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An Initial Study of Starch-g-polystyrene Foam Prepared by a Steaming Process

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ABSTRACT

The fundamental objective of the present study was to determine appropriate conditions for the preparation of a starch-g-polystyrene foam sample by a steaming process using water as a blowing agent. This study was undertaken to assess the physical properties using a variety of techniques including visual inspection, density measurement, and scanning electron microscopy. The starch-g-polystyrene copolymer was prepared from the synthesis of cassava starch and styrene monomer by free radical polymerization using benzoyl peroxide as an initiator in an aqueous medium. An FT-IR technique was employed to characterize the chemical structure of the graft copolymers. The experimental results revealed that the appropriate ratio of starch-g-polystyrene and water was 30:70 and the appropriate steaming time was 5 min since this condition generated foam with a more uniform cell size and cell distribution. The open-cell foam was obtained from this technique. In addition, the foam density tended to decrease with increasing water ratio.

Keywords: cassava starch, polystyrene, starch-g-polystyrene copolymer, foam, steaming process

INTRODUCTION

Consumption of single-use foam packaging is promptly increased for various segments of business and daily life, particularly in the food industry. Expanded polystyrene has been commercially accepted for this certain application deriving from the excellent thermal insulation, low density, weight-to-strength ratio, ease of process and low cost (AFPR, 1999). Notwithstanding, the disposal of the post-consumer foam packaging is becoming a serious problem in consideration of their recalcitrance to microbial attach and inability to self-decompose. These concerns have led to improvements in the manufacturing process, the implementation of a recycling program and the development of alternative raw materials that are derived from renewable resources and are more degradable.

Starch is desirable as an environmentally friendly alternative material for making foam (Shogren, *et al.* 1993). The use of this material as a substitute for plastics confronts some limitations due to its brittleness and hydrophilicity (Bader, *et al.* 1994; and Kirby, *et al.* 1993). Moreover, articles made from starch are brittle at low humidity, and swell and deform upon exposure to humidity (Walia, *et al.* 2002). Several feasible solutions are by blending starch with a synthetic polymer, by modification of the chemical structure of starch with chemical substances or by using a graft copolymerization technique. Recently, Kiratitanavit (2002) studied the technique for the synthesis of graft copolymers of cassava starch and styrene monomer by free radical polymerization using benzoyl peroxide as an initiator in an aqueous medium. This graft copolymer showed a higher tendency to be friendly to an environment and relatively low cost in production. Consequently, the starch-g-polystyrene obtained from this technique was used in this study.

Starch-based foams have been processed in various techniques (Shogren, *et al.* 1998; Glenn, *et al.* 2001; Glenn, *et al.* 2001; Glenn, *et al.* 1997; Tienfenbacher, 1993; and Shorgen, *et al.* 1998a). A commercially successful starch-based foam product designed for an industrial application is loose-fill packaging made by extrusion. Lacourse and Altieri (1989) developed the extruded starch-based foam as an alternative to PS-based loose-fill packaging. Explosion puffing is an alternative process to extrusion for creating starch-based foam from starch feedstock containing low moisture levels (Hoseney, *et al.* 1983). Tienfenbacher (1993) developed a technology for producing moulded starch-based foam containers using a baking technology. Glenn and Orts (2001) investigated the properties of starch-based foam made by a compression/ explosion process.

The present study describes an alternative technique for producing starch-g-polystyrene foam where the starch-g-polystyrene was prepared according to Kiratitanavit's technique (Shorgen, *et al.* 1998a). The foam samples were prepared by a steaming process using water as a blowing agent. The objective of this initial study was to determine the appropriate ratio of starch-g-polystyrene and water, and steaming time in accordance with the morphology of the cell structure.

MATERIALS AND METHODS

Materials for synthesis of starch-g-polystyrene

Cassava starch, containing 13% moisture content, was obtained from the Thai Wah Public Co., Ltd. Styrene monomer, supplied from the Dow Chemical Co Ltd., was purified by 10% NaOH and washed with distilled water until the pH reached approximately 7. A solution of benzoyl peroxide (BPO), employed as a radical initiator, was prepared by dissolving 4.0 g of BPO in 40 cm^3 of acetone. Other chemicals including water, toluene, 1.5 N HCl, and methanol were also used for this synthesis.

Synthesis of starch-g-polystyrene

A four-necked round bottom flask, was placed in a heating mantle and equipped with a mechanical stirrer, condenser, thermometer, and nitrogen gas inlet and 360 cm^3 of distilled water was added with stirring by a mechanical stirrer at room temperature under a nitrogen atmosphere for 10 mins. 20 g of cassava starch was then added into the distilled water and stirring was continued for another 30 mins until starch sturry was obtained. The BPO solution and 40 cm^3 of distilled water were added, respectively, into starch slurry with constant stirring for 10 more mins. Subsequently, 20 g of styrene monomer and 20 cm^3 of distilled water were added, respectively. The mixture was heated up to 80^{o}C and maintained at this temperature for 2 hrs. To discharge unreacted monomer and initiator, the mixture was poured into methanol and kept at room temperature for 24 hrs, followed by filtering through Whatman filter paper No. 40, and dried in an oven at 60^{o}C for 24 hrs.

The dried product was ground and added into the thimble inserted in the Soxhlet extraction. 500 cm^3 of toluene, used as the solvent for extracting homopolystyrene from product, was poured into a 1000 cm^3 four-neck round bottom flask, and heated up to the temperature that toluene volatized for 24 hrs. Then the product was removed, filtered, washed with methanol, and dried in an oven at 60^{o}C for 24 hrs.

Following homopolystyrene extraction, the product was added into a 250 cm^3 Erlenmeyer flask, containing 200 cm^3 of 1.5 N HCl, equipped with a condenser. The mixture was stirred and refluxed for 2 hrs. The water-insoluble polymer was filtered and washed with distilled water until pH became 7. Then it was dried in an oven at 60^{o}C for 24 hrs.

Characterization of starch-g-polystyrene

The chemical structure of the obtained sample was characterized using a Fourier Transform Infrared Spectroscopy (FT-IR) technique on a Perkin Elmer 1760X spectrometer. The dried powder samples were mixed with KBr and pressed into a disc form by hydraulic compression. Each spectrum was recorded at a resolution of 4 cm^{-1} with 32 scans at a frequency range of 400-4000 cm^{-1}. A Perkin Elmer 1760X spectrometer was used.

Starch-g-polystyrene Foam Preparation

Starch-g-polystyrene, prepared from the previous part, was used to prepare foam by a steaming process using water as a blowing agent. Starch-g-polystyrene and water were mixed in a 400 cm^3 beaker and heated at 60^{o}C using a water bath and stirred for 15 min until the mixture became slurry. Then the slurry was poured into a 60 mm diameter petri dish and placed in a steamer at a temperature of about 100°C for 5 min. To determine an appropriate steaming time, the steaming period was varied in a range of 3, 5, and 7 min. Various ratios of starch-g-polystyrene and water, as presented in Table 1, were investigated.

Table 1 The ratios of starch-g-polystyrene and water

Percentage of starch-g-polystyrene	Percentage of water
30	70
20	80
10	90

Determination of the Physical Properties of the Foam Sample

The measurement of foam density was calculated from the mass and volume of the tubular specimen. The dimensions of the specimen were measured using vernier calipers and weighed to an accuracy of 0.1 mg.

Scanning Electron Microscopy (SEM) was used to obtain the image of the cell structures and the cell distribution of the foam. The foam sample was cut perpendicular to the rise direction and mounted on aluminum stubs with nail polish. To obtain a sufficient signal, the mounted foam samples were coated with gold-palladium under a vacuum atmosphere. Foam samples were viewed using a JEOL JSM 6400 at a voltage of 15 kV.

RESULTS AND DISCUSSION

Characterization of starch-g-polystyrene

The FT-IR technique was employed to analyze roughly the chemical structure and the functional groups of starch-g-polystyrene. Figures 1-3 present the spectra of starch-g-polystyrene before extraction, after extraction, and hydrolyzed product, respectively.

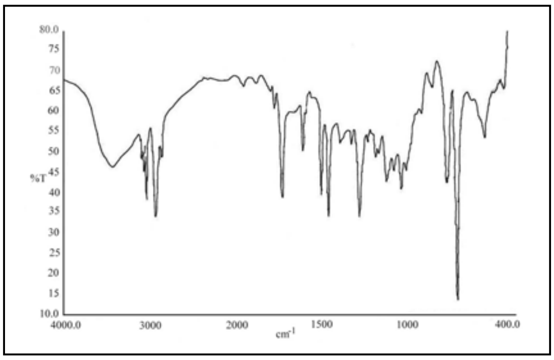


Figure 1 FT-IR spectrum of starch-g-polystyrene before extraction

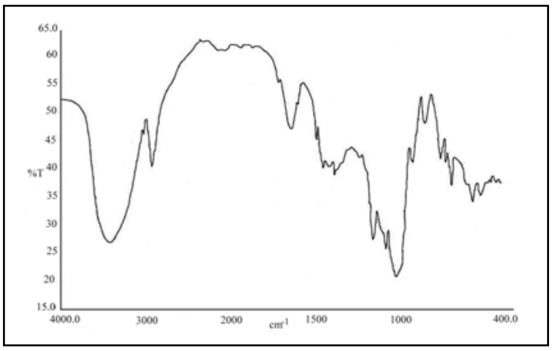


Figure 2 FT-IR spectrum of starch-g-polystyrene after extraction

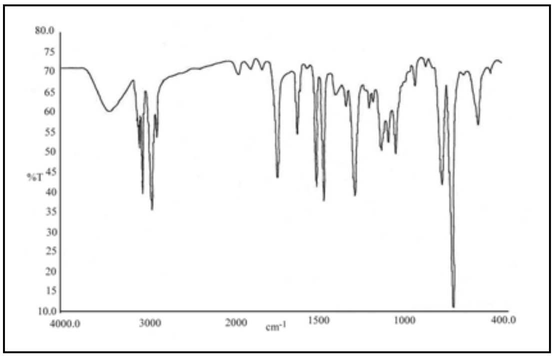


Figure 3 FT-IR spectrum of hydrolyzed product

From Figure 1, the characteristic peak close to 3400 cm^{-1} is attributed to an O-H stretching peak representing the functional group of starch. While the functional groups of polystyrene are exhibited at 3020 cm^{-1} designating aromatic C–H stretching, and at 1600 cm^{-1} designating aromatic C–C stretching. It is clearly seen that the product shows the characteristic peaks of both starch and polystyrene suggesting the possibility of grafting. Following Soxhlet extraction in Figure 2, lower intensity characteristic peaks at 3020 cm^{-1} and 1600 cm^{-1} and higher intensity characteristic peaks at 3400 cm^{-1} are detected. This indicates that the homopolystyrene was removed. After acid hydrolysis of the copolymer, the spectrum of hydrolyzed product in Figure 3 exhibits higher intensity characteristic peaks at 3020 cm^{-1} and 1600 cm^{-1} suggesting an occurrence of the graft copolymer of starch and styrene monomer. Whereas a low intensity characteristic peak at 3400 cm^{-1} indicates some starch existing in the system which may correspond to an incomplete reaction.

Starch-g-polystyrene Foam Preparation and Physical Properties Determination

It should be stated that the starch-g-polystyrene prior to Soxhlet extraction was used during the foam preparation by the steaming process at 102°C. The investigation of various ratios of starch-g-polystyrene and water, and a suitable steaming time were undertaken. Figure 4 exhibits the photographs of foam sample with different ratios of starch-g-polystyrene and water using 5 min steaming time.

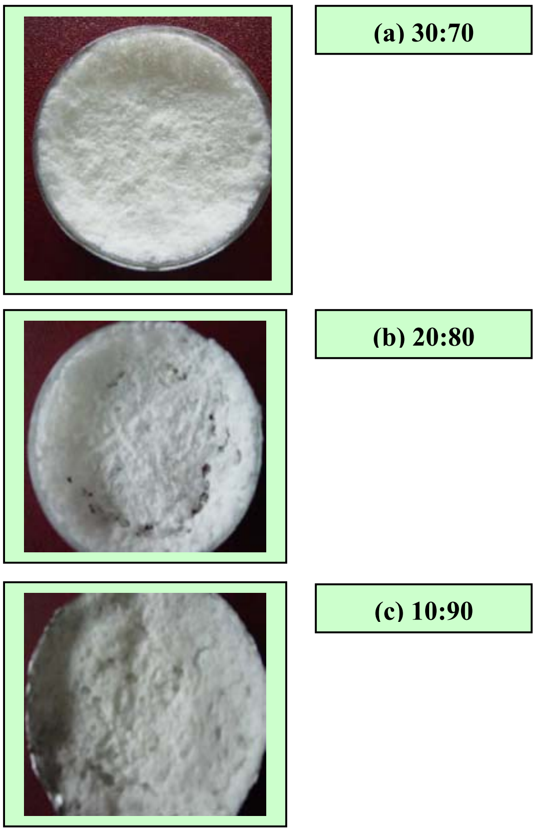


Figure 4 Photographs of foam samples with various ratios of starch-g-polystyrene and water (a) 30:70, (b) 20:80, and (c) 10:90

It can be visually seen that a broader cell size distribution and a less uniform cell size were detected as increasing the water ratio. Moreover, the foam samples tended to be more brittle as water ratio increased. Each foam sample was further characterized by SEM in Figure 5 where for comparison purposes all micrographs are shown at the same magnification. All SEM micrographs showed the voids coalesced so that both the solid and the gaseous phases were continuous (i.e. open-cell foams). The images from the micrographs also verified the previous statement from the visual inspection. This may be caused by an increasing water ratio resulting in a higher vapour pressure inside the mixture during steaming.

The density of each foam sample is shown in Table 2. It was apparent that the density decreased slightly with increasing ratio of water. From these results it appeared that, in foam preparation, the amount of water, acted as a blowing agent, had a significant influence on foam density resulting from the effect of water on the molecular interaction force of starch-g-polystyrene. A higher amount of water tended to provide a more gaseous component in the starch-g-polystyrene foam structure.

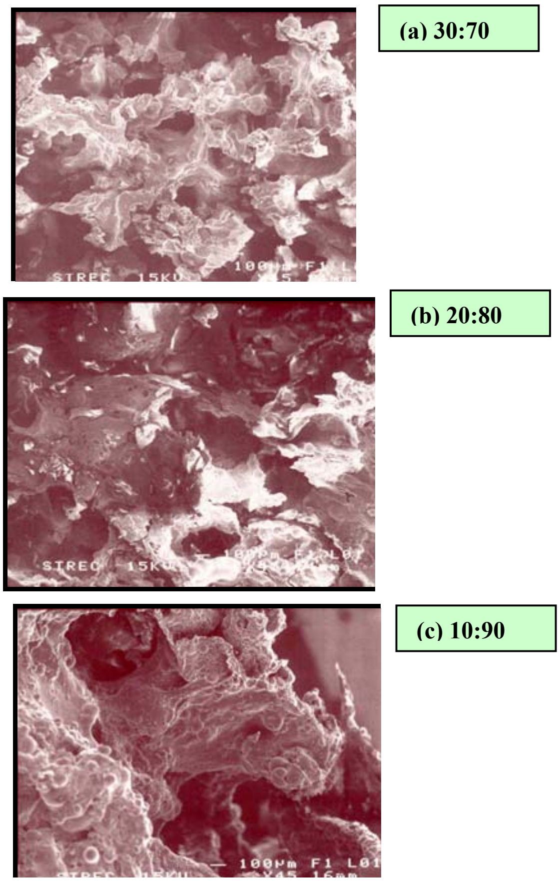
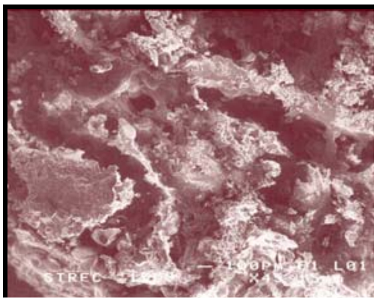


Figure 5 SEM micrographs of foam samples with various ratios of starch-g-polystyrene and water (a) 30:70, (b) 20:80, and (c) 10:90

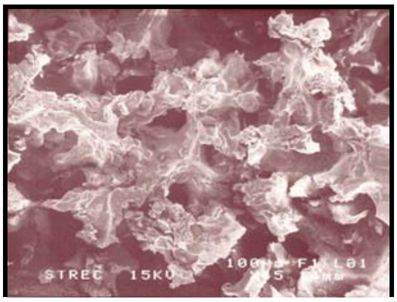
Table 2 Density of foam samples

Starch-g-polystyrene : water	Density (g/mm^3)
30:70	0.2594
20:80	0.2110
10:90	0.1482

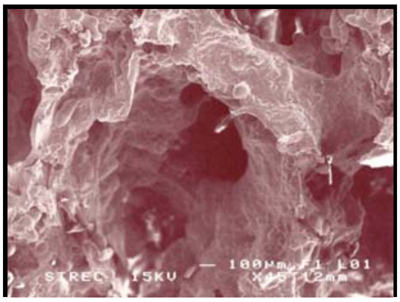
The 30:70 ratio of starch-g-polystyrene and water was further used to determine an appropriate steaming time in a range of 3, 5, and 7 min in accordance with the SEM micrographs, as presented in Figure 6. With increasing steaming time, a larger cell size was detected possibly as a result of vapour pressure inside the system. However, a more uniform cell size and cell distribution was perceived for 5 min steaming time.



(a) 3 min



(b) 5 min



(c) 7 min

Figure 6 SEM micrographs of foam samples with different steaming times

CONCLUSIONS

It appeared that the starch-g-polystyrene had the potential to be processed in a cellular form using water, as a blowing agent, via steaming process. The results from the SEM led to the conclusion that the most appropriate ratio of starch-g-polystyrene and water for foam preparation is 30:70 using a 5 min steaming time. This is because a more uniform cell size and cell distribution of foam sample was detected when compared with other conditions. In addition, the cell size of foam sample seemed to be controlled by the water content.

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