

# Thermoplasticization of sago residue by esterification with plant oil

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**Abstract** In order to establish sago residue as new woody resource for making plastic sheets, the reactivity with plant oil, thermoplasticity, and the solvent suitable for washing the reaction products were evaluated.

Methanol-water mixture solvent and methanol-hexane mixture solvent were used to extract unreacted products from the esterified sago residue (ESR). In case of methanol-water mixture solvent, the washed ESR showed higher weight increases than samples which were washed with other solvents and it was indicated that the palm oil used as esterification reagent still remained. With methanol-hexane mixture solvent at 8: 2 v/v, the weight of washed ESR was decreased. This indicates that a portion of reaction products must have been dissolved in this solvent. On the other hand, in case of methanol-hexane solvent at 9: 1 v/v, the weight of washed ESR was increased and unreactive palm oil was removed. The methanol-hexane mixture solvent (9: 1 v/v) is, therefore, more suitable than other solvent for washing reaction products. As regards esterification, results of IR spectroscopy and measurement of fatty acids showed that reaction conditions at 140°C for 4 hours and 160°C for 2 hours were more suitable than other conditions. Thermoplasticity of plastic sheets made from ESR improved with the addition of glycerol. The plastic sheets from the reaction at 140°C for 4 hours showed better thermoplasticity than other sheets. The sheets from ESR showed higher modulus of elasticity with glycerol addition.

**Key words:** Esterification, Plasticizer, Sago residue, Thermoplasticity

## 植物油脂によるサゴヤシ澱粉抽出残渣のエステル化と熱可塑性の付与

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**要約** 本研究ではプラスチックシート原料として、サゴヤシ澱粉抽出残渣の有効利用法の確立を目指し、化学修飾後の反応生成物の洗浄に適した溶媒の検討、熱可塑性に及ぼす可塑剤添加の効果及びシートの力学的特性の評価を試みた。

メタノール-水混合溶媒及びメタノール-ヘキサン混合溶媒を用いて反応生成物の洗浄について検討を行った。メタノール-水混合溶媒では反応前後での質量増加率は著しく増加したが、エステル化剤として用いたパーム油の未反応部分が残存していることが認められた。メタノール-ヘキサン混合溶媒 (8: 2 v/v) では質量増加率がマイナスを示し、成分の一部が可溶化していることが認められた。混合比 (9: 1 v/v) では、未反応のパーム油の残存が認められず、質量増加率もプラスを示した。よって、メタノール-ヘキサン (9: 1 v/v) 混合溶媒が、他のメタノール-水混合溶媒などより反応生成物の洗浄溶媒として適していることが明らかになった。エステル化の反応条件については、ケン化による遊離脂肪酸の定量及び赤外線分光分析から 140°C で 4 時間、及び 160°C で 2 時間の条件が他のものよりも適していた。熱可塑性の目視評価では、グリセリンの添加量に伴って熱可塑性が向上し、グリセリンの可塑剤としての効果が確認された。また、140°C 4 時間の反応条件でエステル化された試料が、他の反応条件でエステル化されたものよりも熱可塑性

が高い傾向がみられた。シートの弾性率測定においては、熱可塑性の評価と同様に、140°C 4時間の反応条件でエステル化された試料が比較的他のものよりも高い値を示した。

キーワード エステル化, 可塑剤, サゴヤシ澱粉抽出残渣, 熱可塑性

## Introduction

Sago palm is used for food in Southeast Asia for its starch that accumulate in the stem. Moreover, the starch is industrially utilized (Yatugi 1984). The residue after extraction of starch from pith is, however, not utilized and becomes a disposal problem. This sago residue contains cellulose, hemicellulose, lignin, and residual starch that could not be extracted. Utilization of this residue as new woody resource is thought possible (Watanabe and Ohmi 1997). Therefore, thermoplasticization of sago residue for making plastic sheet was tried in this study.

Esterification is one of the chemical modifications that add thermoplasticity to plant resource (Ogura 1984, Feuge, et al. 1970, Rizzi, et al. 1978). However, most of the reagents used are petroleum-based (Funakoshi, et al. 1979). On the other hand, there is a large number of ester compounds, which can be esterification reagent, such as plant oils and fats in natural products.

This study experimented on making plastic sheet from sago residue esterified with plant oil. For examining the possibility of using plant biomass to chemically modify the sago residue, sago residue was esterified by ester interchange reaction (alcoholysis) with plant oil (Sonntag 1979). The reactivity, thermoplasticity, and mechanical properties of the reaction products were evaluated.

## Experiment

### Materials

Sago residue (provided by Nistei Sago Industry, Sarawak, Malaysia) was dried at 50°C. Thereafter, the dried sago residue was extracted by ethanol-benzene mixture (1: 2 v/v) in Soxhlet extractor for 24 hours for the purpose of removing lipid. The extracted sago residue was air-dried then vacuum-dried at 50°C. Sago residue sample was milled through 60-mesh sieve. Palm oil was used as esterification chemical.

### Esterification

Esterification of sago residue was conducted by ester interchange reaction. Palm oil containing a large amount of triglyceride, was used as esterification chemical. N/2 HCl was used as the acid catalyst from the results of Ohmi's study (Ohmi 1998).

The mixture of sago residue (10 g), palm oil (120 g), and N/2 HCl (2.5 g) were heated and stirred in a separable flask attached with a reflux condenser, agitator, and thermometer at 140°C or 160°C for 2 or 4 hours. The weight ratio of sago residue and palm oil was minimum to be mixed and stirred in flask from pre-experiments. The reaction was conducted in atmosphere of nitrogen to prevent the oxidation of palm oil.

### Examination of solvent to remove unreacted palm oil

After the reaction, the esterified sago residue (ESR) was pre-washed with methanol, and extracted with six kinds of solvents in Soxhlet extractor for 24 hours to remove unreacted palm oil. After the solvent extraction, the product was air-dried, vacuum-dried at 50°C and weighed.

### Determination of fatty acid generated by saponification

The mixture of washed ESR (0.3 g) and N/2 KOH (ethanol solution, 25 ml) was put in a flask attached to a reflux condenser and heated at 60°C in water bath for 1 hour. After cooling, N/2 HCl (25 ml) and phenolphthalein were added in the flask. Amounts of fatty acid which were generated by saponification, were determined by neutralization with N/10 KOH (Kuwata 1969).

### Infrared spectroscopy

Infrared spectra were measured to evaluate the presence of ester bond. The measurement was conducted with SHIMAZU FT-IR 8100 following the

KBr tablet method.

### Preparation of plastic sheets

The reaction product ESR (about 2 g) and glycerol (0 g, 0.2 g, 0.3 g, 0.4 g) were mixed and put into the steel molding box (diameter: 80 mm) and hot-pressed. The conditions for hot-pressing were 5 min under 215 kPa, 2 min under 53.7 kPa, and 10 min under 215 kPa, all at 140°C. After hot-pressing, the plastic sheets were cold-pressed at 102 kPa for 10 min. Thermoplasticity of plastic sheets was evaluated visually on the section that was changed by pressing.

### Measurements of modulus elasticity

Plastic sheets were cut to 24 mm × 4 mm × 0.3 mm dimensions. Modulus of elasticity (MOE) of the sheets was measured by DVE-V4 (Rheology Co. Ltd). MOE was determined under conditions of auto pressure and displacement amplitude (2.0 μm) of sine wave at 900 Hz. Commercial polyethylene sheet was also measured as control.

## Results and discussion

### Investigation of solvent to remove unreacted palm oil

Table 1 shows weight increases of ESR samples,

which was esterified at 140°C for 4 hours, with various extraction solvents. The weight increases of samples washed with methanol or water-methanol mixture solvents were high and the washed ESRs were oily. On the other hand, the weight increases of samples washed with methanol-hexane mixture solvent were very low, and the washed ESRs were not oily. It was therefore obvious that methanol and water-methanol mixture solvent could not extract unreacted palm oil. In case of methanol-hexane (8:2) mixture solvent, the decrease of the weight was considered due to solubilization of a part of the reaction product. Therefore, methanol-hexane (8:2) mixture solvent was not suitable.

Table 2 shows the amount of 10 / N KOH to neutralize the fatty acid generated from sample by saponification. It shows that the washed ESR with methanol-hexane (9:1) was required more of the titre.

Figure 1 shows the infrared spectra of washed samples. The sample washed with methanol-hexane (9:1) mixture solvent shows the higher adsorption peak of ester bond at 1750 cm<sup>-1</sup>.

Therefore, it was suggested that the methanol-hexane (9:1) mixture solvent was the most suitable to wash the ESR.

**Table 1** Weight increase of ESR after solvent extraction

Solvent (v/v)	Weight increase (%)	SD*
Methanol	133.1	14.9
Water - methanol (5 : 5)	231.4	18.9
Water - methanol (7 : 3)	254.8	36.6
Water - methanol (3 : 7)	259.2	6.1
Methanol - hexane (8 : 2)	-2.1	3.1
Methanol - hexane (9 : 1)	6.6	0.9

\* SD: standard deviation.

**Table 2** Amount of 10 / N KOH to neutralize fatty acid

Solvent (v/v)	10 / N KOH (ml/g)	SD**
Control*	12.9	1.2
Methanol - hexane (8 : 2)	17.0	0.9
Methanol - hexane (9 : 1)	17.5	0.9

\* Control: untreated sago residue.

\*\* SD: standard deviation.

### Qualitative and quantitative analyses of esterification

Table 3 shows the weight increases and the amounts of 10 / N KOH to neutralize the fatty acid generated by saponification. As for titre of saponification, all reaction products were higher than untreated sample. However, no distinct correlation was found between the weight increases and the amounts of 10 / N KOH. Figure 2 and 3 shows the infrared spectra of the reaction products according to the reaction times. Both of the reaction products reacted at 140°C and 160°C showed the adsorption peak of ester bond (about 1750 cm<sup>-1</sup>). The reaction product that obtained at 160°C for 2 hours showed the highest adsorption

peak of ester bond.

From the results of the above qualitative and quantitative analyses, it is suggested that esterification of sago residue with palm oil at either 160°C for 2 hours or 140°C for 4 hours, is more effective than other reaction conditions.

### Evaluation of thermoplasticity of reaction products

The plastic sheets were prepared for visual evaluation of thermoplasticity of reaction products. The sheets were put on a mesh sheet with lighting from the backside (mesh side). Thermoplasticization was evaluated according to the visibility of the lattice of mesh sheet from the front side of the plastic sheets.

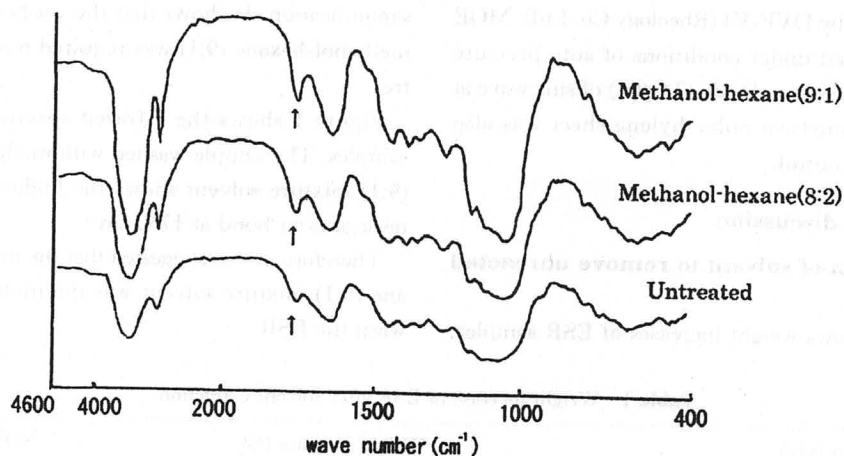


Fig. 1 Infrared spectra of reaction products that was washed by methanol-hexane mixture solvent.

Table 3 Weight increase and amount of 10 / N KOH to neutralize fatty acid of the reaction product

Temperature (°C)	Reaction time (hrs)	Weight increase (%)	SD**	10/N KOH (ml / g)	SD***
Control*	—	—	—	12.9	1.2
140	2	6.6	0.9	17.5	0.9
	4	2.4	1.7	19.9	3.9
160	2	3.7	1.8	20.1	1.4
	4	0.3	1.1	19.5	3.3

\* Control: untreated sago residue.

\*\* SD: standard deviation of the weight increase (%).

\*\*\* SD: standard deviation of the amount of 10 / N KOH (ml / g).

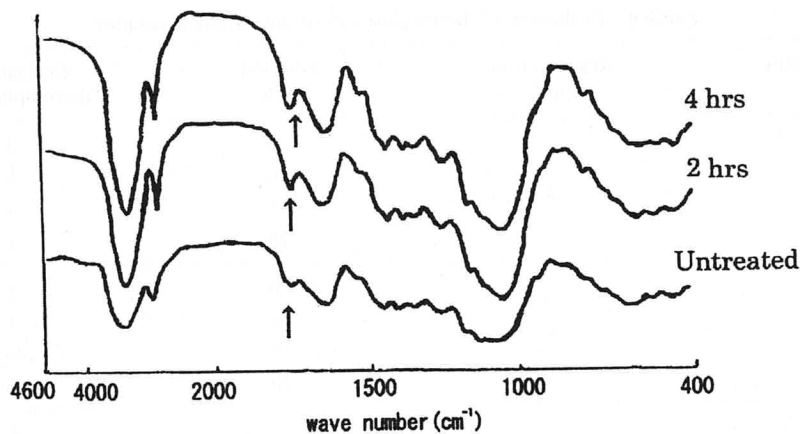


Fig. 2 Infrared spectra of reaction products at 140°C.

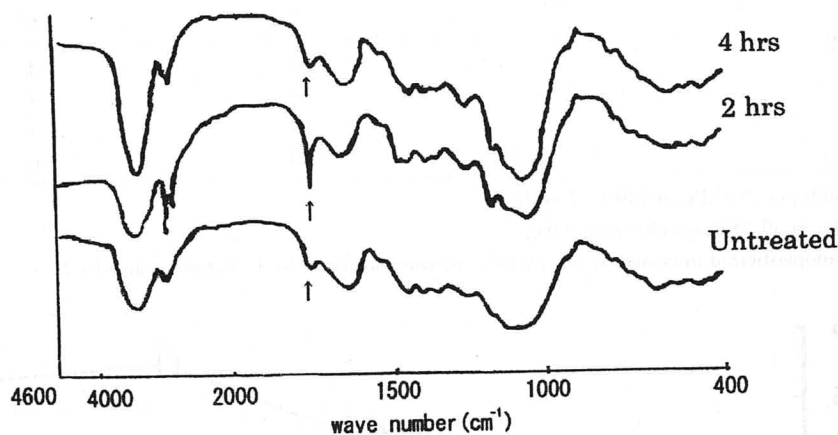


Fig. 3 Infrared spectra of reaction products at 160°C.

Without glycerol, the sheet from 2 g of the reaction product did not show plasticity. However, even without glycerol the sheet indicated thermoplasticity when the weight of reaction product was 1.5 g. This indicates that sago residue was thermoplasticized by esterification. Table 4 shows the result of evaluation of thermoplasticity. Well thermoplasticized indicated by ++; partially thermoplasticized by +; and no change by  $\pm$ . The thermoplasticity of the sheets increased with increases of glycerol content. This suggests that glycerol was effective plasticizer for thermoplasticization of these reaction products.

#### Modulus of elasticity of the sheet

Figure 4 shows the MOEs of the sheets. MOEs of

the sheets were higher than that of polyethylene. The sheets prepared from the reaction product that were reacted at 140°C for 4 hours, tend to be of higher elastic modulus than others. This result agrees with the evaluation of thermoplasticity. The elastic modulus curves tend to increase with glycerol content.

The above results suggest that the MOEs of the sheets and the thermoplasticization are directly related, and that the MOEs of the sheets increased with glycerol content.

#### Conclusion

For utilizing sago residue, reactivity of palm oil on sago residue, thermoplasticity, and mechanical properties of the esterified products were evaluated,

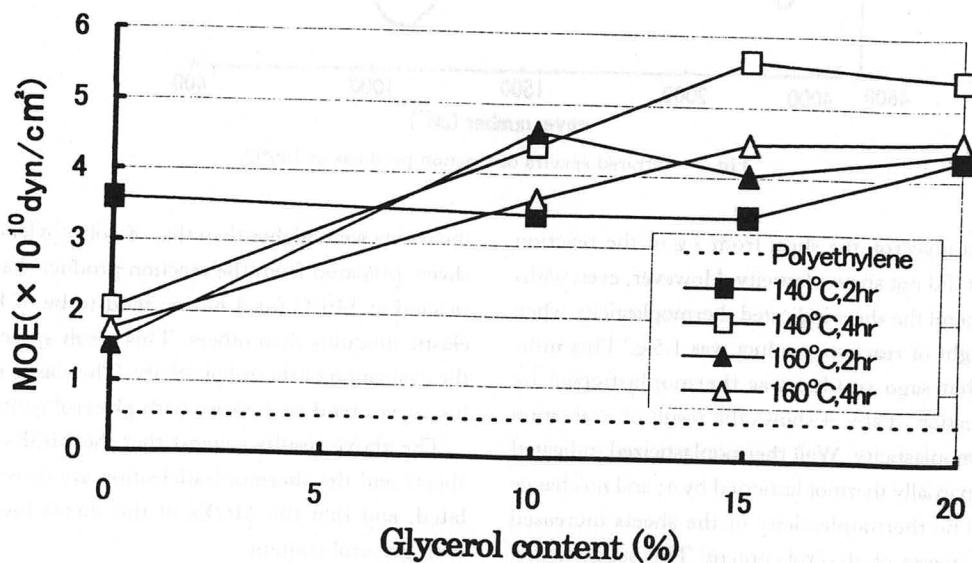
**Table 4** Evaluation of thermoplasticity of the esterified samples\*

Temperature (°C)	Reaction time (hrs)	Glycerol (wt%)	Evaluation of thermoplasticity**
140	2	0	±
		10	+
		15	+
		20	+
140	4	0	±
		10	+
		15	++
		20	++
160	2	0	±
		10	+
		15	+
		20	++
160	4	0	±
		10	+
		15	+
		20	++

Hot-press condition: 215 kPa, at 140°C, 2 cycle.

\* The weight of all ESR samples were 2.0 g.

\*\* Well thermoplasticized indicated by ++; partially thermoplasticized by +; and no change by ±.

**Fig. 4** Modulus of elasticity curves of the sheets.

the following conclusion was confirmed.

- 1) It is possible to esterify sago residue with plant oil.
- 2) Methanol-hexane (9:1) mixture solvent is more effective solvent than other methanol, water-methanol, and methanol-hexane (8:2) mixture

solvent to remove unreacted palm oil.

- 3) The ESR, from the reaction at 140°C for 4 hours, is more suitable for preparing plastic sheet than those from other reaction conditions.
- 4) MOEs of plastic sheets from the ESR were higher than that of polyethylene and increased with an increase in the amount of glycerol added.

In this paper, reaction condition and properties of plastic sheet were mainly discussed. Therefore, there are some problems such as amounts and recover of esterification reagent, washing with organic solvent, and equipment for practical process. In order to establish the sago residue as new material of plastic, henceforward, it may be necessary to study about practical processing and more effective esterification.

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