Effect of Potassium Persulfate on Graft Copolymerization and Mechanical Properties of Cassava Starch/Natural Rubber Foams

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ABSTRACT: The aim of this study was to improve the mechanical properties of thermoplastic starch foams prepared from cassava starch blended with natural rubber latex by reactive blending. Potassium persulfate was used as an initiator for graft copolymerization between the starch and natural rubber during baking. The starch–natural rubber graft copolymer (starch-*g*-NR copolymer) was successfully produced during both suspension and melt blending based on ^{1}H-NMR and FTIR characterization. Natural rubber increased the flexural modulus of starch/natural rubber foams without potassium persulfate, thus indicating the compatibility of the blends. The starch-*g*-NR copolymer, acting as a compatibilizing agent, enhanced the impact strength of foams, but it did not improve the flexural modulus. This may be due to the potassium persulfate decreasing the molecular weight of the natural rubber. Relative humidity also played an important role on the mechanical properties. Foams became more ductile at higher relative humidities. Since foam density increased with an increasing natural rubber content, the specific impact strength was also considered. A soil burial test showed that the cassava starch foams and foams containing 15 pph of natural rubber were fully biodegraded within 8 and 18 weeks, respectively. The starch-*g*-NR copolymer delayed biodegradation of foams and foams containing high natural rubber content, i.e., 35 pph, showed a low ability to be biodegraded. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 93–105, 2010

Key words: thermoplastic starch foams; cassava starch; natural rubber latex; biodegradable polymer; renewable resources

INTRODUCTION

Currently, there is a great deal of interest in biodegradable polymers because of environmental concerns, especially polymers derived from renewable resources. As a result, thermoplastic starch has been widely studied in recent years. Thermoplastic starch foams have been prepared from many kinds of starch such as maize starch,[1,2] potato starch,[1,3–6] cassava starch,[2,3,7] rice starch,[7] wheat starch,[2–5,8,9] and corn starch.[2–5,10–12] Because of the brittleness and hygroscopic characteristics of thermoplastic starch, starch has been blended with other polymers prior to foam processing. Both biodegradable and nonbiodegradable polymers have been blended with starch to make thermoplastic starch foams. These include polymers such as polystyrene,[13,14] poly(methyl methacrylate),[14] low-density polyethylene,[15] polyurethane,[16] polystyrene blended with poly(ethylene-*co*-vinyl alcohol),[17] biodegradable copolyester,[18,19] poly(lactic acid),[20–26] poly(lactic acid) blended with poly(hydroxyester ether),[5] poly(ε-caprolactone),[27] poly(vinyl alcohol),[28–31] and natural rubber latex.[32,33] Kiatkamjornwong et al.[32] used gelatinized cassava starch and used benzoyl peroxide to vulcanize the natural rubber. The natural rubber latex was stabilized with a nonionic surfactant. It was found that the compressive stress increased as the natural rubber content increased but there was no result reported for their density and impact strength. Shey et al.[33] used potato starch, wheat starch, and waxy corn starch and added a stabilizer to the natural rubber latex. They described the tensile properties and the densities of the foams but made no mention of the elongation at break. They also found that changes in the yield strain were not high. For example, the yield strain of potato starch foam with and without natural rubber latex was 2.63% and 1.78%, respectively. They concluded that natural rubber latex increases flexibility and the moisture resistance

of baked starch foams. Tensile properties of thermoplastic starch blended with glycerol and natural rubber latex were also reported.[34] The researchers reported that the modulus and tensile strength of thermoplastic starch decreased as the natural rubber content increased. The elongation at break of starch/natural rubber blends depended on the glycerol content. The blends containing 20% glycerol showed an increase in elongation at break after adding 2.5% natural rubber and higher rubber content decreased the elongation at break of the blends. The blends containing higher glycerol content, i.e., 30 and 40%, exhibited a decrease in the elongation at break for all blend compositions. It should be noted that it is necessary to add a plasticizer such as glycerol for producing thermoplastic starch foams but the plasticized thermoplastic starch foams are still relatively brittle so that there has been much research work on starch-based polymer blends as described earlier. Based on previous articles,[32–34] natural rubber is not a plasticizer of starch. It is known that natural rubber is an impact modifier. Although foams prepared from starch blended with natural rubber have been reported,[32,33] the application of natural rubber as the impact modifier of thermoplastic starch foams has not been published. Therefore, it is of interest to investigate the effect of the natural rubber content on the impact strength of the thermoplastic starch foams. As starch is a hydrophilic polymer, whereas natural rubber is a nonpolar polymer, a compatibilizer should be employed to improve the mechanical properties of blends of starch and natural rubber. There are many methods for compatibilization in the polymer blends. One of the more efficient methods for compatibilization is reactive blending that produces a graft copolymer at the interphase between the polymer A phase, i.e., starch, and the polymer B phase, i.e., natural rubber, during baking (foam preparation). This graft copolymer, sometimes, is called the *in situ* graft copolymer which means that the graft copolymer is synthesized during melt blending. In this case, both polymers (starch and natural rubber) must have a functional or reactive group to provide a chemical reaction. It is assumed that the double bonds in natural rubber and the hydroxyl groups in starch do interact and lead to a starch-*g*-NR graft copolymer. The hydroxyl groups in starch are active and can be used to prepare graft copolymers with other polymers such as polyacrylamide, polycaprolactone, poly(lactic acid), polystyrene, poly(methyl acrylate), polyacrylonitrile, and low-density polyethylene. Many initiators have been used to synthesize starch-based graft copolymers such as ceric ammonium nitrate,[35–39] potassium persulfate,[40,41] potassium permanganate,[42] a mixture of potassium persulfate and benzoyl peroxide,[43–46] and a mixture of

cerium sulfate and potassium persulfate.[45] Because of the following reasons, we believe that potassium persulfate is a suitable agent to generate the graft copolymer in the starch/natural rubber blends. First, potassium persulfate is a good initiator for both starch and natural rubber. Double bonds in natural rubber and hydroxyl group in starch are activated by free radicals produced from potassium persulfate. Second, potassium persulfate is a water-soluble initiator that can disperse very well in the mixture of starch and natural rubber latex. Additionally, based on our knowledge, there has been no publication of graft copolymerization in the cassava starch/natural rubber foams by using potassium persulfate as an initiator.

The objectives of this research were, therefore, to evaluate the effect of potassium persulfate on graft copolymerization between native cassava starch and natural rubber latex and to determine the mechanical properties and characteristics of any prepared foams. The effect of natural rubber content and relative humidity were also studied. Foam density was uncontrolled so as to be in the same range after loading the natural rubber latex to observe the real effect of natural rubber on cassava starch foam under the same foam formulation. The effect of density on the impact strength was considered in terms of the specific impact strength derived from the impact strength normalized with the density. The article will be divided into two parts. The first part will focus on the synthesis and characterization of the starch-*g*-NR copolymer obtained from suspension grafting to verify the efficiency of potassium persulfate in graft copolymerization. The second part will describe the morphology, density, mechanical properties, and results of a soil burial test for foams. The presence of the starch-*g*-NR copolymer in the foams will be described in the first part.

EXPERIMENTAL

Materials

Native cassava starch containing 32% amylose was purchased from General Starch Co., Bangkok, Thailand. High ammonia grade natural rubber (NR) latex (60% dry rubber content) was purchased from Chalong Concentrated Latex Co., Songkla, Thailand. Foam formulation is listed in Table I. All chemicals including the NR content (dry rubber content) were weighed based on 100 parts by weight of starch. The concentration units of all chemicals and NR in the foams are given as parts per hundred (pph). NR latex was used as received and no latex stabilizer was employed.

TABLE I
Foam Formulation

Material	Weight
Cassava starch	100
Sodium bicarbonate	0.1
Guar gum	1
Magnesium stearate	2
Glycerol	5
Natural rubber	0–35
Water	100

Synthesis of the starch-g-NR copolymer in suspension blending

To prove that the starch-g-NR copolymer occurred due to potassium persulfate (PPS), synthesis of this graft copolymer in the suspension blending was executed. Starch and water were added into a round bottomed three-necked flask at 50°C and stirred for 15 min to obtain homogeneous slurry. Continuous stirring was maintained at a constant speed for the entire experiment. NR latex, diluted with water, was added into the flask and stirred for 15 min before adding PPS into the solution. The PPS content was based on the total weight of starch and NR, i.e., 0.5 pph of PPS required 0.5 g of PPS in 100 g of starch/NR blend. The reaction time was 2 h. Polymer blends were precipitated by methanol, filtered, and then dried at 60°C until the weight was constant. The NR/starch blend was kept in the desiccator before characterization.

Investigation of graft copolymer

Nonreacted NR in the starch/NR blend was extracted by Soxhlet extraction in toluene at 110°C. Complete extraction was determined by dropping the extracted solution in methanol which is a nonsolvent of NR. If no precipitation was observed or methanol was clear, complete extraction had been performed. To substantiate the validity of the Soxhlet extraction technique, the same extraction method was applied to the starch/NR blend without PPS. The residue after extraction was dried at 60°C until the weight was constant and kept in the desiccator before use. FTIR and ^{1}H-NMR were employed to investigate the presence of the starch-g-NR copolymer. Starch, NR and the blend without extraction of nonreacted NR were also investigated by FTIR and ^{1}H-NMR. Deuterated chloroform and deuterated dimethyl sulfoxide were used as a solvent of NR and starch, respectively, for the ^{1}H-NMR analyses. Investigation of the graft copolymer in the foam samples with and without PPS was also carried out. Foam samples were extracted and characterized in a similar way to the methods described earlier.

Foam preparation

Starch was mixed with other solid chemicals as listed in Table I at room temperature for 10 min before adding the aqueous glycerol solution and the NR latex. In the case of adding PPS, the PPS aqueous solution was mixed with the aqueous glycerol solution and then added into the mixture. Foams were prepared by compression molding at 180°C under a pressure of 1000 psi (70 kg/cm^2) for 5 min and the foam thickness was ~ 4 mm.

Mechanical properties test and characterization of foams

An Izod impact test was performed according to ASTM D256. Dimensions of the un-notched specimens were 12.7 mm $\times$ 63.5 mm $\times$ 4 mm. The experiment was carried out by using a 2 J pendulum and six to eight specimens were tested for one sample. Flexural properties were determined based on ASTM D790 (three point bending test). The dimension of the specimens was 30 mm $\times$ 150 mm $\times$ 4 mm and the length of the support span was 80 mm. Testing speed was 2.5 mm/min and 10 specimens were tested for one sample. Mechanical properties were tested at 25°C $\pm$ 1°C and 60% $\pm$ 5% RH. Density was determined as a ratio between the mass (weight) and volume and investigated at 27°C $\pm$ 1°C and 70% $\pm$ 5% RH. The specimen dimension was 30 mm $\times$ 150 mm $\times$ 4 mm. Before testing of the mechanical properties, specimens were stored for 7 days at ambient temperature (28°C $\pm$ 1°C) and at two different relative humidities: 40% $\pm$ 3% RH and 70% $\pm$ 8% RH. The lower RH was controlled by silica gel in the desiccator. The higher RH was the relative humidity of the ambient environment in the laboratory. Temperature and relative humidity were recorded every day at 8 am, 12 pm, 3 pm, and 6 pm. The average values have been reported.

A fractured surface of the foam was recorded by a scanning electron microscope. The molecular weight of the NR extracted from the foam specimens was evaluated by gel permeation chromatography. Foam specimens were ground to a powder and dissolved by stirring in toluene at 60°C for 48 h. The solution was filtered using a 325 mesh stainless steel sieve. Then, the NR solution was precipitated in methanol and dried at 60°C. NR was dissolved in tetrahydrofuran to obtain the solution concentration of a 0.5 wt %. The polymer solution was filtered by using a nylon filter before injection into the equipment that had a refractive index detector. The flow rate of the solvent (mobile phase) was 1 mL/min and the temperature of the column was 40°C. The standard curve was obtained from standard polystyrene (known molecular weight polystyrene).
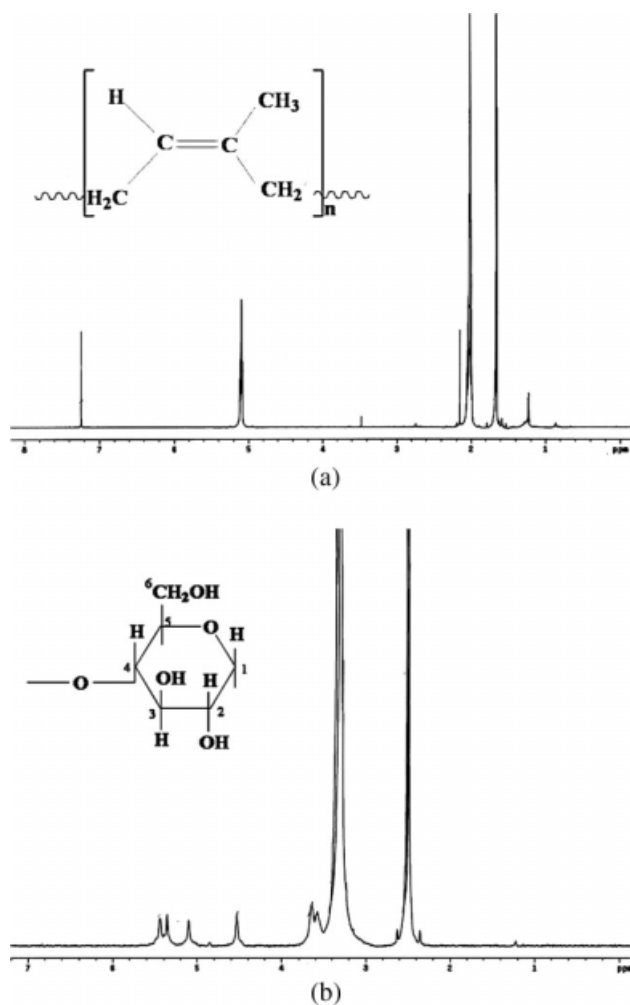
Figure 1 ^{1}H-NMR spectra of NR dissolved in deuterated chloroform (a) and starch dissolved in deuterated dimethyl sulfoxide (b).

Soil burial test of foams

Soil was packed into 40 cm × 60 cm × 20 cm (width × length × height) baskets. The specimen width and length was 30 mm and 150 mm, respectively, specimens were placed in the middle of the basket and six specimens were used for each sample. Baskets of soil were exposed to sunlight and rain, and the dampness of the soil was observed and controlled by watering every 4 days if necessary. Specimens were removed every 2 weeks and cleaned by brushing and blown dry with air. Changes in the specimens were observed by eye and recorded by a digital camera. Cleaning with water was not possible because starch absorbs water. Changes in specimen weight after soil burial were not measured because it was not possible to remove soil completely from the specimens without cleaning with water. After observation, specimens were replaced into the soil.

## RESULTS AND DISCUSSION

Graft copolymer

The assumption that the addition of PPS into the starch/NR blend led to the starch-g-NR should be verified before preparing the foams. Generally, synthesis of the graft copolymer using melt blending is rather difficult. Therefore, suspension blending was carried out between starch and the NR latex.

The starch-g-NR copolymer was successfully produced by suspension blending based on its NMR and FTIR characteristics. The ^{1}H-NMR spectrum of NR dissolved in deuterated chloroform and starch dissolved in deuterated dimethyl sulfoxide are demonstrated in Figure 1(a,b), respectively. The ^{1}H-NMR assignment of NR and starch are listed in Table II.[47–49] As described in the experimental section, validation of the Soxhlet extraction requires a sample without PPS. In this case, no NR must be observed in the sample after extraction. The residue obtained after Soxhlet extraction was dissolved in deuterated dimethyl sulfoxide and deuterated chloroform to investigate the presence of starch and natural rubber in the residue. Figure 2 shows ^{1}H-NMR spectra of this residue. It was found that the sample without PPS after Soxhlet extraction contained only starch, represented by the spectrum "a" in Figure 2 which showed all chemical shifts of starch as described in Table II. In contrast, the residue dissolved in deuterated chloroform (the spectrum "b" in Fig. 2) did not show the characteristics of NR. This result confirmed that there was no NR in the

TABLE II
^{1}H-NMR Assignments for NR and Cassava Starch

| Material	Solvent	δ (ppm)	Assignment
NR	Deuterated chloroform (CDCl₃)	5.10	C=CH
		2.01	CH₂
		1.65	CH₃
Cassava starch	Deuterated dimethyl sulfoxide (DMSO-d_6)	5.10	H-1
		5.44, 5.36	OH-3,2
		4.53	OH-6
		3.65–3.30	H-6,5,4,3,2
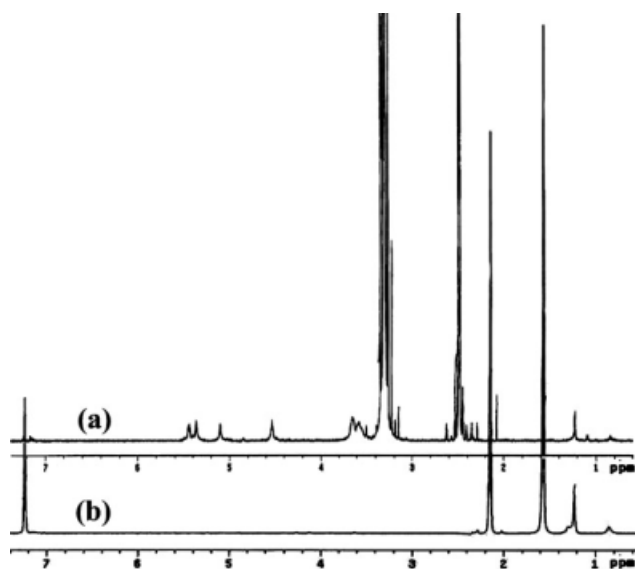
Figure 2 ^{1}H-NMR spectra of the residue from a Soxhlet extraction of a starch/NR blend without PPS dissolved in deuterated dimethyl sulfoxide (a) and in deuterated chloroform (b).

blend without PPS after Soxhlet extraction and also proved that the Soxhlet extraction procedure was valid.

The presence of starch-g-NR copolymer was proved by Figure 3. Figure 3 represents the spectra obtained from the residue after Soxhlet extraction of the blend containing PPS and shows that it composed of both starch and NR. The starch component was observed in the spectrum "a" which derived from the residue dissolved in deuterated dimethyl sulfoxide, and this spectrum looked similar to the spectrum in Figure 1(b) and the spectrum "a" in Figure 2. The spectrum "b" was derived from the residue dissolved in deuterated chloroform and it showed the chemical shifts at δ 5.10 ppm, 2.01 ppm, and 1.65 ppm which are the characteristics of NR. It should be noted that the spectrum "b" in both Figures 2 and 3 were derived
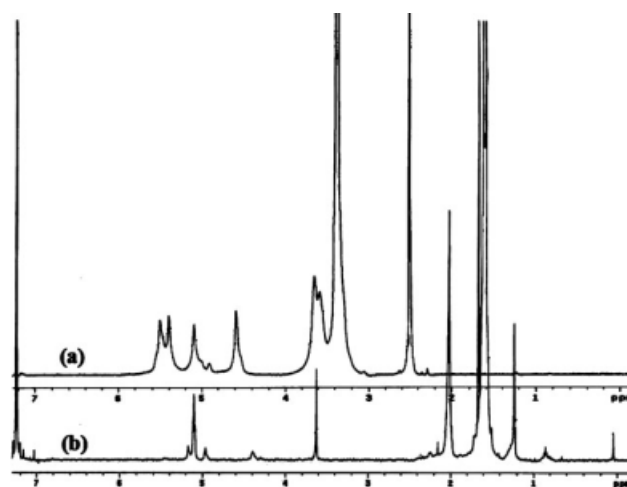

Figure 3 ^{1}H-NMR spectra of the residue from a Soxhlet extraction of a starch/NR blend containing 0.5 pph of PPS dissolved in deuterated dimethyl sulfoxide (a) and in deuterated chloroform (b).

from the residue dissolved in deuterated chloroform which is a solvent of NR but they showed different characteristic. The blend containing PPS after Soxhlet extraction still exhibited NR due to grafting reaction between NR and starch resulting in the nonextractable NR in the residue. On the other hand, after Soxhlet extraction, NR in the blend without PPS was completely removed from the blend as shown in Figure 2 (spectrum "b"). The ^{1}H-NMR spectrum of virgin starch dissolved in deuterated chloroform was investigated to confirm the appearance of the spectrum "b" in Figure 2. The virgin starch was dispersed in deuterated chloroform for 24 h, filtered, and characterized by NMR. The derived ^{1}H-NMR spectrum of the solution was identical to the spectrum "b" in Figure 2 but is not shown in this article.

FTIR characterization was performed by using the samples before and after Soxhlet extraction. Table III shows the FTIR assignment of NR and starch.[40,50,51]

TABLE III
FTIR Assignments for NR and Cassava Starch

| Material	Wavenumber (cm^{-1})	Assignment
NR	3429	O—H stretching
	2926, 2925, 2854	C—H stretching
	1720, 1666	C=C stretching
	1448	C—H deformation (CH$_3$)
	1374	C—H deformation (CH$_2$)
	836	C—H stretching (C=CH)
Cassava starch	3417	O—H stretching
	2930	C—H asymmetric stretching
	1646	O—H bending (H$_2$O)
	1458, 1370	C—H deformation (CH$_2$ bending)
	1159, 1084, 1010	C—O stretching (C—O—C, C—O—H)
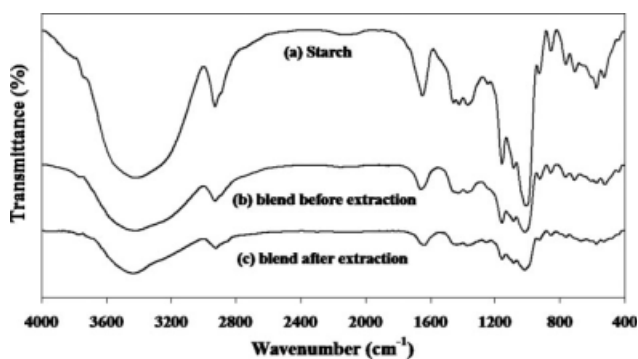
Figure 4 FTIR spectra of virgin starch (a), a starch/NR blend containing 0.5 pph of PPS before Soxhlet extraction (b), and after Soxhlet extraction (c).

Figure 5 FTIR spectra of NR (a), a starch/NR blend containing 0.5 pph of PPS after Soxhlet extraction (b), and the subtraction between starch and the blend after Soxhlet extraction (c).

The FTIR spectra of the blends before and after Soxhlet extraction were similar to that of starch alone as shown in Figure 4. As a result, a spectrum subtraction was applied as shown in Figure 5. The spectrum of the blend after Soxhlet extraction (residue) was subtracted from the spectrum of starch (spectrum "c": starch-subtraction in Fig. 5). There was a trace of an NR component in this subtracted spectrum as appeared at 2926–2854 cm^{-1}. Therefore, it was confirmed that there had been a starch-g-NR copolymer formed during blending of the starch and NR in the presence of PPS.

Although there was a graft copolymer synthesized during the suspension blending, it may not occur during the melt blending. Foam specimens containing PPS were investigated for the presence of the starch-g-NR copolymer. ^{1}H-NMR spectra of the foam residue after extraction and being dissolved in deuterated chloroform are shown in Figure 6. Foam containing PPS (the spectrum "a") showed strong peaks at δ 5.10 ppm, 2.01 ppm, and 1.65 ppm which were assigned to NR. On the other hand, no NR traces was observed in the foam without PPS (the spectrum "b") and this spectrum was similar to the spectrum "b" in Figure 2. These results confirmed that there was a graft copolymer present in the prepared foams.
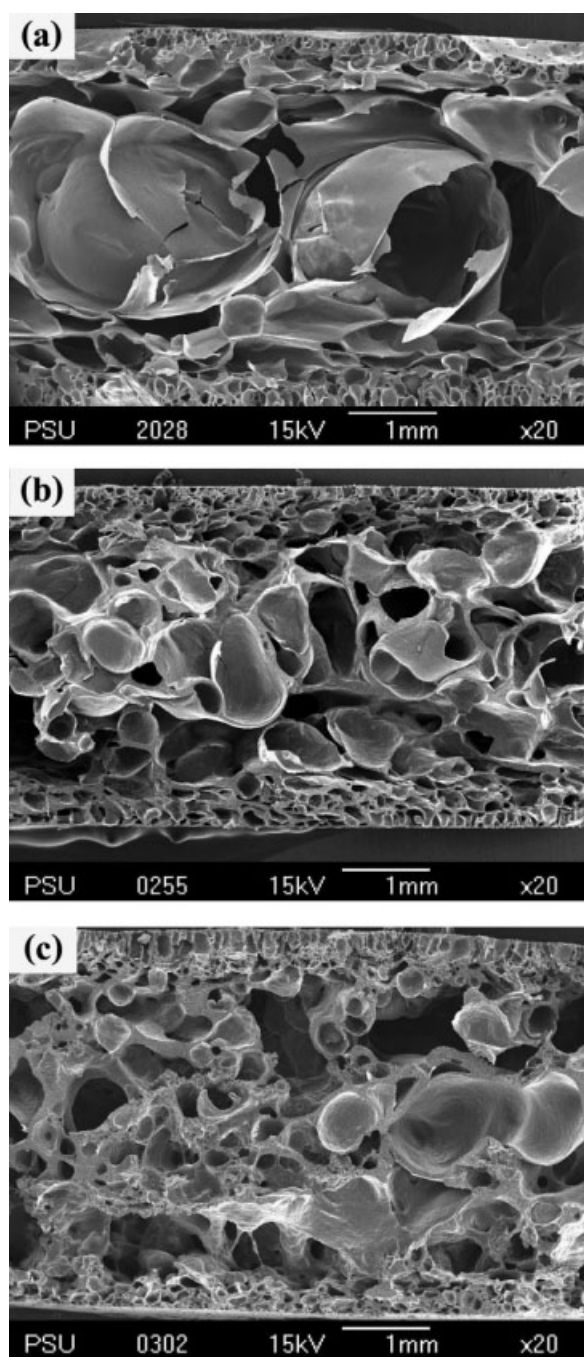
Foam morphology

SEM micrographs of foams containing 0, 15, and 35 pph of NR are demonstrated in Figure 7(a–c), respectively. Generally, all foams showed skin-core morphology. The depth of a skin layer was ∼ 0.5 mm and much smaller cellular structures were noticed in the skin layer. The most remarkable change due to the addition of NR was the cellular structure in the core portion. The cell size became smaller and denser as the NR content increased. A phase separation of NR and starch was clearly seen
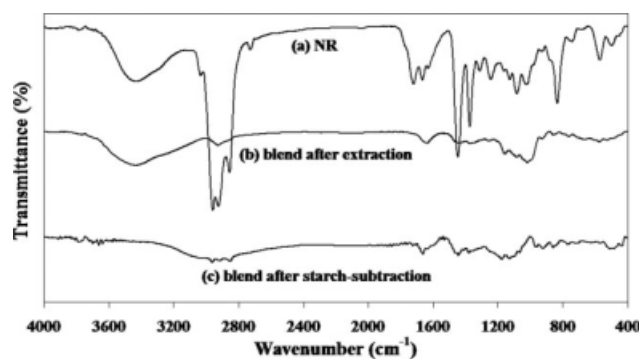
in the foam containing 35 pph of NR [Fig. 7(c)]. A phase separation in thermoplastic starch blended with NR latex has been reported elsewhere.[34] This study did not add any stabilizer with the NR latex, whereas other researchers[32,33] stabilized NR latex by adding nonionic surfactants.

The effect of the NR content on foam morphology observed in the core area is presented in Figure 8. Thermoplastic starch foam showed a smooth and homogeneous surface as demonstrated in Figure 8(a). The thicker cell wall and inhomogeneous surface were derived after adding 15 pph of NR as shown in Figure 8(b,c), respectively. It appeared that the cell wall and phase separation increased with an increasing NR content. A very thick cell wall [Fig. 8(d)] and a higher phase separation [Fig. 8(e)] were found in the foams containing 35 pph of NR. Some specimens of this composition showed gross phase
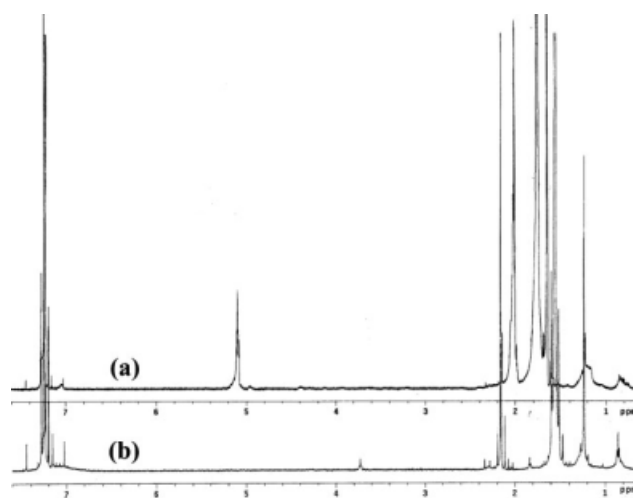
Figure 6 ^{1}H-NMR spectra of starch/NR foams after Soxhlet extraction and dissolved in dueterated chloroform: the foam containing 0.025 pph of PPS (a) and the foam without PPS (b).

Figure 7 SEM micrographs of starch/NR foams containing different NR contents, showing foam morphology: 0 pph (a), 15 pph (b), and 35 pph (c).

segregation as shown in Figure 8(f). As the content of the blowing agent did not increase with increasing NR content, the formation of foam might be different. Furthermore, sodium bicarbonate may not be a good blowing agent for NR. These led to a more dense foam and thicker cell wall in the foams containing NR. However, based on a preliminary study, an increase in sodium bicarbonate content from 0.1

to 0.5 pph did not significantly decrease the density of foams with and without NR.

Effect of NR content on mechanical properties

It is well known that NR is an impact modifier for plastics; therefore, addition of NR into thermoplastic starch should increase its impact strength. Undoubtedly, the impact strength of starch/NR foams increased with increasing NR content (Fig. 9). With regard to the foam morphology described earlier, a thicker foam cell wall was obtained after adding NR. This resulted in a higher toughness of the starch/NR foams than found in the pure thermoplastic starch foams. The high-phase separation of NR did not diminish the impact strength of the foams. The relative humidity had a significant effect on the impact strength of foams with and without NR. Storing the samples at higher relative humidity produced higher impact strength. This was because starch absorbed moisture from the environment and water is a plasticizer of thermoplastic starch. A greater toughness is obtained from plasticized thermoplastic starch.

The foam density increased with increasing NR content and there was little effect of relative humidity on the foam density (Table IV). The density of the cassava starch foam prepared in this study was in the same range as the wheat starch foam,[33] i.e., 0.20 g/cm^3. By adding NR latex (27 wt % of water),[33] the density of that wheat starch foam increased to 0.22 g/cm^3 and was comparable to the foam described here that contained 15 pph of NR. As foams have shown significant discrepancies in density, this may provide for a contradictory opinion of the effect of the NR content. Consequently, the specific impact strength (impact strength (J/m^2) normalized with density (g/cm^3)) was considered and is listed in Table V. It was found that the specific impact strength of foams was enhanced by the addition of NR. All blends showed higher specific impact strength than thermoplastic starch foams stored at 40% RH. Only the high NR content (30 and 35 pph) improved its specific impact strength after storage at 70% RH. The addition of a low NR content, i.e., 15–25 pph, exhibited a slight decrease in the specific impact strength. There were two factors involved in the enhancement of the impact strength of foams stored at 70% RH: absorption of moisture by the thermoplastic starch and the contribution made by the NR content. The lower specific impact strength at relatively low NR content (15–25 pph) may be due to the NR reducing the absorption of moisture by the foam. The higher NR content (30 and 35 pph) provided more phase separation so that the thermoplastic starch phase could absorb more moisture.
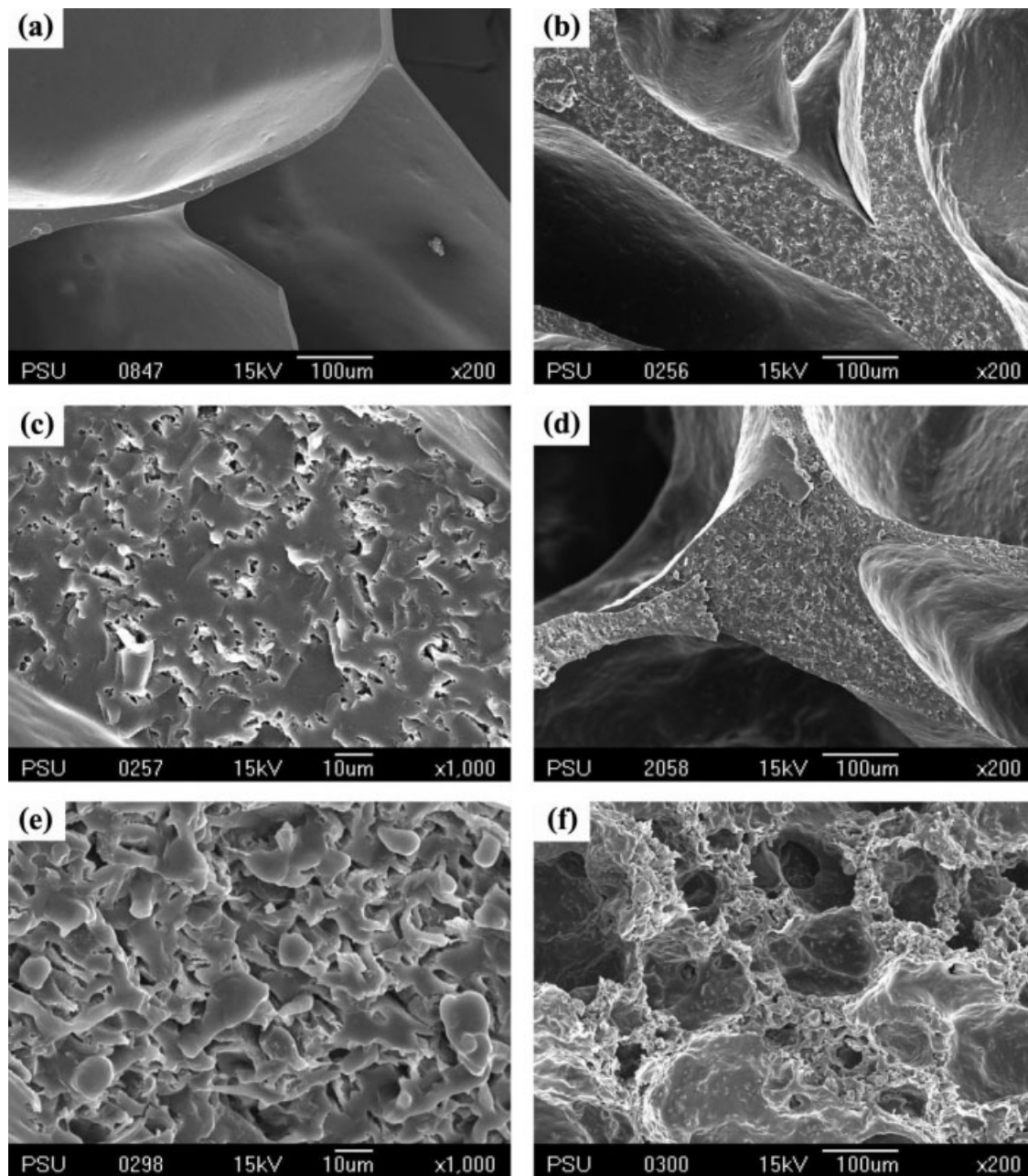
Figure 8 SEM micrographs at the core area of foams containing different NR contents, showing more phase separation as the NR content increased: 0 pph (a), 15 pph (b and c), and 35 pph (d–f).

The effect of NR on the flexural properties is tabulated in Table IV. Unexpectedly, the flexural modulus (E) of thermoplastic starch foam increased after blending with NR and there was a maximum modulus for each relative humidity. It appeared that 15 and 20 pph were the optimum content of NR for improving the flexural properties when stored at 40 and 70% RH, respectively. The lower flexural modulus of foams containing the higher NR content was probably due to more phase separation. However, the modulus values of foams containing NR were

not much different after passing the maximum modulus. All foams containing NR showed higher flexural modulus than foams without NR. This behavior was unique because normally addition of a softer polymer (NR) should not increase the modulus of a hard matrix (thermoplastic starch). The reduction in the tensile modulus of thermoplastic starch due to the addition of NR has been reported.[33,34] As the density increased when the NR content increased, one might claim that the higher density caused a higher modulus. As a result, the
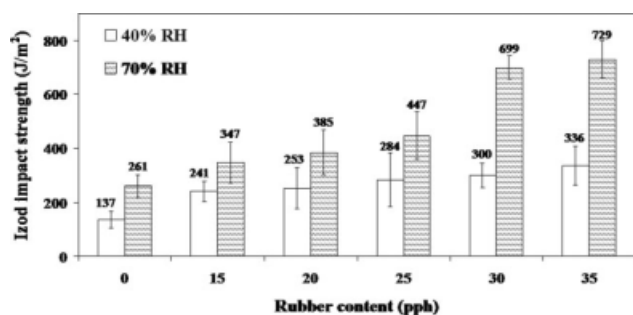
Figure 9 Effect of relative humidity of the storage conditions on the impact strength of starch/NR foams without PPS.

specific modulus was taken into account. It was found that the specific modulus decreased as the NR content increased when foams were stored at 40% RH, but foams containing 15 and 20 pph of NR showed a higher specific modulus than foams without NR when stored at 70% RH. The specific modulus was 802, 1025, and 890 MPa cm^3/g for foams containing 0, 15, and 20 pph of NR, respectively. This was a synergistic behavior of the present foams and the result revealed that the prepared starch/NR blend was compatible at a certain composition with regard to the flexural modulus. Foams without NR stored at 40% RH exhibited a higher flexural modulus than those stored at 70% RH. A similar result has been reported.[33] This was most likely due to the moisture effect: lower humidity providing lower plasticization. The relative humidity produced a lower effect on the flexural modulus in foams containing NR. In practice, the addition of NR should reduce the ability of the foams to absorb water and this effect was proven by the soil burial test. The addition of NR did not show significant changes in the maximum flexural stress (σ_{max}). The maximum value appeared in foams containing 15 and 20 pph of NR when stored at 40 and 70% RH, respectively. The maximum flexural stress at 40% RH tended to be higher than the one at 70% RH. As predicted, the specific flexural strength of foams decreased as the

NR content increased. This agreed with the general knowledge that rubber will toughen plastics, whereas rubber reduces the strength of the blends. The flexural strain (ε_b) recorded at the strain at break was in the same range for all foams. Thermoplastic starch foams prepared by Shey et al.[33] also showed a slight increase in tensile yield stress and tensile yield strain after adding NR latex and those values are in the same range as in this study. However, a comparison between the tensile and the flexural properties should not be made due to different type of loading. In this study, NR acted as only an impact modifier and did not notably increase the flexural strain of the thermoplastic starch. Relative humidity also showed no influence on the flexural strain.

Obviously, although the impact strength increased with increasing density, the flexural properties did not relate to the density in the same manner as the impact strength. It could be expected that a higher foam density should provide a higher flexural modulus in addition to its strength. Remember that there are many factors involved in the mechanical properties such as the homogeneity of the foams and the type of polymer and rubber. In addition, the NR/starch blend in this study was one kind of rubber toughened plastic and, in general, not all mechanical properties are improved in the rubber toughened plastics. For example, epoxidized NR had increased impact strength but decreased the tensile properties of nylon 6.[52] The higher specific flexural modulus in foams revealed good interfacial adhesion between the continuous phase (starch) and the discontinuous phase (NR). As mentioned earlier, the effect of foam density was questionable. Because the aim of this study was to determine how much NR was able to be added into the same formulation of the starch compound, it was unnecessary to obtain a similar range of foam density and the effect of foam density on the mechanical properties has been already discussed in terms of the specific impact strength. For that reason, it can be clearly stated that NR was able to increase the impact strength and the flexural modulus of thermoplastic starch foams.

TABLE IV
Density and Flexural Properties of Starch/NR Foams Without PPS and Stored at 40 and 70% RH for 7 Days Before Testing

NR (pph)	Density (g/cm^3)		E (MPa)		σ_{max} (MPa)		ε_b (%)	
	40% RH	70% RH	40% RH	70% RH	40% RH	70% RH	40% RH	70% RH
0	0.1838 ± 0.0178	0.1845 ± 0.0112	249 ± 47	148 ± 19	3.34 ± 0.77	2.98 ± 0.27	1.75 ± 0.34	1.80 ± 0.21
15	0.2706 ± 0.0155	0.2723 ± 0.0155	325 ± 34	279 ± 42	4.29 ± 0.59	3.19 ± 0.55	1.68 ± 0.13	1.46 ± 0.13
20	0.3103 ± 0.0137	0.3178 ± 0.0209	296 ± 35	283 ± 25	3.82 ± 0.46	3.35 ± 0.42	1.85 ± 0.31	1.85 ± 0.46
25	0.3434 ± 0.0156	0.3680 ± 0.0176	257 ± 30	251 ± 26	3.19 ± 0.50	3.15 ± 0.51	1.69 ± 0.26	1.70 ± 0.21
30	0.3896 ± 0.0209	0.4108 ± 0.0206	265 ± 30	221 ± 32	3.28 ± 0.46	2.47 ± 0.44	2.26 ± 0.20	2.00 ± 0.23
35	0.4201 ± 0.0147	0.4215 ± 0.0149	261 ± 25	219 ± 25	3.07 ± 0.32	2.56 ± 0.31	2.06 ± 0.23	2.37 ± 0.18

Relative humidity (%)	NR (pph)	Specific impact strength ($\times 10^{-3}$ J m/kg)	
		0 pph of PPS	0.025 pph of PPS
40	0	745	–
	15	891	1095
	20	815	961
	25	827	1091
	30	770	1412
	35	800	1255
70	0	1415	–
	15	1274	1563
	20	1211	1585
	25	1215	2026
	30	1702	1910
	35	1730	2107

Effect of PPS on mechanical properties

The density of foams containing PPS is revealed in Table VI and was similar to that of foams without PPS. The addition of PPS increased the impact strength of all foams stored at 40 and 70% RH and the impact strength increased with increasing NR content (Fig. 10). This was due to the presence of the graft copolymer (starch-g-NR copolymer) in the foam samples. The graft copolymer occurred at the interphase between NR and starch and acted as a compatibilizer of the starch/NR blend, leading to higher compatibility of the blends. The starch-g-NR copolymer also increased the interfacial adhesion between NR and starch. Theoretically, the *in situ* graft copolymer will transfer the applied load from the weaker phase (NR) to the stronger phase (starch), resulting in a higher toughness. The impact strength of foams stored at 70% RH was still higher than those stored at 40% RH. The specific impact strength of all foams increased after adding PPS as shown in Table V. All blends exhibited higher specific impact strength than the thermoplastic starch

and the improvement appeared in the samples stored at both low and high relative humidity. These data substantiated the strong influence of the starch-g-NR copolymer on the impact strength of starch/NR foams.

Flexural properties of foams containing PPS are listed in Table VI. Trends of changes in flexural properties due to the NR content were similar to foams without PPS as described previously. The 20 pph of NR seemed to be the best foam owing to its flexural modulus and flexural strength. Insignificant changes in the flexural strain were noticed and all remaining foams showed low strain at break. Comparing the results in Tables IV and VI, PPS decreased the flexural modulus and the flexural strength of foams. It was suspected that chain scission of NR may have taken place after adding PPS because foam samples became slightly yellowish. Foams containing 15 pph of NR and 0.025–0.10 pph of PPS were investigated. Nonreacted NR was extracted from foam samples and characterized by GPC. The average molecular weight (M_n and M_w) and molecular weight distribution (M_w/M_n) of free NR (nongrafted NR) are displayed in Table VII. The molecular weight of the starch-g-NR copolymer was not determined because of the presence of starch in the graft copolymer that resulted in no dissolution in tetrahydrofuran. Undoubtedly, PPS caused a decrease in the molecular weight of NR. This was attributed to its lower flexural modulus and strength. The reduction in molecular weight of NR reduced only the flexural properties, whereas the foam toughness was improved by adding PPS. These results indicated that the starch-g-NR copolymer and NR played different roles in different mechanical properties. As stated earlier, NR is the impact modifier and always improves the impact strength of polymer blends. The impact modifier may not, however, increase the ductility or flexibility of the blends, as occurred in this study. There is no doubt that NR was a good impact modifier for thermoplastic starch and the starch-g-NR copolymer had increased impact strength but not flexural

TABLE VI
Density and Flexural Properties of Starch/NR Foams Containing 0.025 pph of PPS and Stored at 40 and 70% RH for 7 Days Before Testing

| NR (pph)	Density (g/cm^3)		E (MPa)		σ_{max} (MPa)		ε_b (%)	
	40% RH	70% RH	40% RH	70% RH	40% RH	70% RH	40% RH	70% RH
15	0.2320 ± 0.0096	0.2393 ± 0.0132	230 ± 25	164 ± 15	2.96 ± 0.38	1.49 ± 0.14	1.91 ± 0.39	1.36 ± 0.21
20	0.3110 ± 0.0295	0.3117 ± 0.0226	292 ± 30	202 ± 22	3.68 ± 0.38	2.52 ± 0.33	1.69 ± 0.21	2.29 ± 0.21
25	0.3438 ± 0.0289	0.3460 ± 0.0434	270 ± 27	205 ± 18	3.49 ± 0.40	2.54 ± 0.23	1.80 ± 0.36	2.32 ± 0.18
30	0.3889 ± 0.0231	0.3901 ± 0.0250	225 ± 31	154 ± 22	2.79 ± 0.29	1.79 ± 0.23	1.79 ± 0.22	2.92 ± 0.52
35	0.4000 ± 0.0185	0.4035 ± 0.0231	180 ± 18	175 ± 28	2.07 ± 0.26	1.97 ± 0.39	2.66 ± 0.28	2.12 ± 0.25
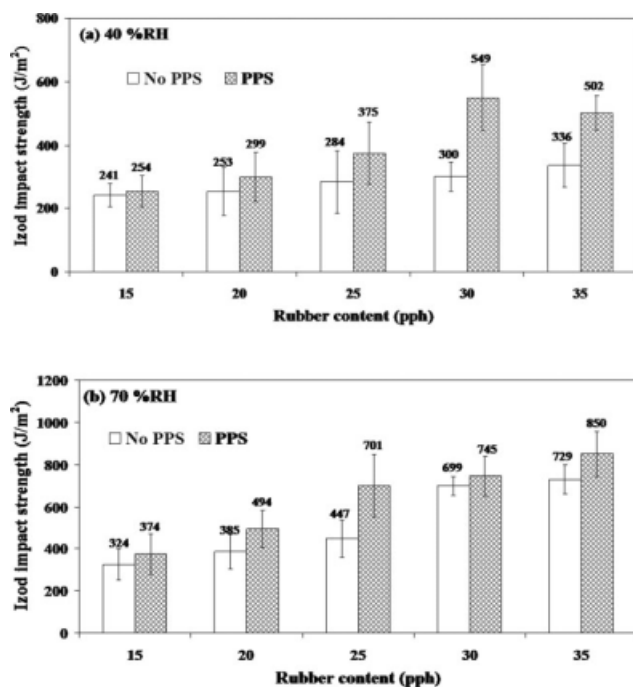
Figure 10 Effect of PPS on the impact strength of starch/ NR foams stored for 7 days at 40% RH (a) and 70% RH (b).

properties. Flexural properties of foams were seemingly governed by NR content, the molecular weight of NR and foam morphology.

It was reasonable to compare samples containing 15 pph of NR to that without NR due to their small difference in density, i.e., density of the foam with and without NR was 0.27 and 0.18 g/cm^3, respectively. For this comparison, it was remarkable that NR increased the impact strength from 137 to 241 J/m^2 and from 261 to 347 J/m^2 when stored at 40 and 70% RH, respectively. Moreover, the presence of the starch-g-NR copolymer provided a higher toughness, i.e., from 137 to 254 J/m^2 and from 261 to 374 J/m^2 when stored at 40 and 70% RH, respectively.

Benzoyl peroxide (BPO) was used as an initiator in a preliminary study. It was found that foam density of the blends increased with increasing BPO content because NR phase was crosslinked by BPO. BPO provided lower impact strength than PPS

TABLE VII
Effect of PPS Content on the Molecular Weight of NR in Starch/NR Foams

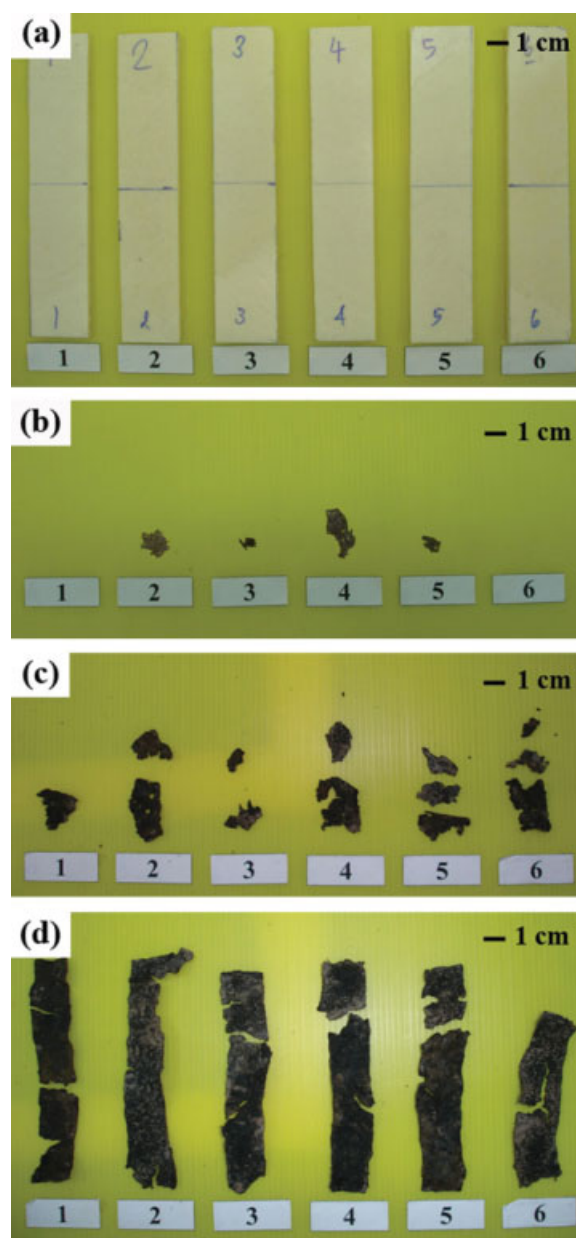| PPS (pph)	M_w	M_n	M_w/M_n
0	1,990,000	669,000	2.97
0.025	1,131,000	389,000	2.91
0.05	313,000	111,000	2.82
0.10	256,000	106,000	2.42

Figure 11 Specimens before and during soil burial testing: foams before testing (a), foams containing 15 pph of NR at the 16th week (b), foams containing 15 pph of NR and 0.025 pph of PPS at the 22nd week (c), and foams containing 35 pph of NR at the 22nd week (d). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

although BPO provided higher foam density than PPS. It is not the scope of this article to compare different initiators, particularly one showing lower impact resistance.

Degradation of foams

Degradation was evaluated by the soil burial testing. Observations of the physical changes of the foams

were the major criterion for determining degradation. It was not difficult to find foam specimens in soil after burial although soil adhered to the foam surfaces. Figure 11(a) represents a foam specimen before the soil burial test. The original dimension was 30 mm × 150 mm × 4 mm (width × length × thickness). It was found that the cassava starch foam was completely biodegraded after the 8th week because the foam specimens could not be found. Figure 11(b) shows photographs of foams containing 15 pph of NR after the burial test for 16 weeks. These starch/NR foams were almost fully biodegraded. Specimen no. 1 and 6 were not found in the soil and the other specimens were reduced to a tiny piece. Specimen no. 2–5 could not be found after the 18th week, to indicate full biodegradation. The addition of PPS delayed the biodegradation of starch/NR foams. Figure 11(c) shows foams containing 15 pph of NR and 0.025 pph of PPS after a soil burial test for 22 weeks. Biodegradation took place by ∼ 80% based on the remaining specimens. The impediment on the biodegradation of polymer blends due to the *in situ* graft copolymer has also been observed with LDPE/cassava starch blends containing PPS.[53] A higher NR content needed a longer time for degradation. Figure 11(d) shows foams containing 35 pph of NR after a soil burial test for 22 weeks. Approximately 20% biodegradation occurred and most degradation was observed on the surface of the specimens. The presence of NR reduced the water absorption of foams. The decrease in water absorption caused a lower biodegradation rate of starch because water is essential for fungus growth and the physical factors affecting the activity of the enzymes. As a consequence of the differences in the chemical structures and composition of starch and NR, their biodegradation mechanisms should be dissimilar. It was not in the scope of this study to elucidate their biodegradation mechanisms.

CONCLUSIONS

It was confirmed that the graft copolymer (starch-*g*-NR copolymer) was produced in this study by suspension blending and melt blending. NR acted as an impact modifier for thermoplastic starch and also increased the flexural modulus of the foams. No enhancement in ductility or elongation at break was noticed. A higher NR content provided higher impact strength under certain conditions. The graft copolymer had enhanced impact strength but decreased flexural properties because PPS reduced the molecular weight of NR. Although the density of the foams was different due to their different NR contents, it was confirmed that NR and the starch-*g*-NR copolymer increased the impact strength and the flexural modulus of thermoplastic starch foams with

regard to the specific impact strength and the specific flexural modulus. The soil burial tests indicated that foams containing 15 pph of NR were classifiable as a biodegradable polymer because it was biodegraded within 18 weeks after soil burial.

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