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Thermoplasticization of Sago Palm by Acetylation

Takako Watanabe and Masaharu Ohmi

Tokyo University of Agriculture and Technology, Fuchu, Tokyo, 183 Japan

Abstract It has recently become evident that plastics derived from petroleum have accumulated in the natural environment and seriously affected ecosystems. This has led to the desire for the development of degradable plastics. Sago palms are planted as a food resource in Southeast Asia because they have a lot of starch in their pith. Because of their component characteristics, they could be a good raw-material for biodegradable plastics. This paper describes an attempt at thermoplasticization of the sago palm with some chemical modification.

A chemical component analysis was conducted with a view to utilizing the sago palm as a new woody resource. The components of sago palm were affected by soil characteristics. In particular, the starch contents varied with soil type and growth stage. Thermoplasticization of the sago palm was done by acetylation, which is an esterification method. Thermoplasticity after acetylation was evaluated by making sheets on an experimental basis by hot-pressing acetylated materials. Furthermore, the thermal behavior of these sheets was determined by thermogravimetry analysis (TG) and thermomechanical analysis (TMA). The sample with the lower starch content showed higher acetyl content. The sheets made by hot-pressing showed thermoplasticity at 180 °C, and thermal softening point of the sheet made from sago growing in peat soil appeared at about 150 °C. It was suggested that thermoplasticity of sago palm could be achieved by chemical modification. As a result, it was also suggested that biodegradable plastics could be produced from the sago palm.

Key words: Acetylation, Chemical modification, Sago biomass, Thermoplasticization

アセチル化によるサゴヤシ材への熱可塑性の付与

渡辺尊子・近江正陽

東京農工大学農学部 〒183 東京都府中市幸町 3–5–8

要約 今日，石油由来のプラスチックが自然環境下で蓄積され，生態系に多くの影響を与えることが問題として指摘されてきており，環境中を循環する生分解性プラスチックの開発が望まれている．一方，サゴヤシは，その髄中に多量のデンプンを蓄積することから，食糧資源として東南アジアを中心として栽培されてきているが，その成分的特性から生分解性プラスチックの原材料として利用されうることが期待できる．また，サゴヤシからデンプンを抽出した後の残渣は現在，そのほとんどが利用されずに廃棄されており，その利用法の確立が必要とされている．本研究では上記の背景を踏まえ，サゴヤシ材に化学修飾により熱可塑性を付与することを目的とした．

サゴヤシ材を新たな木質資源として用いるために，成分分析を行った．その成分組成は生育土壌に影響を受け，特に，主成分であるデンプンの含有量が大きく異なっていた．また，アセチル化によって熱可塑性を付与することを試み，熱圧締によりシートを試作し，その熱可塑性の評価を行った．さらに，シートの熱的挙動を熱重量分析および熱機械分析により明らかにした．

実験の結果，本研究で用いられたアセチル化法においては，デンプン含有量の少ない方が，多いものに比べエステル含有率が高くなる傾向にあった．また，熱圧締により作製されたシートからは，180 °C 付近で最もよく熱可塑化が起きているのが明らかになった．シートの熱軟化曲線からは，泥炭土壌で生育したサゴヤシ材から調製されたシートにお

いて 150 °C 付近に熱軟化点が見られた．本研究の結果から，サゴヤシ材へ熱可塑性を付与することができ，生分解性プラスチックの原材料として用いることが可能であることが示唆された．
キーワード　アセチル化，化学修飾，サゴバイオマス，熱可塑化

Introduction

Plastics derived from petroleum are light, strong and durable, and they are easy and inexpensive to manifacture. Thus, a large quantity of plastics are used for many pursposes in our daily lives. In recent years, however, the disposal of petroleum-based plastic wastes has created serious environmental problems at a global level. Burning them causes air pollution and their undegradablility makes it impractical to bury them. Furthermore, they adversely affect the ecosystem. One way to solve this problem is to use biodegradable plastics made from biomass such as cellulose or starch.

Recently, plasticization of wood, a natural resource mainly consisting of cellulose, has been developed for production of biodegradable plastics (Shiraishi 1995). Thermoplasticization of wood substitutes bulky and non-polarizing functional groups for hydroxyl groups with etherification and/or esterification (Shiraishi 1983). Biodegradability of cellulose acetate has also been studied (Buchanan et al. 1993). However, because of its lower crystallinity, starch is biodegrades more easily than cellulose.

The sago palm contains large amounts of starch (more than 200 kg) in its pith and the starch is used for food and applied to industry, though it has been difficult to expand the use of sago starch in Japan because it is more expensive than tapioca starch (Ohno 1994). After extraction of starch in industrial process, a certain amount of starch remains in the pith residue. There have been a few reports in relation to the utility of the pith residue (Horigome et al. 1991; Haryanto et al.1991), but in fact almost all pith residue from starch factories is thrown away, causing environmental pollution in the near future. Therefore, it is important to find new ways to utilize the residue of sago palm.

It has been attempted to produce biodegradable plastics from the sago palm. The objective of this study was to investigate the possibilities of thermoplasicization of the sago palm by chemical modification for the purpose of applying a thermoplasticization method to apply it to sago pith residue.

Experiment

Materials

Sago palms (*Metroxylon sagu*) seven years old in mineral soil in Teh, Sarawak Malaysia and eight years old in peat soil in Dalat, Sarawak Malaysia were cut in 1993 and used in this experiment. The sago palm samples were taken from about 1.5 m above the ground and ground into meal after air-drying.

Component Analyses

Component analysis of sago palm was conducted for use as woody plant resources. Therefore, the method of component analysis for wood (Yasuda 1985) was used without determination of 80% ethanol extractive and starch.

Five chemical components were determined: alcohol-benzene extractive, 80% ethanol extractive, starch, holocellulose and lignin. Alcohol-benzene extractive was extracted from untreated meal for 6 hours with an alcohol-benzene mixture (volume ratio: 1:2) in a Soxlet extractor. The extractive was then dried and weighed. 80% ethanol extractive was extracted from extracted alcohol-benzene meal with 80% (wt.) ethanol aqueous solution three times at 80 °C for 15 minutes. The extractive was then dried and weighed after filtration. Starch was determined by the anthrone-sulfuric acid method after perchloric acid extraction (Sasaki 1979). Holocellulose and lignin were determined by the chlorite and sulfuric acid methods after extracting alcohol-benzene extractive and starch.

Acetylation

Sago palm meal (12.5 g) extracted with the alcohol-benzene mixture was heated and stirred with acetic anhydride (40 g) and pyridine (100 g) in a

Table 1 Components of sago palm and sugi

	Sago palm		Sugi (Haraguchi et al. 1985)
	mineral soil	peat soil	
Alcohol-benzene extractive (%)*1	2.9	13.0	3.2
80% ethanol extractive (%)*2	15.1	31.1	—
Starch (%)*2	76.3	37.3	—
Holocellulose (%)*2	7.5	23.3	70.1
Lignin (%)*2	1.8	5.6	31.4

*1 Weight ratio for ovendry weight of untreated sample.

*2 Weight ratio for ovendry weight of alcohol-benzene extracted sample.

separable flask attached to a reflux condenser, an agitator and, a thermometer at 100 °C for 4 hours. After the reaction, the meal was washed once with ethanol, and then three times with methanol (Ogura 1979). Thereafter, the weight percent gain was calculated from the weights before and after reaction and the acetyl content was determined by the saponification method (Shiraishi et al. 1972).

Preparation of sheet from acetylated meal

The acetylated and untreated sago palm meal (about 3 g) was put into the molding box (diameter: 80 mm) and hot-pressed. Hot pressing was performed under 215 kPa at 160 °C, 160 kPa at 180 °C, and 107 kPa at 200 °C. In one hot-press cycle, the sample was hot- pressed for 1 hour and cooled for 1 hour under zero pressure.

Thermal behavior analysis

The thermal behavior of sago plastic sheets was measured by TG and TMA. The gravimetric behavior, including thermal degradation of sheets, was measured from room temperature to 600 °C by a thermal gravimetric analyzer (SHIMADZU TG-20). The measurement was conducted in a nitrogen atmosphere (50 ml/min), at a temperature increase rate of 10 °C/min. Then, the thermal softening point of the sheets was measured with a thermomechanical analyzer (SHIMADZU TMA-50). The measurement was conducted from room temperature to 350 °C in a nitrogen atmosphere (about 75 ml/min), at a temperature increase rate of 5 °C/min and a load of 10 g.

Results and Discussion

Component analysis

Table 1 shows the results of component analysis of sago palm and sugi (*Cryptmeria japonica* D. DON), (a common Japanese tree) (Haraguchi et al. 1985). The sago palm grown in mineral soil contained more starch than that grown in peat soil. The one grown in peat soil contained more alcohol-benzene extractive and 80% ethanol extractive than the one grown in mineral soil. Starch (main component of sago palm) content was higher in the sago palm grown in mineral soil than that grown in peat soil. Comparing the components of sago palm with those of sugi , the sago palm contained less holocellulose and lignin than sugi. The sago palm was characterized by a large amount of starch; the sago palm contained less cellulose, a highly crystalline polymer, and much more starch, a lower crystalline polymer. Therefore, the thermoplasticization of the sago palm is expected to be easier than that of common woody plants.

Evaluation of thermoplasticity

The weight percent gains and the ester contents of sago palms by acetylation are shown in Table 2. The weight percent gain of the sample grown in

Table 2 Weight percent gains and ester contents of acetylated sago palm wood meals

Soil	Weight percetn gains (%)	Ester contents (%)
Mimeral	2.5	4.9
Peat	−8.0	26.2

Table 3 Hot press conditions and evaluation of thermoplasticity of samples

Sample	Soil	Hot-press conditions			Evaluation of thermoplasticity
		Temperature (°C)	Pressure (kPa)	Cycle	
No. 1	mineral	160	215	1	±
No. 2	mineral	160	215	3	±
No. 3	mineral	180	160	1	+
No. 4	mineral	180	160	2	++
No. 5	mineral	180	160	7	+++
No. 6	mineral	200	107	1	—
untreated	mineral	180	160	1	—
No. 7	peat	160	160	1	++
No. 8	peat	160	215	1	++
No. 9	peat	180	160	1	+++
untreated	peat	180	160	1	—

mineral soil was 2.5%, but the ester content was only 5%. On the other hand, the weight gain of the sample grown in peat soil was −8%, but its ester content was as high as 26%. The loss of weight was caused by the loss of low molecular sugar, which could not be recollected after the washing with ethanol and methanol. Thus, the lower starch content is better for acetylating the sago palm in the reaction system used in this study.

Table 3 shows the evaluation of thermoplasiticy of sheet samples with press temperature and the number of the press cycle. The thermoplasticies of the sheet samples were evaluated, focusing on the section which is changed by hot-pressing; the marks, +++, ++, +, ±, −, −−, −−− , in the Table 3 mean very well plasticizing, well plasticizing, plasticizing, no change, burnt, well burnt, and very well burnt, respectively. The acetylated sago palm meals were plasticized at about 180 °C, while the untreated meals were not plasticized. This suggests that the sago palm meals were thermoplastic after acetylation. In the results of acetylated samples, No. 9 sheet was thermoplasi-cized after only one cycle of hot-pressing at 180 °C, whereas seven-cycle hot-pressing was required to thermoplasticize No. 5 sheet. Furthermore, the sago palm grown in peat soil was thermoplasticized at a lower temperature than that grown in mineral soil. The difference in thermoplasticization temperature was based on the ester content (Funakoshi et al. 1979). The ester content greatly affected the thermoplasticity and the sago palm could be remarkably thermoplasticized with acetylation. Though the thermofloat of acetylated wood (for example, sugi), depending on the degree of substitution, is incomplete at temperatures even higher than 250 °C (Shiraishi et al. 1980; Aoki et al. 1980), the sago palm could be plasiticized at lower temperatures.

Thermal behavior of sheets made from acetylaed sago palm

Figure 1 shows thermal gravimetoric (TG) curves of sample sheets (No. 3 and No. 9 in Table 3). The large weight losses seemed to be derived from thermal degradation of holocellulose and starch, which were found in both sample sheets at about 270 °C. No weight loss occurred in either sample in the range of 100 to 200 °C near the hot-pressing temperature.

Figures 2 and 3 show thermal softening curves for sample sheets. The curves for the sheet made from acetylated sago palm (No. 9) has a broad shoulder at about 150 °C (arrow in Fig. 3). However, the curve for sheet (No. 3) had no shoulder. This peak is thought to have been derived from the thermal softening point, since there was no weight

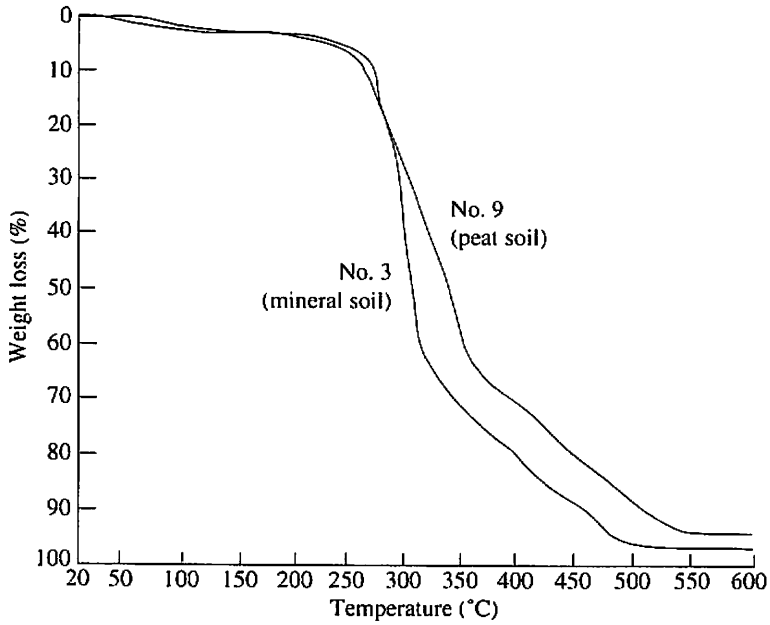

Fig. 1 Thermal gravimetric curves of the sheets of No. 3 (mineral soil) and No. 9 (peat soil)

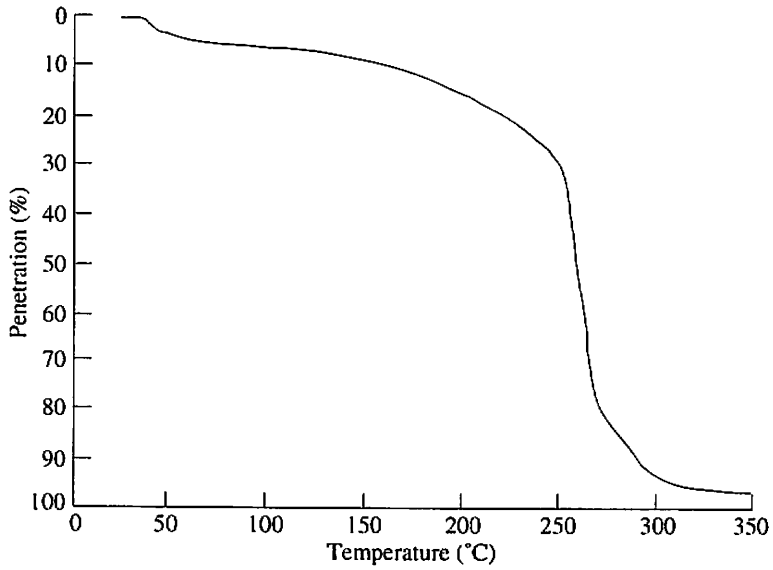

Fig. 2 Thermal softening curve of the sheet made of sago growing on mineral soil (No. 3)

loss in the TG curves at this temperature. It is considered that the thermoplasticity of sago palm was affected by the esterification because the starch, cellulose and lignin, which are the main components of the sago palm do not have any physical transition point in the range from 120 °C to 200 °C. (Arima

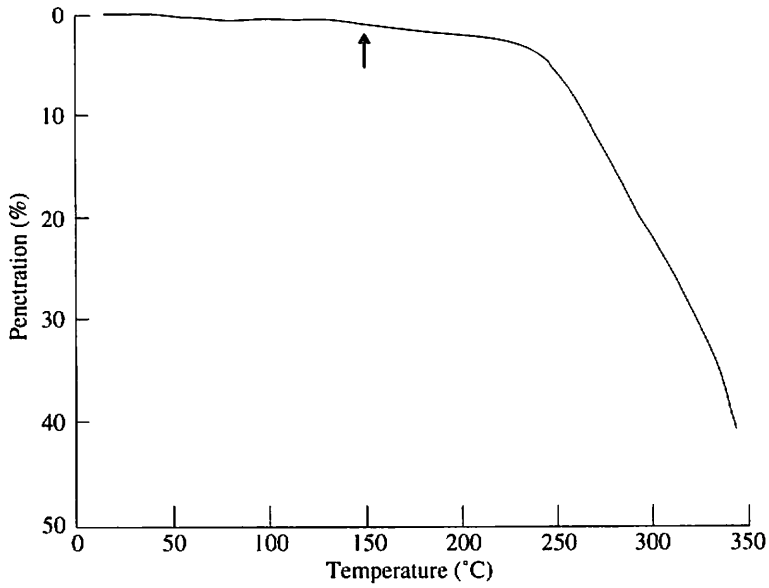

Fig. 3 Thermal softening curve of the sheet made of sago growing on peat soil (No. 9)

1973; Collison et al. 1971; Ueno et al. 1977)

It is thus suggested that a suitable press condition for the wood after small chemical modification allowed the sago palm to thermoplasticize.

Conclusions

Thermoplasticization of sago palm was attempted in order to introduce a new method to utilize sago biomass. The following conclusions were obtained through this study:

(1) The chemical components of the sago palm differed, depending on soil type.

(2) Acetyl content was affected by starch content in the reaction system used in this study.

(3) The thermal softening point of the acetylated sago palm grown in peat soil was about 150 °C.

(4) The sago palm could be thermoplasticized by acetylation.

(5) It was suggested that the thermoplasticization method used in this study can be applied to sago pith residue.

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References

Aoki, T., Shiraishi, N., Tanahashi, M., Yokota, T., and Yamada, T. 1980 Thermal softening of wood and cellulose. Mokuzai kenkyu shiryo No. 15: 61. (in Japanese)

Arima,T. 1973 Differential Scanning Calorimetry of wood and wood components (II). Mokuzai Gakkaishi 19: 443–450. (in Japanese with English summary)

Buchanan, C. M., Gardner, R. M., and Komarek, R. J 1993 Aerobic biodegradation of cellulose acetate. J. Appl. Polym. Sci. 47: 1709–1719.

Collison, R. and Dickson, A. 1971 Heats of starch dehydration by differential thermal analysis. Stärke 23: 45–48.

Funakosi, H., Shiraishi, N., Norimoto, M., Aoki, T., Hayashi, H., and Yokota, T. 1979 Studies of the thermoplasticization of wood. Horzforchung 33: 159–166.

Haraguchi, T. 1985 Mokuzai no Sosei In: Mokuzai no Kagaku (Haraguchi, T., Terashima, N., Usuda, M.,

Kosizima, T., Sakai, K., Morohoshi, N., Teratani, F., Kai, Y., Shimizu, K., and Sakakibara, A.) Buneidou Syuppan , Tokyo, 1–5. (in Japanese)

Haryanto, B., Royaningsih, S., Pabgloli, P. 1991 The use of fibrous residue and the bark of sago for making particle board. Proceedings of the Fourth International Sago Symposium, Kuching, Sarawak, 203–206.

Horigome, T., Sakaguchi, E., Takamura, Y., Bintaro, M. H. 1991 The feeding value of pith and residue from sago palm. Proceedings of the Fourth International Sago Symposium, Kuching, Sarawak, 195–200. (in Japanese)

Ogura, N. 1979 Sakusan denpun. In: Denpun Kagaku Jikken-Hou (Suzuki, S., Nakamura, M. ed.) Asakura Shyoten, Tokyo, 250–252. (in Japanese)

Ohno, M. 1994 On the sago starch production. SAGO PALM 2: 36–40. (in Japanese)

Sasaki, A. 1979 Syokubutu shiryou-tyu no denpun no teiryou: Denpun Kagakku Jikken-Hou (Suzuki, S., and Nakamura, M. ed.) Asakura Syoten, Tokyo, 1–7. (in Japanese)

Shiraishi, N., Yokota, T., Kimura, T., and Sumizawa, K. 1972 The interaction of wood with organic solvents (III). Mokuzai Gakkaishi 18: 215–222. (in Japanese with English summary)

Shiraishi, N., Tubotuchi, K., Matunaga, T., Yokota, T., and Aoki, T. 1980 Mokuzai no purasuchikkuka ni kansurukenkyu III. Preprints of the 30th Annual Meeting of the Japan Wood Research Society, Kyoto, Japan, 34. (in Japanese)

Shiraishi, N. 1983 Mokuzai no purasuchikkuka. *In*: Mokuzai Riyou no Kagaku (Imamura, H., Okamoto, H., Goto, T., Yasue, M., Yokota, T., and Yosimoto T. ed.) Kyoritsu Suppan, Tokyo, 294–303. (in Japanese)

Shiraishi, N. 1995 Biodegradable plastic. Mokuzai Gakkaishi 41: 621–630. (in Japanese)

Ueno, Y. Izumi, M. and Kato, K. 1977 Studies on pyrodextrinization of corn starch: Part II: A scanning electron microscopic study. Stärke 29: 329–335.

Yasuda, S. 1985 Mokuzai Bunseki. *In*: Mokuzai Kagaku Jikken-Shyo (Usuta, M., Mizumachi, H., Iiyama, K., Morohoshi, N., and Yamaguchi, A. eds.) Tyugai Sangyou Tyousa-Kai , Tokyo, 149–156. (in Japanese)