

Development of Biodegradable Plastic Composite Blends Based on Sago Derived Starch and Natural Rubber

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ABSTRACT

Polyethylene is a widely used packaging material, but its non-biodegradable nature can lead to waste disposal problems. This increases the concern in research and development of biodegradable plastics from natural resource as alternatives to petroleum-derived plastics. In this study, biodegradable plastic composites were prepared by blending thermoplastic starch with natural rubber in the present of glycerol as plasticizer. Local sago starch was cast with 0.5 to 10% of natural rubber to prepare the bioplastic. The products were characterized by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), water absorption test, biodegradable test, hydrolysis test, and mechanical analysis. Meanwhile, composite with natural rubber latex was increased from 0.5 to 10% showing that the melting temperature is in the range of 120 to 150°C, but with no significant difference. The water absorption characteristics, biodegradability, and tensile strength decreased by 11.21%, 30.18%, and 20.733 MPa, respectively. However, the elongation at break was increased from 26.67 to 503.3%. The findings of this study showed that sago starch has a great potential in bioplastic production with good miscibility and compatibility.

Keywords: Biodegradable, sago starch, thermoplastic starch (TPS), natural rubber latex

INTRODUCTION

Polyethylene is a widely used packaging material due to its good material properties and low cost. However, these qualities have overshadowed its non-biodegradable nature, leading to waste disposal problems. Moreover, this has led to the research and development of biodegradable plastics from natural resources as alternatives to petroleum-derived plastics (Kim *et al.*, 2000).

One biopolymer showing a great promise is starch. Starch, obtained from renewable resources, has many advantages which include low cost, abundant supply, and environmental amity (Takahashi, 1986). Starch is composed of amylose and amylopectin, which are both polysaccharides made up of α -D-glucopyranosy units (French, 1984). Amylose is a linear (1-4) linked α -D-glucan and amylopectin, a highly branched molecule consisting of short chains of (1-4) linked α -D-glucose with (1-6) linked α -linked branches (Kennedy *et al.*, 1983). The ratio of amylase and amylopectin varies with the starch source, but it is typically 20:80 amylose to amylopectin (Orford *et al.*, 1987).

Sago palm is one of the important starch production crops in which *M. longispinum*, *M. sylvestre*, *M. microcanthum*, *M. sagu*, and *M. rumphii* are the important species widely used. Sago starch consists of oval granules with diameters in the range of 20 to 40 μ m, and moisture contents ranging between 10.6% and 20.0%. The total amylose contents (lipid free starch) in sago starch

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ranged between 24% and 31%, whereas the apparent amylose content (starch with lipid) was slightly lower, i.e. in the range of 24% to 30%. The gelatinization temperature for sago starch is high as compared to corn, peas and potatoes, but low than sweet potatoes, Tania and yam (Tian *et al.*, 1991; Veletudie *et al.*, 1995). These led to important properties of sago starch such as ease to gelatinize, high viscosity with proper extraction and easily moulded (Takahashi, 1986). Therefore, it shows that starch has a great potential to be produced into biodegradable polymer.

However, starch properties need to be improved with physical and/or chemical additions due to poor mechanical properties, processability, and water sensitivity (Choi and Kim, 1999). Common method used to improve these properties is the use of polymer blending. It is a method designed to generate materials with optimized chemical, structural, mechanical, morphological, and biological properties. Polymer blending can be defined as a mixture of two or more polymers in order to achieve a material that has certain properties of each of the compositions of the blend. Some researchers have previously reported on some polymer blends like starch/synthetic polymer blends which only enable partial environmental degradability (Martina and Herbert, 1996; Evangelista *et al.*, 1991).

Due to the increased concern over environmental pollution caused by non-biodegradable materials, the development of biodegradable materials for wide application is on demand. As starch-based materials have been proven to be good biodegradable sources, sago starch (which is readily available in Sarawak) was chosen to be used in developing biodegradable plastic composite with a natural rubber blend. Natural rubber latex is used because it is a renewable resource which can be biodegraded and it contains natural stabilizers (i.e. proteins and lipids) that could help compatibilization with starch (Antoine *et al.*, 2004). Therefore, the objectives of the present study were to develop starch-rubber composite using sago starch and biodegradable plastic composite blend with good compatibility, miscibility, and biodegradability.

MATERIALS AND METHODS

Natural rubber latex was extracted from *Hevea brasiliensis* tree in UPMKB field and it was stabilized by adding 2.5% of ammonia solution. Meanwhile, sago starch was supplied by MuiHiong Foodstuff Company. Glycerol (Fisher Scientific) and sodium hydroxides (System) used were analytical grade reagents.

Film preparation

The method used was modified from that of Antoine *et al.* (2004). Sago starch (3% wt/wt) was gelatinized at 75°C and continuous stirred before it was dissolute in an autoclave at 120°C, 110 kPa for 30 minutes. Glycerol was added as plasticizer with 30% w/w relative to starch (dry basis). Thermoplastic starch-latex samples, in the ratios of 100:0, 99.5:0.5, 98.5:1.5, 97.5:2.5, 96.5:3.5, 95:5 and 90:10, were prepared. The mixture was then homogenized using an ultrasonic homogenizer (OMNI Rupter 250) under 30% power for 6 minutes. The products were dried at room temperature for 3 days before they were oven dried at 50°C overnight.

Film Characterization

Mechanical properties

Film products were tested for their tensile strength and elongation at break in accordance with the ASTM D 638M standard.

Differential scanning calorimetry

The film products of 10 mg were encapsulated in Tzeroaluminum pans. The sample pan was then heated at 20°C/min from 20°C to 200°C. The melting temperatures (T_m) were also recorded.

Fourier transform infrared spectroscopy

The fourier transform infrared (FTIR) spectra of the film products was recorded to be between 4000 and 500 cm^{-1} of wavelength.

Water absorption

The method used was according to Chandra and Rustgi's (1996). The film products, in the size of 2.0 x 3.5 cm, were dried for 6 hours at 50°C before they were cooled and weighed. The samples were soaked in distilled water at $23 \pm 1^\circ\text{C}$. The samples were periodically weighted every 4 weeks to record any change in their weights. The percentage of the water absorption by films was then calculated using the following formula: $W_f = \frac{W_w - W_c}{W_c} \times 100$, where W_c represents conditioned weight, W_w is wet weight, and % W_f represents the % of the final weight increase.

Film Biodegradability

Simple hydrolysis

The method used was according to the one proposed by Arvanitoyannis *et al.* (1997). The samples in the size of 1.5 x 3.0 cm were soaked in 20 ml distilled water at 70°C. The changes in the weight were measured every 2 hours in order to record the weight losses versus time.

Alkali hydrolysis

The method used was that of Arvanitoyannis *et al.* (1997). The samples with the size of 1.5 x 3.0 cm were soaked in 20 ml sodium hydroxide at 70°C. The changes in weight were measured every 2 hours to record the weight losses versus time.

Soil burial

The method employed was according to that of Arvanitoyannis *et al.* (1997). For this purpose, some film products, in the size of 3.0 x 4.0 cm, were buried into mineral soil. The films were removed, rinsed with distilled water and dried in an oven at 50°C for 24 hours before they were weighed. The test was conducted every 30 days up to 90 days of soil burial.

RESULTS AND DISCUSSION

Mechanical Properties

Both the tensile strength and elongation at break of thermoplastic starch/ natural rubber latex blends are summarized in Table 1. The mechanical profiles show that the tensile strength reduced as the percentage of the natural rubber in films increased, whereas the elongation at break was increased with the increase in the percentage of the natural rubber used in the films. Films with natural rubber contents, ranging from 0.5 to 10%, showed significantly less tensile strength as compared to the ones without any natural rubber. In particular, TPS90.0NR10.0 and TPS95.0NR5.0 exhibited a high elongation at break with the values of 420.00 and 503.33%, respectively. The results that showed

natural rubber which was used as a reinforcement agent in starch blends could cause a reverse effect on the mechanical strength. In addition, poor interfacial interaction between natural rubber and starch matrix limits the mechanical solicitation of the blends.

TABLE 1
The effect of NR treatment on the tensile strength and elongation at break of TPS films

Treatment	Mechanical properties	
	Tensile strength (MPa)	Elongation at break (%)
TPS100NR0	25.200 ^a	26.67 ^b
TPS99.5NR0.5	16.000 ^b	30.00 ^b
TPS98.5NR1.5	10.233 ^{bc}	23.33 ^b
TPS97.5NR2.5	8.600 ^c	23.33 ^b
TPS96.5NR3.5	7.200 ^c	23.33 ^b
TPS95.0NR5.0	5.367 ^c	420.00 ^a
TPS90.0NR10.0	4.467 ^c	503.33 ^a

Note: The same alphabets (within column) indicate no significant difference between mean using Tukey's test at P=0.05

Water Absorption Properties

The effect of the NR treatment on the TPS films under water absorption test is shown in Table 2. It can be seen that the ability of film to absorb water generally decreases with the (high) amount of NR blended with the TPS film. According to data analysis, however, the water absorption capacity was not significantly affected by the increases in natural rubber content from 0 to 10%. Meanwhile, water absorption capacity plays an important role in the degradability of bio-based materials. The films with a high amount of starch readily absorbed water due to the present of hydroxyl groups. Although water absorption capacity is an advantage for bio-based materials, it also becomes a drawback when applied as packaging materials. According to Zhao *et al.* (2005), this disadvantage could be overcome by methylation of starch molecule where hydrophobic of the films would be increased by replacing the hydroxyl group with the methyl group.

TABLE 2
The effect of the NR treatment on the TPS films under water absorption test

Treatment	Water absorption capacity (%)			
	1 st week	2 nd week	3 rd week	4 th week
TPS100 NR0	47.751 ^{ab}	38.882 ^a	34.732 ^{ab}	34.656 ^{ab}
TPS99.5NR0.5	47.199 ^{ab}	45.632 ^a	44.021 ^a	44.095 ^a
TPS98.5NR1.5	50.913 ^a	44.784 ^a	42.454 ^{ab}	42.439 ^{ab}
TPS97.5NR2.5	48.300 ^a	38.176 ^a	39.328 ^{ab}	42.537 ^{ab}
TPS96.5NR3.5	42.531 ^{ab}	44.386 ^a	34.866 ^{ab}	34.983 ^{ab}
TPS95.0NR5.0	41.609 ^{ab}	36.933 ^a	34.039 ^{ab}	34.084 ^{ab}
TPS90.0NR10.0	30.314 ^b	26.026 ^a	23.454 ^b	23.446 ^b

Note: The same alphabets (within column) indicate no significant difference between mean using Tukey's test at P=0.05

The Thermal Profile

The thermal profile of TPS/NR film is shown in Table 3. The thermal profile of the film products showed no significant difference in melting point with increase in natural rubber content from 0.5% to 10%. TPS films showed the melting points in the range of 120 to 150°C. Nevertheless, there was no significant difference in the melting points, and this was probably due to the low amount of rubber present in the entire TPS films. However, TPS films without natural rubber also showed the melting points of more than 100°C. This characteristic may enable the application of TPS films as packaging materials which could be heat over 100°C.

TABLE 3
Effect of NR treatment on melting point of TPS films

Treatment	Melting temperature (°C)
TPS100NR0	120.273 ^a
TPS99.5NR0.5	129.407 ^a
TPS98.5NR1.5	130.397 ^a
TPS97.5NR2.5	133.643 ^a
TPS96.5NR3.5	131.433 ^a
TPS95.0NR5.0	134.250 ^a
TPS90.0NR10.0	149.130 ^a

Note: The same alphabets (within column) indicate no significant difference between mean using Tukey's test at P=0.05

The FTIR Analysis

The FTIR spectroscopic analysis of the entire TPS films did not exhibit any drastic changes in the spectra. Meanwhile, the FTIR spectrum of films exhibited a wide O-H stretching absorbance centred around 3400 cm⁻¹, a slight C-H stretching band at 2921 cm⁻¹, and a characteristic set of strong C-O stretching bands between 960-1190 cm⁻¹. The TPS films buried in the soil showed a drastic reduction in the absorption of peaks corresponding to both the hydroxyl and fingerprint regions of the spectra. However, the changes in the absorption peaks were comparatively less in TPS97.5NR2.5, TPS96.5NR3.5, TPS95NR5, and TPS90NR10. The FTIR data in this study proved that the loss of starch material was due to biodegradation alone. Meanwhile, natural rubber functions as a coating material that protects the films from degradation. Hence, the films with high amounts of NR showed less change in the FTIR spectra. The weight loss was due to the microbial invasion and not because of the physical action alone. *Fig. 1* shows some FTIR spectra of the films before and after soil burial for 90 days.

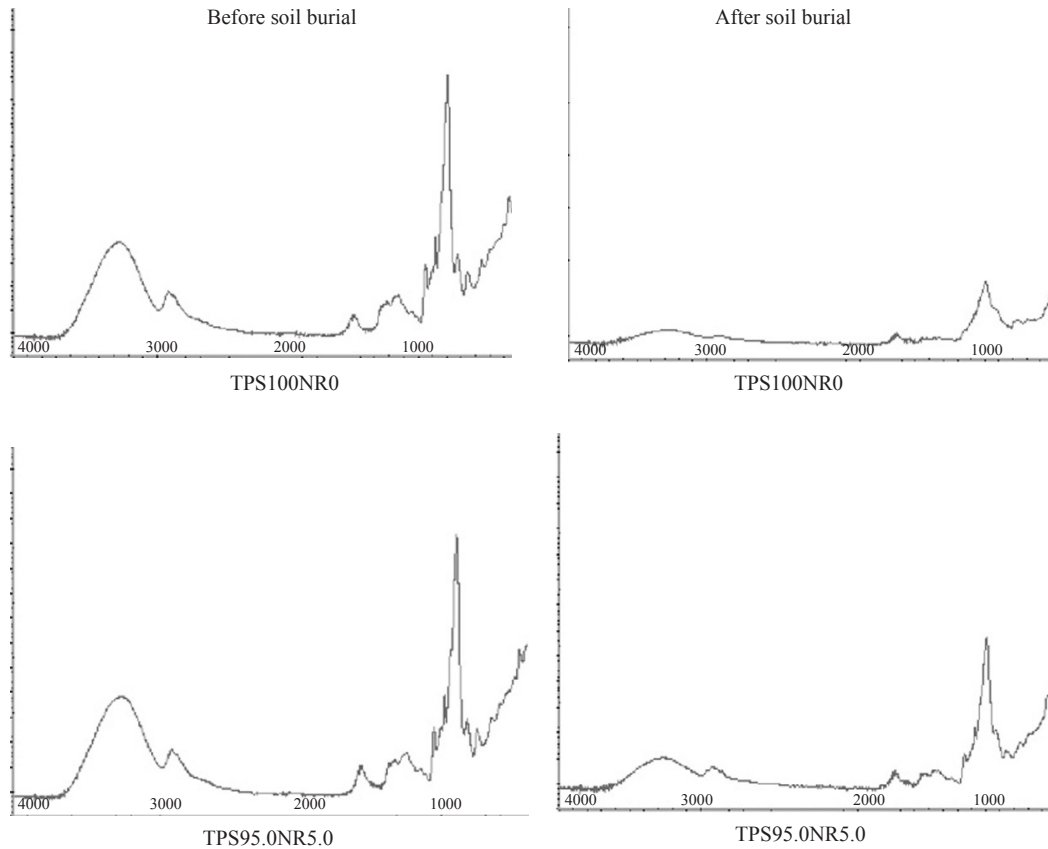


Fig. 1: Fourier Transform Infrared (FTIR) analyses before and after the soil burial for 90 days

Film Biodegradability

The data obtained from the simple hydrolysis test are shown in Table 4. Films with natural rubber content (i.e. from 3.5% to 10%) significantly experienced a slower weight loss as compared to the rest of the films. Films with higher amount of starch showed higher weight losses. This might be due to the loss of starch which got dissolved in water. Table 5 illustrates the results of the alkali hydrolysis test. All the films showed a drastic weight loss, particularly the TPS film without rubber. The alkali hydrolysis caused a higher weight loss as compared to the simple hydrolysis. Thus, NaOH was found to enhance the solubilization of gelatinized starch in the polymer blend (Arvanitoyannis *et al.*, 1997). The purpose of using these methods for assessing the biodegradability of film was to prove that the synthesized film could be degraded in water with different values of pH. Higher pH values could accelerate the degradability of starch based film.

TABLE 4
Effect of the NR treatment on the TPS films under simple hydrolysis test

Treatment	Weight loss (%)					
	2 hours	4 hours	6 hours	8 hours	10 hours	12 hours
TPS100 NR0	55.278 ^a	58.689 ^a	60.849 ^a	63.663 ^a	66.933 ^a	69.679 ^a
TPS99.5NR0.5	49.812 ^a	53.326 ^{ab}	57.528 ^{ab}	60.981 ^a	62.876 ^a	64.376 ^a
TPS98.5NR1.5	46.342 ^{ab}	49.812 ^{ab}	55.736 ^{ab}	57.709 ^{ab}	58.148 ^{ab}	61.264 ^{ab}
TPS97.5NR2.5	40.198 ^{abc}	42.035 ^{bc}	42.566 ^{bc}	42.590 ^{bc}	42.626 ^{bc}	42.703 ^{bc}
TPS96.5NR3.5	28.599 ^{bcd}	29.262 ^{cd}	29.654 ^{cd}	29.681 ^c	29.843 ^c	29.891 ^c
TPS95.0NR5.0	32.605 ^{bcd}	33.490 ^{cd}	33.711 ^{cd}	33.675 ^c	34.032 ^c	34.051 ^c
TPS90.0NR10.0	21.268 ^d	23.574 ^d	24.461 ^d	28.096 ^c	28.270 ^c	28.340 ^c

Note: The same alphabets (within the column) indicate no significant difference between the mean using Tukey's test at P=0.05

TABLE 5
Effect of the NR treatment on the TPS films under alkali hydrolysis test

Treatment	Weight loss (%)					
	30 min	60 min	90 min	120 min	150 min	180 min
TPS100NR0	100.000 ^a	100.000 ^a	100.000 ^a	100.000 ^a	100.000 ^a	100.000 ^a
TPS99.5NR0.5	41.900 ^b	64.773 ^{bc}	71.361 ^{bc}	73.501 ^b	75.441 ^b	76.843 ^b
TPS98.5NR1.5	53.290 ^b	75.098 ^{ab}	77.006 ^{ab}	77.542 ^{ab}	78.288 ^{ab}	78.864 ^b
TPS97.0NR2.5	43.280 ^b	54.983 ^{bc}	57.348 ^{bcd}	58.410 ^{bc}	59.756 ^{bc}	60.369 ^{bc}
TPS96.0NR3.5	52.290 ^b	57.241 ^{bc}	58.100 ^{bcd}	58.388 ^{bc}	58.901 ^{bc}	59.238 ^{bcd}
TPS95.0NR5.0	44.140 ^b	48.009 ^{bc}	48.558 ^{cd}	48.833 ^c	49.101 ^c	49.316 ^{cd}
TPS90.0NR10.0	36.410 ^b	37.977 ^c	38.049 ^d	38.174 ^c	38.275 ^c	38.589 ^d

Note: The same alphabets (within the column) indicate no significant difference between the mean using Tukey's test at P=0.05

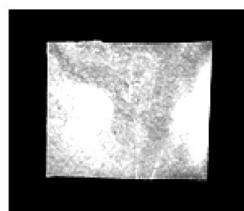
The soil burial test provides a real environment for the polymer to biodegrade. A rapid weight loss was observed in all the films with different compositions during the first 30 days of the experiment as shown in Table 6. After 90 days of exposure to soil, the films were found to have reduced in size and become hard and fragile. The film deterioration was indicated by the loss in their total weight after soil burial for the three-month period. There were black and red spots on the surface of the films indicating the soil microbial invasion. *Fig. 2* shows films without natural rubber which had experienced a rapid degradation as compared to the rest of the films.

TABLE 6
Effect of the NR treatment on the TPS films in the soil burial test

Treatment	Weight loss (%)		
	30 th days	60 th days	90 th days
TPS100.0NR0	44.64 ^a	50.46 ^a	59.35 ^a
TPS99.5NR0.5	23.50 ^a	46.58 ^a	59.95 ^a
TPS98.5NR1.5	20.19 ^a	58.59 ^a	59.21 ^a
TPS97.5NR2.5	24.33 ^a	42.34 ^a	43.81 ^a
TPS96.5NR3.5	21.21 ^a	32.30 ^a	33.21 ^a
TPS95.0NR5.0	26.77 ^a	38.59 ^a	42.56 ^a
TPS90.0NR10.0	18.94 ^a	28.29 ^a	29.17 ^a

Note: The same alphabets (within the column) indicate no significant difference between the means using Tukey's test at P=0.05

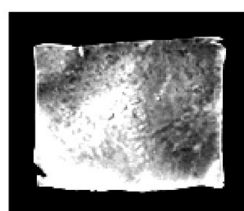
TPS100.0NR0



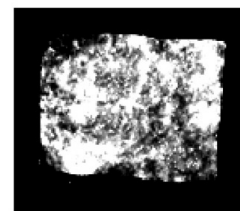
Before soil burial



After 90 days of soil burial



Before soil burial



After 90 days of soil burial

Fig. 2: The evolution of the physical state of the TPS films before the soil burial during 90 days of the experiment

CONCLUSIONS

Sago starch and rubber latex blends showed a wide range of physical and mechanical properties. This shows that sago starch has a good potential in producing bioplastic with good miscibility and compatibility. Further study using different plasticizers may produce blends with the optimum properties for different applications.

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