

Thermal Behavior and Surface Morphology Studies on Polystyrene Grafted Sago Starch

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ABSTRACT: Polystyrene grafting onto sago starch was carried out by using ceric ammonium nitrate as a redox initiator. The grafted copolymers were characterized by FTIR, thermogravimetry (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). FTIR spectra analysis of the grafted chain and commercial polystyrene was identical, indicating that styrene was successfully grafted onto sago starch. TGA thermograms and analysis of DSC curves showed that the thermal stability of

starch increases as a result of grafting. SEM micrographs showed the deformed prolate ellipsoidal shape of sago starch particles and this shape disappeared in polystyrene grafted sago starch being replaced with a spongy surface with pores. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2053–2058, 2003

Key words: graft copolymers; biodegradable; radical polymerization; sago starch; polystyrene

INTRODUCTION

Chemically modified starches with improved properties are gaining increasing importance in industry not only because they are low in cost, but mainly because the polysaccharide portion of the product is biodegradable.¹ The study of thermal properties is a useful tool for monitoring not only various kinds of synthetic polymer–starch interactions, but also important processing and end-use properties of grafted copolymers. Extensive studies on the graft copolymerization of vinyl monomers onto various types of starch have shown that grafting may cause slight to drastic changes in thermal behavior, the extent depending on various parameters such as the kind of monomer, grafting conditions and grafting percentage, and so forth.² The study of surface morphology using a scanning electron microscope is a very popular technique, used extensively to investigate the morphology of grafted copolymers.^{2–6}

The present work is a study of characterizing polystyrene grafted sago starch by using FTIR, thermogravimetry (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Sago starch was supplied from PPES Sago Industries (Mukah; Sdn Bhd. Sarawak, Malaysia). Styrene was

purchased from Fluka Chemie (Buchs, Switzerland) and purified by passing it through an alumina column to remove the stabilizer. Ceric ammonium nitrate (CAN), concentrated nitric acid, and hydrochloric acid were obtained from BDH Chemical Ltd. (Poole, UK). Chloroform and methanol were purchased from Mallinkrodt Baker (Phillipsburg, NJ). Methanol (commercial grade) was obtained from Chemie-Link Enterprise (Selangor, Malaysia). Distilled water was used for graft copolymerization and all other chemicals were of analytical grade.

Preparation of polystyrene grafted sago starch

Copolymerization

Polystyrene grafted sago starch was obtained by radical copolymerization of polystyrene onto gelatinized sago starch, initiated by CAN, in aqueous solution. Gelatinized sago starch solution was prepared by heating 5 g of dried sago starch in 165 mL distilled water for 0.5 h at 80°C under N₂ atmosphere in a three-neck conical flask. The gelatinized sago starch solution was then cooled to 50°C before grafting. To graft the starch with styrene, the solution was mixed with 0.92 g of CAN dissolved in 8.0 mL of 0.01M HNO₃ and stirred for 10 min. Then 20 mL of purified styrene was added and the solution was deoxygenated by passing nitrogen gas through the mixture. The mixture was heated at 50°C under reflux for 2 h and stirred throughout the experiment. The reaction mixture was then poured into 400 mL of commercial methanol to precipitate the polystyrene grafted sago starch. The precipitate was filtered, washed with an

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TABLE I
Removal of Polystyrene from 8.65 g of Unextracted Sago Starch-g-Polystyrene at 25°C in Chloroform by Shaking^a

Number of shaking	Weight of polystyrene removed/g	Percentage of polystyrene removed
1	0.60	6.9
2	0.83	9.6
3	0.95	11.0
4	0.95	11.0

^a Reaction conditions: temperature, 25°C; shaking period, 4 h (3 times).

excess of methanol, and dried in an oven at 60°C until reaching a constant weight.⁵

Sago starch used for TGA, DSC, and SEM characterizing underwent the same treatment used for polymerization, except in the absence of monomer.

Extraction of homopolymer

Polystyrene grafted sago starch was purified from polystyrene (PS) formed during the grafting reaction by an extraction process. The homopolymer was extracted by shaking 8.65 g of crude product in 30 mL of chloroform for 4 h and filtered. The filtered polystyrene grafted sago starch was washed with methanol and dried in an oven at 60°C for 24 h and then dried in a vacuum oven at 60°C to a constant weight. This process was repeated for another three times.⁶

Characterization of polystyrene grafted sago starch

The polystyrene grafted sago starch was characterized by FTIR, TGA, DSC, and SEM.

Fourier transform infrared analysis

FTIR was useful in elucidating the molecular structure, particularly in recognition of the functional groups. Infrared (IR) spectra in the range of 4000–400

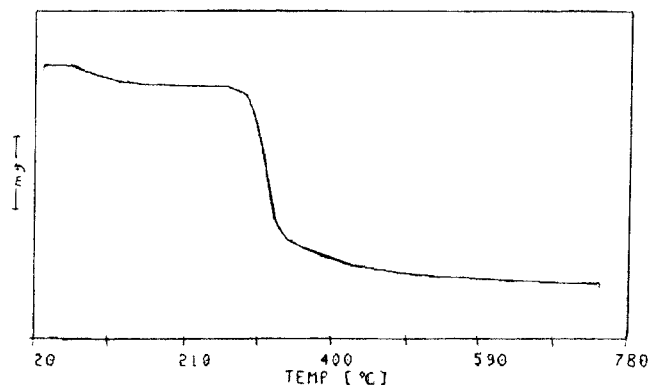


Figure 2 TGA thermogram of sago starch that has undergone the same treatment used for polymerization, except in the absence of monomer.

cm⁻¹ of polymer sample were recorded on an FTIR Perkin–Elmer model 1650 spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT) using the KBr pellet technique for sample preparation. The polystyrene grafted sago starch was hydrolyzed to obtain the polystyrene chain because the presence of styrene in the FTIR spectrum of polystyrene grafted sago starch could not be detected. The grafted polystyrene was separated from the sago starch backbone by acid hydrolysis. This was carried out by refluxing 5.0 g of polystyrene grafted sago starch in 100 mL of 0.5M HCl for 6 h. The polystyrene obtained was collected by filtration, washed with dimethyl formamide to ensure complete removal of the hydrolyzed sago starch, and finally dried in a vacuum oven until a constant weight was recorded. Loosely attached polystyrene on the polystyrene grafted sago starch was extracted during the extraction process by shaking in the chloroform. The polystyrene obtained from the acid hydrolysis process is the polystyrene produced from the breaking of the chemical bond in the copolymer.

Thermogravimetry analysis

A Shimadzu thermogravimetry model DT-40 (Shimadzu, Kyoto, Japan) was used to perform TGA of

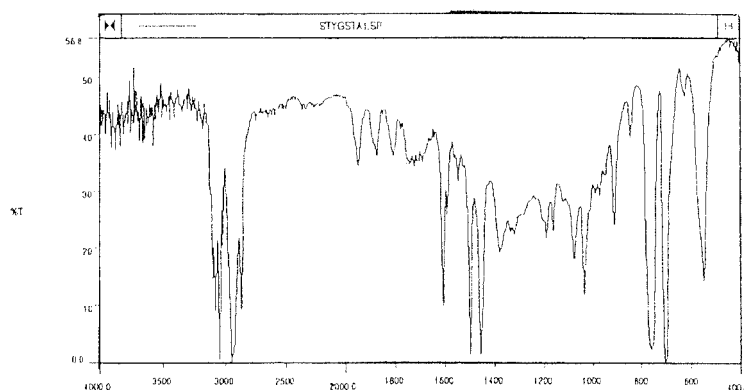


Figure 1 FTIR spectrum of grafted polystyrene.

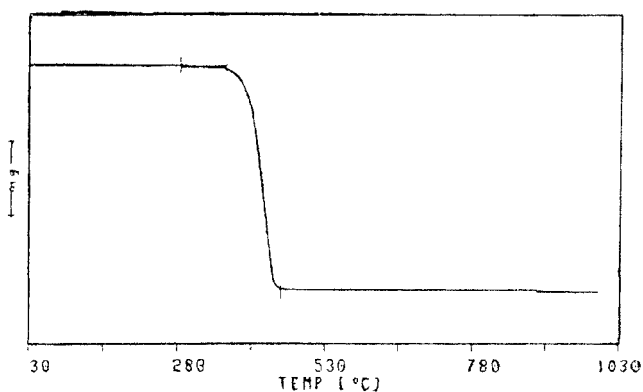


Figure 3 TGA thermogram of polystyrene.

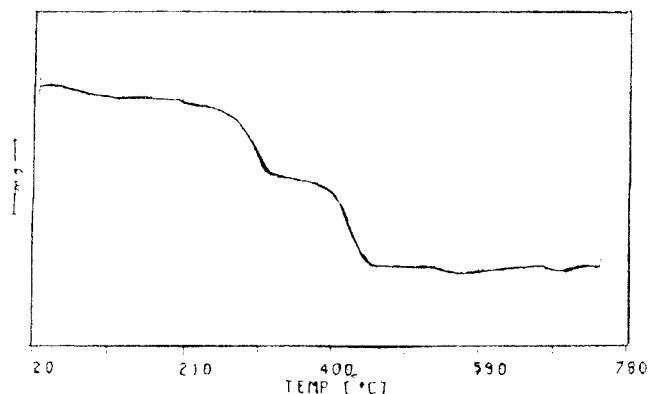


Figure 4 TGA thermogram of polystyrene grafted sago starch.

sago starch, polystyrene, and polystyrene grafted sago starch. Samples between 10 and 20 mg were heated at a rate of 15°C/min from room temperature to 950°C under the flow of N₂ gas.

Differential scanning calorimetry analysis

A PL-DSC instrument was used to characterize sago starch, polystyrene, and polystyrene grafted sago starch. Samples (40 mg) were heated at a rate of 10°C/min from room temperature to 600°C under nitrogen atmosphere. DSC curves were recorded using a Shimadzu DT-40 thermal analyzer.

Scanning electron microscopy

A scanning electron microscope (JSM-6400) was used to study the surface morphology of granular sago starch, sago starch that underwent the same treatment used for polymerization except in the absence of monomer, and polystyrene grafted sago starch samples. The samples were first coated with a thin layer of gold and observed at magnifications of $\times 25$, $\times 80$, and $\times 400$.

RESULTS AND DISCUSSION

Extraction of homopolymer

The graft copolymerization of styrene grafting onto sago starch produces polystyrene grafted sago starch and polystyrene. Polystyrene was removed from the polystyrene grafted sago starch by shaking in chloroform. For the first shaking, 6.9% of ungrafted polystyrene was extracted (Table I). The percentage of extracted polystyrene increased with the increase in the number of shaking and then leveled off. This was attributed to the polystyrene, which was loosely deposited onto the polystyrene grafted sago starch when dissolved in the chloroform. Any polystyrene remaining in polystyrene grafted sago starch was assumed to be grafted. From this result, it could be concluded that three courses of shaking in chloroform for the homopolymer extraction was sufficient to remove the homopolymer successfully. Trimnell et al.⁶ reported the use of a similar method to extract ungrafted polymethyl acrylate from starch-g-methyl acrylate by using acetone.

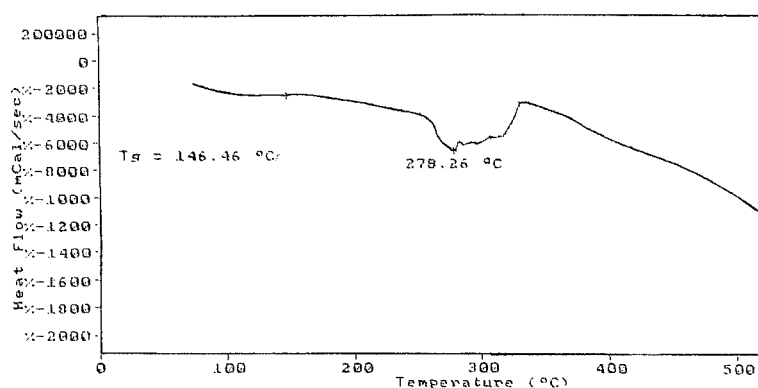


Figure 5 DSC curve of sago starch that has undergone the same treatment used for polymerization, except in the absence of monomer.

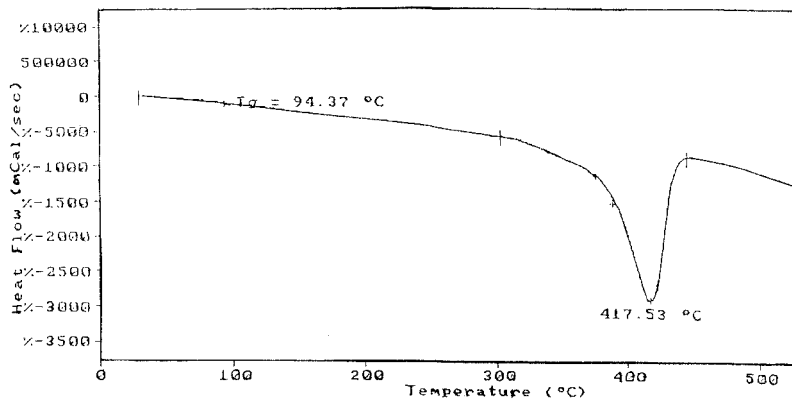


Figure 6 DSC curve of polystyrene.

Fourier transform infrared analysis

The infrared spectrum of grafted polystyrene is shown in Figure 1. The polystyrene grafted sago starch was hydrolyzed to obtain the polystyrene chain because the presence of styrene in the FTIR spectrum of polystyrene grafted sago starch could not be detected. This could be because the small amount of styrene in the grafted copolymer or because the grafted copolymer did not grind well with KBr in the preparation of the sample for FTIR analysis.

The FTIR spectrum of grafted polystyrene (Fig. 1) shows the appearance of peaks at $1600\text{--}1450\text{ cm}^{-1}$, attributed to C=C of the vinyl group, and the C=C in the aromatic ring was observed at $2000\text{--}1600\text{ cm}^{-1}$. This result (Fig. 1) showed that the spectrum of grafted polystyrene was identical to that of polystyrene, indicating that styrene was successfully grafted onto sago starch.

Thermogravimetry analysis

TGA is based on continuous measurements of weight on a sensitive balance (microbalance) as the sample temperature is increased in an inert atmosphere.⁹ The TGA thermogram of sago starch (Fig. 2) shows the

weight loss from 41 to 163°C that could be the result of water evaporation. Weight loss from 163 to 349°C could be attributed to the decomposition of sago starch. Figure 3 shows the TGA thermogram of polystyrene; the weight loss observed from 285 to 457°C was probably caused by the decomposition of polystyrene.

The TGA thermogram in Figure 4 shows the decomposition of polystyrene grafted sago starch. There was a slight weight loss at $29\text{--}130^{\circ}\text{C}$, which could be the moisture content loss in the polystyrene grafted sago starch. There were two zones of weight loss corresponding to the decomposition of polystyrene grafted sago starch. The first weight loss from $130\text{ to }318^{\circ}\text{C}$ was probably caused by the decomposition of sago starch, whereas the second weight loss from $318\text{ to }459^{\circ}\text{C}$ could be attributed to the presence of styrene in the grafted sago starch.

Differential scanning calorimetry analysis

In differential scanning calorimetry (DSC) analysis, a polymer sample and an inert reference are heated in a nitrogen atmosphere and thermal transitions in the sample are detected and measured.⁹ The DSC curves

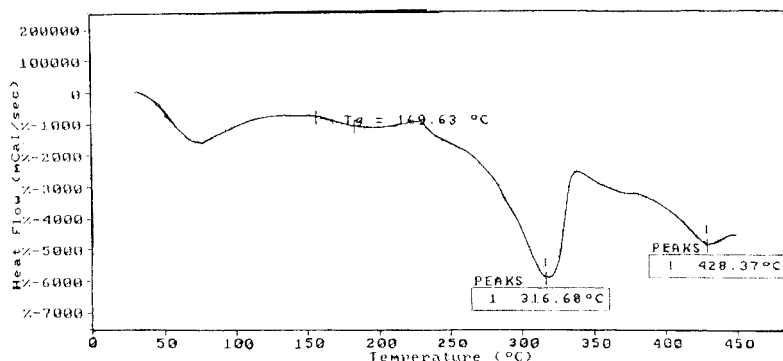


Figure 7 DSC curve of polystyrene grafted sago starch.

of sago starch, polystyrene, and polystyrene grafted sago starch are shown in Figures 5, 6, and 7, respectively. The sago starch DSC curve (Fig. 5) shows a broad endothermic peak at 278°C with the glass-transition temperature (T_g) observed at 146°C. The broad endothermic peak could be the result of the mixture of amorphous and crystalline phases in the starch structure.

In Figure 6, the T_g of polystyrene is at 94°C and the endothermic peak is at 418°C. The DSC curve of polystyrene grafted sago starch (Fig. 7) with two endothermic peaks is observed at 317 and 428°C and T_g at 170°C. It can be seen that polystyrene grafted sago starch has two endothermic peaks, whereas the sago starch and polystyrene have only one endothermic peak. This indicates the presence of styrene in the grafted starch. The melting of polystyrene chains in polystyrene grafted sago starch could have caused the new endothermic peak.² The presence of separate thermal transitions in the DSC curve of polystyrene grafted sago starch may be attributed to the poor compatibility between the starch and grafted polystyrene.²

Scanning electron microscope analysis

The surface morphology of granular sago starch, sago starch that has undergone the same graft polymerization treatment, and polystyrene grafted sago starch was observed by scanning electron microscopy (SEM). Plate 1 shows that the image of sago starch consists of oval granules, in a mixture of sizes between 5 and 10 μm .¹⁰ It was also observed that sago starch under SEM possesses a particle shape called deformed prolate ellipsoidal.¹¹ As can be seen in Plate 2, the sago starch that has undergone the same treatment used for polymerization, except in the absence of monomer, had a smooth and compact surface that might be caused by the formation of crystalline structure after the gelatinization process.

The smooth and compact surface of crystalline structure has disappeared in Plate 3 showing that the

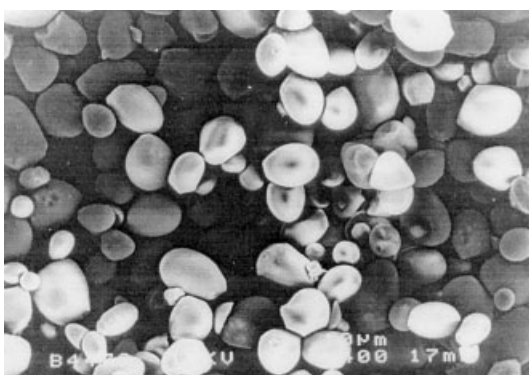


Plate 1 SEM micrograph of granular sago starch at $\times 400$.

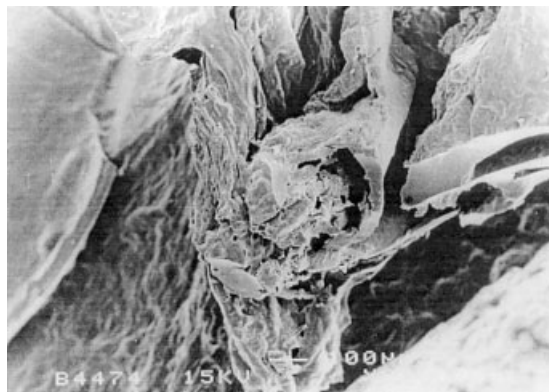


Plate 2 SEM micrograph of sago starch that has undergone the same treatment used for polymerization, except in the absence of monomer at $\times 80$.

grafting process had occurred on the surface of the sago starch, which changed the surface morphology. Polystyrene grafted sago starch also showed a spongy surface with pores, probably as a consequence of the grafting process.²

CONCLUSIONS

Although FTIR analysis of polystyrene grafted sago starch did not clearly show the presence of polystyrene, the FTIR of the polymer obtained from the hydrolysis of polystyrene grafted sago starch is identical to that of polystyrene, thus indicating that styrene was successfully grafted onto sago starch. The DSC study showed that polystyrene grafted sago starch has two endothermic peaks, whereas the sago starch and polystyrene have only one endothermic peak, thus indicating the presence of styrene in the grafted copolymer. TGA thermograms showed there were two zones of weight loss for polystyrene grafted sago starch compared to the original sago starch, which had only one zone of weight loss. These differences in TGA thermograms showed that sago starch had been modified.

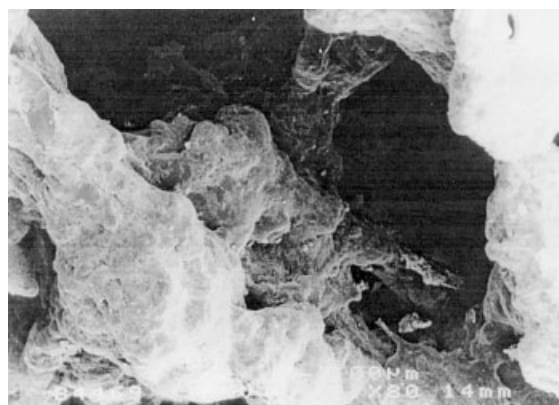


Plate 3 SEM micrograph of polystyrene grafted sago starch at $\times 25$.

The surface morphology of gelatinized sago starch under SEM was shown to be smooth and compact; however, this smooth and compact surface disappeared in the polystyrene grafted sago starch, which instead was characterized by a spongy surface with pores, thus confirming that styrene had been grafted onto the sago starch.

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