, (C) 30, and (D) 50% natural rubber content, respectively.



**Fig. 4.9** Scanning electron micrographs for cross-sections of (A) pure octyl tapioca starch foam and natural rubber/octyl tapioca starch composites foams at (B) 10, (C) 30, and (D) 50% natural rubber content, respectively.

The effects of the cellulose pulp content, reinforcing filler, on specific flexural strength, maximum flexural strain, and specific flexural modulus for both native tapioca starch composite foams and octyl tapioca starch composite foams are illustrated in Fig. 4.10. As evidently shown in Fig. 4.10 (A) and (B), the specific flexural strength and the specific flexural modulus for both native tapioca starch composite foams and octyl tapioca starch composite foams were found to increase with increasing cellulose pulp content (reported at a fixed natural rubber content of 30 wt%). Possible explanation may be lie on the reinforcing effect. Since, the similar chemical functional groups between starch and cellulose fiber good interfacial interaction between matrix and reinforcing filler were promoted. Good interfacial interaction suggests that stress can transfer from the starch matrix to the fibers very effectively during deformation, hence giving rise to higher strength (Averous *et al.*, 2001; Lodha *et al.*, 2002). Furthermore, the presence of fibers in a batter formulation is responsible for an increase in the viscosity of the batter. The increase in the viscosity causes the batter to be less expandable, giving rise to smaller average cell size, thicker cell wall, and higher density (Shogren *et al.*, 2002). According to Table 4.1, the density for all fiber content of cellulose pulp reinforced natural rubber/starch composite foams increased with increasing fiber content. Figs. 4.11 and 4.12 verify that the average cell size for all fiber content of cellulose pulp reinforced natural rubber/starch composite foams decreased with increasing fiber content. As a result of the smaller average cell size, thicker cell wall, higher density, and the presence of reinforcing fibers, cellulose pulp reinforced natural rubber/starch composite foams appeared to exhibit improvement in the specific flexural strength and specific flexural modulus. The maximum flexural strain for both native tapioca starch composite foams and octyl tapioca starch composite foams was shown to increase with increasing fiber content (see Fig. 4.10, C ) due possibly to the increased strength of the materials (Shogren, , Lawton, Tiefenbacher, & Chen, 1998b).

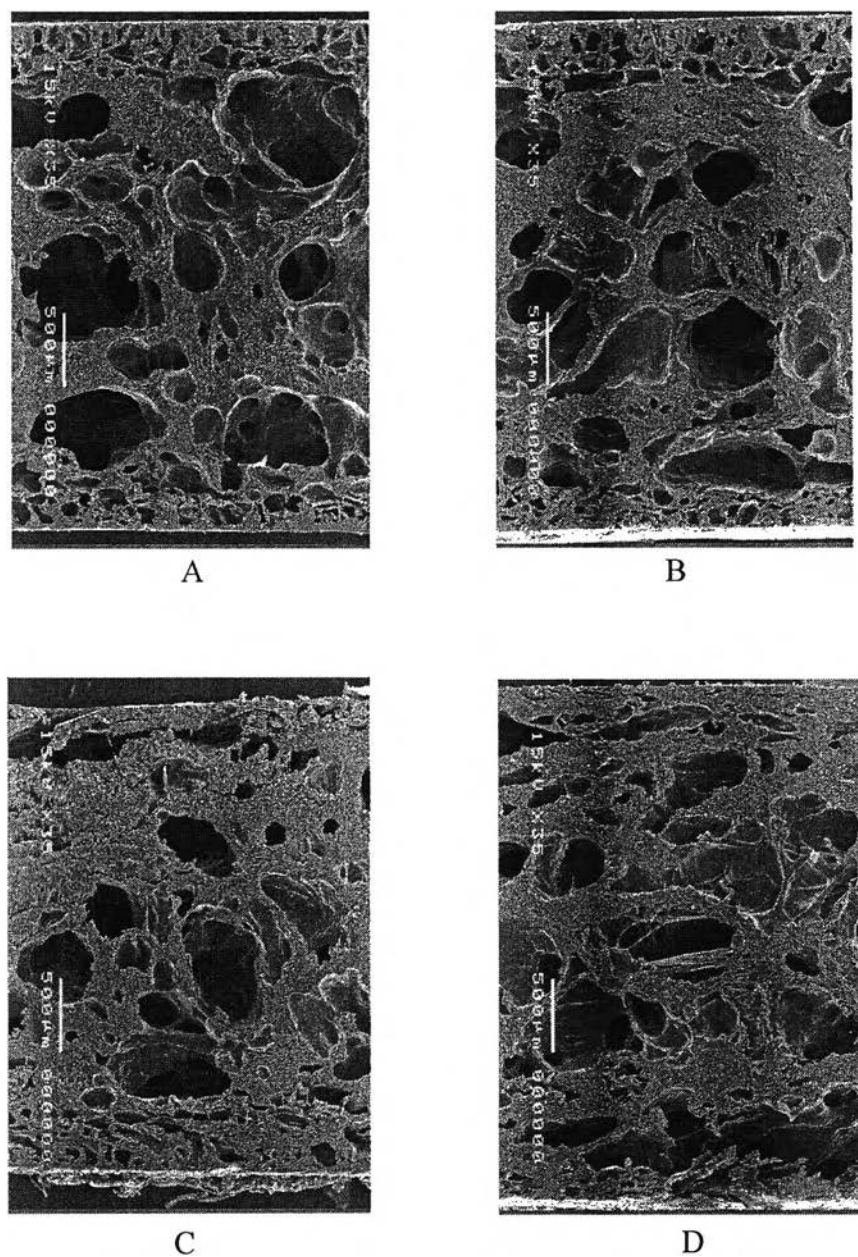




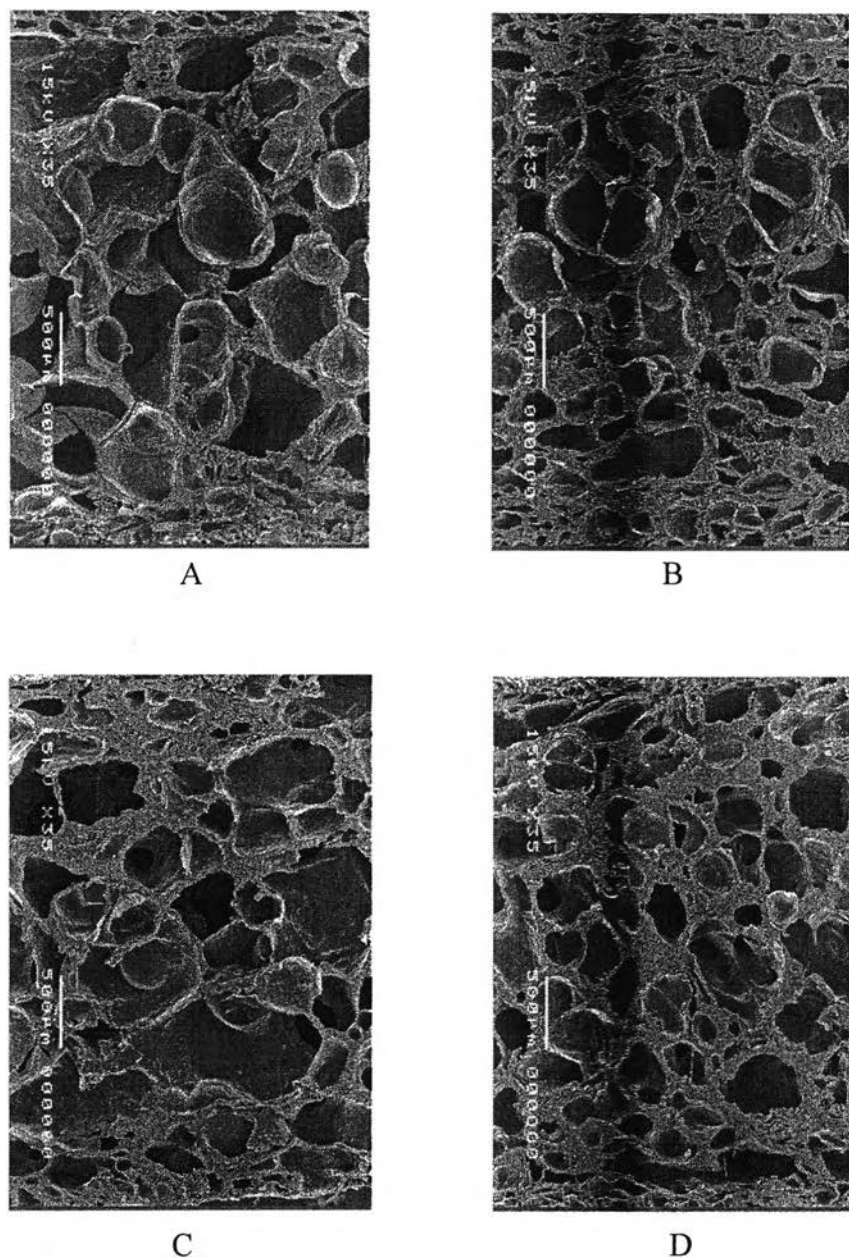
**Fig. 4.10** Effect of cellulose pulp content on the specific flexural strength (A), maximum flexural strain (B) and specific flexural modulus (C) of cellulose pulp reinforced natural rubber/tapioca starch foams.

**Table 4.1** Effect of cellulose pulp content on densities of native tapioca starch composite foams and octyl tapioca starch composite foams (reported with the standard deviation in parentheses)

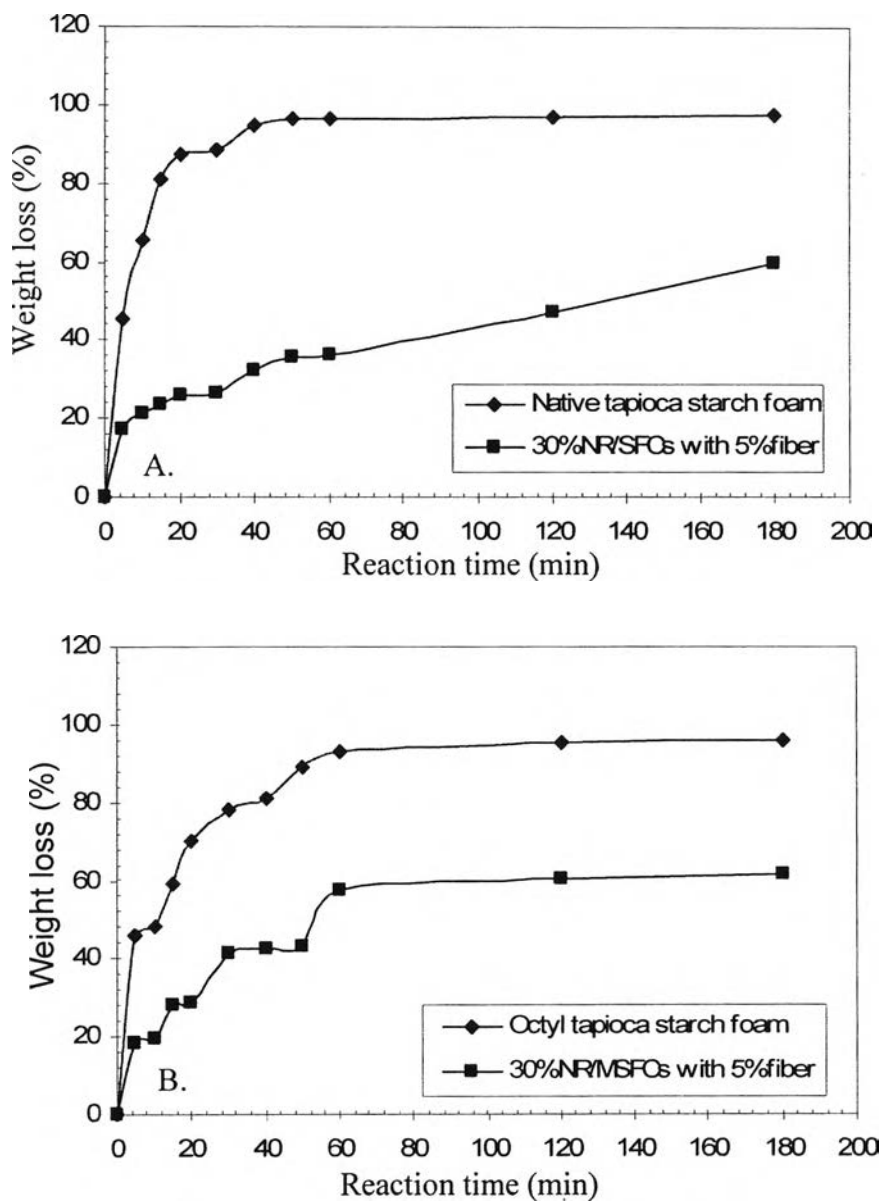
Foam type	Fiber content (%)	Average density (g/cm <sup>3</sup> )
Native tapioca starch composite foam	1	0.43 (0.015)
	3	0.53 (0.0044)
	5	0.55 (0.019)
Octyl tapioca starch composite foam	1	0.27 (0.024)
	3	0.40 (0.029)
	5	0.42 (0.0028)



**Fig. 4.11** Scanning electron micrographs for cross-sections of (A) pure native tapioca starch foam and cellulose pulp reinforced natural rubber/ native tapioca starch composites foams at (B) 1, (C) 3, and (D) 5% cellulose pulp content, respectively.



**Fig. 4.12** Scanning electron micrographs for cross-sections of (A) pure native tapioca starch foam and cellulose pulp reinforced natural rubber/octyl tapioca starch composites foams at (B) 1, (C) 3, and (D) 5% cellulose pulp content, respectively.



**Fig. 4.13** Enzymatic degradation by  $\alpha$ -amylase at 60 °C for (A) native tapioca starch based-foams and (B) octyl tapioca starch based-foam.

Enzymatic degradation of pure starch foam and cellulose pulp reinforced natural rubber/starch composite foams were tested by an in vitro hydrolysis with  $\alpha$ -amylase at 60 °C and the results are expressed as a function of reaction time in Fig. 4.13 of the foam specimens investigated exhibited an increase in the percentage of

weight loss with increasing reaction time. A similar dependence on percentage of weight loss versus reaction time for all foam specimens was observed, in that it initial abrupt increase at the start testing and then the degradation rate reduced as a function of time until after 1 hr the degradation rate for all foam specimens tended to constant. Comparison between the percentage of weight loss curves of pure starch foam and cellulose pulp reinforced natural rubber/starch composite foams suggests that the composite foam exhibited no complete degradation, the final percentage weight loss of the composite foams exhibited at around 60%. This may be a direct result of the addition of natural rubber and cellulose pulp due to its can not hydrolysis via  $\alpha$ -amylase so its still presented in the final component of foam specimen.