

## Degradability of plastic sheeting prepared from esterified sago residue

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**Abstract** In this report, plastic sheeting prepared from esterified sago residue was investigated for its degradability in soil or on fungi and for its insolubility in various solvents.

The esterification conditions for the residue, as adopted in the previous study, were reaction at 140°C for 4 hours or at 160°C for 2 hours. The reaction products were mixed with glycerol (0, 10, 15 and 20wt%) as a plasticizer and then molded into a plastic sheet by a hot-press. Samples of the plastic sheeting were buried in soil for 60 days. After this period, all samples showed a decreasing modulus of elasticity (MOE) and loss of mass. Other plastic sheet samples were placed on a fungus medium. The resulting samples were remarkably biodegraded, regardless of the esterification conditions or the glycerol contents. The results of insolubility tests with various solvents showed clearly that plastic sheeting had low insolubility in acid and alkali solutions. A comparison of insolubility between polar and non-polar solvents, revealed higher insolubility in the non-polar. In addition, the insolubility of the polar solvent decreased with increasing glycerol content.

**Key words:** Biodegrade, Exposure to soil or fungus, Insolubility, Sago residue.

## エステル化したサゴヤシデンプン抽出残渣から調製したプラスチックシートの分解性

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**要約** 本報ではサゴヤシデンプン抽出残渣から調製したプラスチックシートの生分解性を検討するため、土壌環境中での分解性、培養した生菌による分解性、各種溶媒に対する耐性を評価した。

前報のエステル化反応条件で効率の良かった条件(140°C・4時間、160°C・2時間)でサゴヤシデンプン抽出残渣をエステル化し、グリセロールを混合(0, 10, 15, 20wt%)してプラスチックシートを調製した。このシートを土壌環境に60日間曝露して試験した結果、プラスチックシートの弾性率低下・重量減少が確認された。同様に調製したプラスチックシートをカワラタケを培養した培地に60日間静置して生菌分解試験を行った結果、試料はエステル化条件やグリセロールの添加量に関わらず顕著に分解された。各種薬品による耐溶解性試験の結果、プラスチックシートは酸やアルカリに対する耐性は低いことが明らかになった。極性溶媒と無極性溶媒に対する耐溶解性を比較すると、無極性溶媒に対する耐溶解性の方が高く、さらに極性溶媒の耐溶解性はグリセロールの添加により減少することが明らかになった。

**キーワード** 生分解、サゴヤシデンプン抽出残渣、耐溶解性、土壌および生菌への曝露

### Introduction

Because sago palm, found in Southeast Asia, contains a large amount of starch in the stem, it is used

as a food resources in that part of the world. Sago is cultivated on plantations, and after the plant is harvested, the starch is extracted from the milled pith with water. However, the extracted sago residue is treated as a waste, since there has been no known

use for it. Consequently, various studies for utilizing the residue had been carried out (H. M. H. Bintoro et al. 2001, Sasaki et al. 1999, Watanabe and Ohmi 1997). It was cleared that, after the starch is extracted, sago residue consists almost entirely of polysaccharide components, such as starch, hemicellulose and cellulose. These polysaccharides will be important in the development of new uses of sago residue. In our previous paper, we investigated the esterification of sago residue with plant oil and the preparation of plastic sheets (Sasaki et al. 1999). However, that paper did not deal with the behavior of such sheets in the environment after they are discarded. To protect the environment, all new studies of potential bioresources must take into account the biodegradability of materials. From this standpoint, natural polysaccharides, such as starch and cellulose, have often been used to produce biodegradable plastic materials (Dohi 1995, Yoshioka et al. 1996).

Thus, in this paper we expose plastic sheets, prepared from esterified sago residue, to soil or fungi in order to evaluate their biodegradability, and we assess the insolubility of the sheets in various solvents.

## Experiment

### Materials

Sago residue after starch extraction (provided by Nistei Sago Industry, Sarawak, Malaysia) was milled and passed through a 60-mesh sieve. The milled sago residue was extracted with ethanol-benzene (1:2 v/v) mixed solvent and was dried at 60°C *in vacuo*, and was then esterified with palm oil and 1/2N-HCl as an acid catalyst. The esterification was carried out under the reactive conditions of 140°C for 4 hr or 160°C for 2 hr; these were the conditions used in the previous paper (Sasaki et al. 1999). Plastic sheets were prepared from the esterified sago residue by hot-pressing. Another sheets were prepared with the addition of 20wt% of glycerol to preparation, and was also examined.

### Degradability on soil surface and in soil

In order to evaluate the degradation of plastic sheeting in the environment, two tests were carried out, including burial of a sheet in soil and placement of a

sheet on top of soil. Squares measuring 2 × 2 cm were cut from plastic sheeting as samples, and were exposed to Andosols (FAO et al. 1998) for about 60 days in a field belonging to the Tokyo University of Agriculture and Technology. The samples were then packed in polyethylene sheets with either 5-mesh or 24-mesh nets, and were then placed on the soil surface. Other samples were packed in 24-mesh polyethylene sheets and buried in the soil at a depth of 5 cm. In all of these samples, we traced the decreases in the modulus of elasticity (MOE), mass and area every 20 days for a total of 60 days, and we evaluated the degradation occurring in that period either on or in natural soil. The MOE of each sample was measured non-distractively by a DVE-V4 Rheospectoler (Rheology Co. Ltd).

### Exposure to fungus

Other samples, also measuring 2 × 2 cm, were exposed to wood-rot fungus *Trametes versicolor* (FFPRI 1030). The fungus was cultured on Potato Dextrose Agar medium for 20 days at 28°C. Then, weighed samples were put on a fungal mat and were incubated for 60 days at 28°C. The biodegradability was evaluated according to the loss of mass.

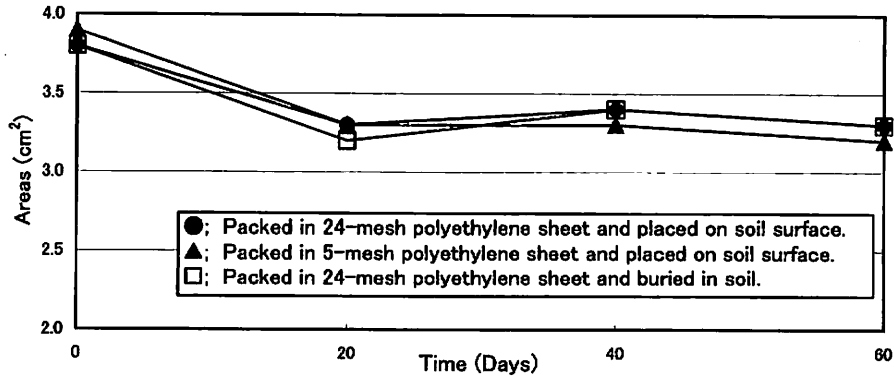
### Insolubility in various solvents

Acid (0.5N-HCl), alkali (0.5N-NaOH), polar (ethanol and dimethylformamide/DMF and water) and non-polar (hexane and benzene) solvents were used as test solvents. A plastic sheet was milled to the size of an 80-mesh pass and was dried. A sample in the amount of 0.3 g was treated with 50 ml of each test solvent. The treatment was carried out by shaking at 25°C. After 24 hours of being shaken, each sample was filtrated and was dried at 50°C for 24 hours *in vacuo*. The insolubility was calculated from the difference in mass before and after treatment.

## Results and discussion

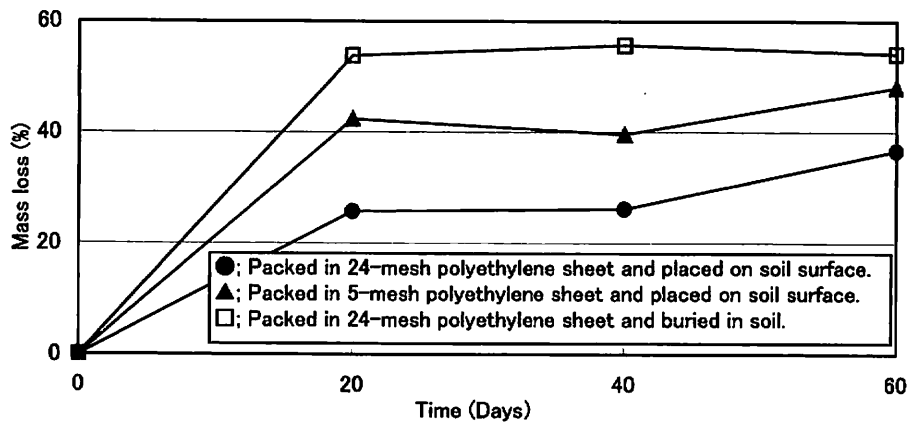
### Biodegradability in Andosols

Figure 1 shows areal changes in the sheet for every 20 days for a total of 60 days. The sample was esterified at 160°C for 2 hours and was then mixed with 20wt% of glycerol to make a plastic sheet by



**Fig. 1** Areal change of plastic sheets placed on and buried in soil.

The plastic sheet was prepared from sago residue, which was esterified at 160°C for 2 hours, and contained 20wt% of glycerol.

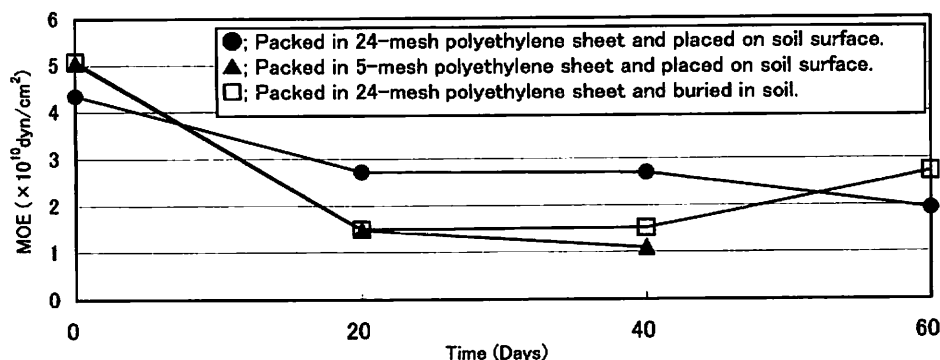


**Fig. 2** Mass loss of plastic sheets placed on and buried in soil.

The plastic sheet was prepared from sago residue, which was esterified at 160°C for 2 hours, and contained 20wt% of glycerol.

hot-pressing. From the results shown in Figure 1, it was clear that all samples placed on or in the soil surface lost area in the first 20 days. However, the area did not reduce any further after the first 20 days. Figures 2 and 3 show the mass losses and the MOE losses of samples under the same experimental conditions as in Figure 1. Similar to the case with the decrease in area, losses of mass and MOE were also considerable within the first 20 days and thereafter did not vary. The buried sample in soil showed the highest loss of mass. The sample that was packed in 5-mesh polyethylene and placed on soil showed

the next-highest loss of mass. Table 1 shows the results of all samples prepared under the various experimental conditions. These results indicated that the sheets rapidly decreased for the first 20 days, and that the sheet mixed with glycerol was more degradable than the sheet without glycerol. For samples placed on the soil surface, the mesh size of the sealing bag affected the degree of the mass loss but not the overall pattern of loss. This result seems to suggest that the area of a sheet exposed to soil was an important factor in degradation. In addition, the samples buried in the soil were more degraded than



**Fig. 3** Modulus of elasticity change of plastic sheets placed on and buried in soil. The plastic sheet was prepared from sago residue, which was esterified at 160°C for 2 hours, and contained 20wt% of glycerol.

**Table 1** Modulus of elasticity and mass loss of all plastic sheets placed on soil surface and buried in soil.

Sample <sup>1)</sup>	Modulus of elasticity (10 <sup>10</sup> dyn/cm <sup>2</sup> ) Time (Days)				Mass loss (%) Time (Days)		
	0 ( $\sigma$ )	20 ( $\sigma$ )	40 ( $\sigma$ )	60 ( $\sigma$ )	20 ( $\sigma$ )	40 ( $\sigma$ )	60 ( $\sigma$ )
40U24	2.63 (0.64)	ND <sup>2)</sup>	ND <sup>2)</sup>	ND <sup>2)</sup>	18 (2.3)	16 (6.9)	26 (5.5)
40U5	2.26 (0.20)	ND <sup>2)</sup>	ND <sup>2)</sup>	ND <sup>2)</sup>	24 (6.2)	25 (7.6)	36 (5.4)
40D24	2.68 (0.41)	2.94 (0.07)	2.51 (0.10)	2.45 (1.6)	23 (0.6)	22 (1.6)	31 (1.7)
42U24	5.31 (0.74)	1.41 (0.89)	1.92 (1.42)	ND <sup>2)</sup>	41 (2.2)	38 (7.4)	47 (2.8)
42U5	6.38 (0.73)	1.55 (0.22)	1.47 (0.16)	ND <sup>2)</sup>	50 (0.0)	45 (7.1)	ND <sup>2)</sup>
42D24	5.97 (0.64)	2.09 (0.23)	2.06 (0.17)	2.93 (0.42)	33 (0.0)	38 (5.9)	42 (11.8)
60U24	2.90 (0.33)	1.54 (0.38)	1.71 (0.37)	1.59 (0.45)	29 (1.6)	26 (5.2)	32 (3.7)
60U5	3.19 (0.11)	1.12 (0.41)	1.43 (0.33)	1.49 (0.21)	12 (3.7)	34 (8.1)	35 (5.8)
60D24	2.95 (0.29)	1.23 (0.29)	1.20 (0.33)	2.31 (0.12)	29 (1.6)	26 (5.2)	35 (5.1)
62U24	4.34 (0.35)	2.72 (0.30)	2.71 (0.33)	1.93 (0.48)	26 (3.9)	26 (5.5)	37 (4.7)
62U5	5.05 (0.69)	1.46 (0.41)	1.09 (0.14)	ND <sup>2)</sup>	42 (2.8)	40 (6.1)	48 (7.4)
62D24	5.09 (1.12)	1.49 (0.00)	1.52 (0.69)	2.73 (0.25)	54 (6.7)	56 (8.2)	54 (7.7)

<sup>1)</sup> The first number is representative of the esterified condition; 4 or 6 show sago residue was esterified at 140°C for 4 hours, or at 160°C for 2 hours. The second number is representative the content of glycerol; 0 or 2 show 0wt%, or 20wt% of glycerol was added to prepare plastic sheet. The third alphabet is representative the place where this analysis was carried out; U or D show sample was placed on the soil surface, or buried in the soil. The last number is representative the mesh size of polyethylene which sealed up with a sample; 24 or 5 show used 24 mesh or 5 mesh polyethylene.

<sup>2)</sup> ND is representative that the value is Not Detected. ( $\sigma$ ) is representative the standard deviation.

those placed on the soil. This was because microorganisms attacked the buried samples more thoroughly than they attacked the non-buried samples. In this study, sheets were degraded accurately, because the mass loss and the decrease of MOE occurred at the same time.

### Biodegradability to fungus

Figure 4 shows the biodegradability of the sheets with white-rot fungus, which degrades lignin, cellulose and hemicellulose. After the period of degradation, the color of the sample sheets had changed markedly, from deep brown to clear. In the control

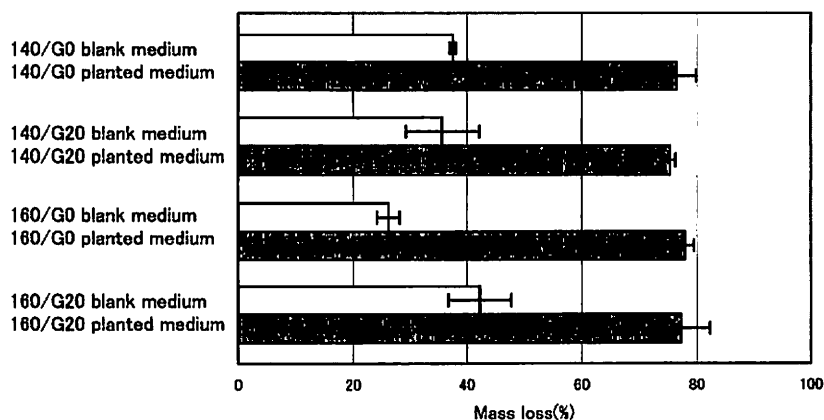


Fig. 4 Biodegradability of plastic sheet with *Trametes versicolor*.

In the mark of vertical pole, the first number such as 140 or 160 is meaning esterificated conditions; [140] shows the conditions of esterification at 140°C for 4 hours and [160] shows the condions of esterification at 160°C for 2 hours, and the second number such as G0 or G20 is meaning the glycerol content when the plastic sheet was prepared.

Table 2 Insolubility of samples in various solvents

Sample <sup>1)</sup>	Insolubility / Residual mass (%)						
	Water ( $\sigma$ )	Hexane ( $\sigma$ )	Benzene ( $\sigma$ )	Ethanol ( $\sigma$ )	DMF ( $\sigma$ )	HCl ( $\sigma$ )	NaOH ( $\sigma$ )
140 / G0	65 (0.8)	90 (0.8)	87 (0.1)	92 (1.0)	64 (5.1)	62 (0.0)	38 (0.4)
140 / G20	54 (0.3)	97 (0.3)	94 (0.1)	84 (0.2)	60 (0.2)	52 (0.1)	35 (0.5)
160 / G0	58 (0.6)	84 (4.0)	92 (0.4)	79 (4.8)	67 (0.4)	53 (0.2)	39 (0.1)
160 / G20	43 (5.4)	92 (0.3)	96 (1.4)	51 (0.3)	52 (0.8)	46 (0.1)	35 (0.6)

<sup>1)</sup> The first number such as 140 or 160 is representative of esterified condition; 140 or 160 show sago residue was esterificated at 140°C for 4 hours, or at 160°C for 4 hours. The second number with G such as G0 or G20 is representative the content of glycerol; G0 or G20 show 0wt% or 20wt% of glycerol was added to prepare plastic sheet. ( $\sigma$ ) is representative standard deviation.

samples, sheets were hydrolyzed somewhat by the moisture from the medium. However, the esterified samples showed a nearly 40 % loss of mass even after the control value was subtracted. From this result, it was clear that the fungus biodegraded the plastic sheet prepared from the esterified sago residue.

#### Insolubility in various solvents

Table 2 shows the insolubility of the samples in each solvent. For each solvent except ethanol, variations in the esterification conditions resulted in only 5–6% difference in the insolubility. This indicated that insolubility in each solvent was almost independent of the esterification conditions, except in the

case of ethanol. In NaOH solvent, the highest mass loss, 60% or more, was observed, and the amount of loss was not influenced by the glycerol content of the sample. HCl solvent had the next-highest ability to dissolve the samples. From those results, it seemed that the sheet was hydrolyzed easily by alkali. In the case of polar solvents such as water and DMF, the more glycerol the samples contained, the lower the insolubility. Also, a comparison between polar and non-polar solvents indicated that insolubility was lower with the polar solvents. In non-polar solvents such as hexane and benzene, the insolubility of the samples was very high. These results indicated that the degree of esterification of samples was not enough.

A highly esterified sample will gain hydrophobic property and insolubility in a polar solvent such as water.

### Conclusion

In order to clarify the degradability of plastic sheeting prepared from esterified sago residue, we investigated the biodegradability of such sheets in soil or on fungus, and assessed their insolubility in various solvents. The following conclusions were confirmed.

- 1) All plastic sheets prepared from esterified sago residue were degraded in Andosols and on the surface. The degradation was most remarkable in the first 20 days and progressed with an increase in the amount of glycerol added.
- 2) All samples biodegraded with *Trametes versicolor*, and the rate of degradation was independent of both the esterification condition of the sago residue and the glycerol content of the plastic sheet.
- 3) The insolubility of samples in alkali and acid solutions was low. Insolubility in polar solvent was lower than that in non-polar solvent, and it decreased with an increase in the amount of glycerol added.

These results indicate that sago residue is a good material for making easily biodegradable plastics. However, the weakness of plastic sheets prepared from esterified sago residue still present a problem for practical utilization. Therefore, further study is needed to improve on this weakness.

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