

Sago Starch and Its Acrylamide Modified Products as Coating Material on Handsheets Made from Recycled Pulp Fibers

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ABSTRACT: This study was carried out to determine the suitability of sago starch as a paper additive. The basic properties (i.e., pH, viscosity, and solid content) of the 5% weight over volume basis of unmodified and modified sago starch (sago starch blended with acrylamide, sago starch grafted with acrylamide in an acidic and adjusted to alkaline conditions) were determined. The starches were then used to coat laboratory handsheets made from recycled pulp fibers. The incorporation of acrylamide into sago starch through grafting significantly reduced the viscosity of the solution. Generally, coating the handsheets with unmodified sago starch significantly improved some properties as com-

pared to the uncoated handsheets. Among the three types of sago starch modification methods, blending gave superior performance when coated on the handsheets, except for smoothness and air permeance, due to insufficient curing shown by the micrographs. FTIR spectra showed that the interactions between the blended acrylamide–starch solutions and the pulp fiber were weak. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 154–158, 2004

Key words: starch; acrylamide; blending; graft-copolymers; mechanical properties

INTRODUCTION

Starch is the most important dry strength additive used in brown grade papers and can exceed 5% of the final paper sheet, excluding starch used as corrugation adhesive. It may also be applied as a sizing agent. Starch improves interfiber bonding through adsorption and the creation of new bonding sites on fiber surfaces. Furthermore, it provides a low-cost method by which recycled grade papers can reach necessary strength properties, and its usage allows lower cost wastepaper grades to be included in the furnish mix.¹

Among the different types of starches, sago starch has some potential as paper additive because of its high amylose content. Nevertheless, sago starch is easily hydrated and swelled, loses viscosity by retrogradation, and produces very cohesive pastes.² Because, in its natural form, sago starch has a limited number of uses, chemical modifications are crucial to widen their usage. Some of these modifications are blending and grafting of sago starch by synthetic polymers to improve properties such as the viscosity and

stability. Therefore, in this article, investigations were made on the suitability of sago starch as an additive to improve the physical and mechanical properties in handsheets and to determine the effects of modification with acrylamide on the properties of starch solutions and handsheets coated with it.

EXPERIMENTAL

Modification and evaluation of sago starch

Commercial grade sago starch flour was obtained from Nitsei Sago Industries Sdn. Bhd., Mukah, Sarawak Malaysia. Acrylamide ($\text{H}_2\text{C}=\text{HCONH}_2$) used was obtained in the form of 97% grade (Aldrich, USA) and stabilized with 25–30 ppm cupric ion. Four types of sago starch solutions were prepared, as follows: (1) unmodified sago starch, (2) sago starch blended with acrylamide, (3) sago starch grafted with acrylamide in acidic condition, and (4) sago starch grafted with acrylamide and adjusted to alkaline condition. The concentration of the mixture was 5% weight over volume basis.

For the unmodified sago starch solutions, sago starch was diluted with distilled water and gelatinized at 80°C for 15 min. A blend of sago starch and acrylamide was prepared by mixing acrylamide and gela-

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TABLE I
Basic Properties of Modified Sago Starch Solutions

Content (% , g/L basis)	pH	Viscosity (mPa. s)	Solid content (%)	Appearance
US	4.16 ^c	1134 ^a	5.16 ^{ns}	Opaque, hardened after a few hours at room temperature
B	4.49 ^b	1371 ^a	5.09 ^{ns}	Opaque, slightly clearer than US sample, hardened after a few hours at room temperature
AC	1.13 ^d	499 ^b	5.20 ^{ns}	Clear
AL	8 ^a	473 ^b	5.12 ^{ns}	Slightly yellowish
Commercial paper resin	4.24	2438	15.92	Clear solution

Note. Values are average of eight replicates; means followed by the different letter (a,b,c,d) in each column for each handsheet property are significantly different ($\alpha = 0.05$) according to Duncan's Multiple Range Test (DMRT), where US is handsheet coated with unmodified sago starch; B is handsheet coated with sago starch blended with acrylamide; AC is handsheet coated with sago starch grafted with acrylamide in acidic condition; AL is handsheet coated with sago starch grafted with acrylamide and adjusted to alkaline condition; ns is not significant.

tinized sago starch solution with high-speed stirring under a fume cupboard at a 1 : 1 ratio and heated for 1 h at 40°C. Graft copolymerization of acrylamide onto sago starch using ceric (IV) ammonium nitrate (Aldrich, USA) as the initiator was done. The average percentage of grafting efficiency was 38.5%. Two grams of starch and 100 mL of distilled water were introduced into a three-necked conical flask before being stirred at 80°C for 30 min for a gelatinization process. The stirred solution was cooled down to the desired grafting temperature of 50°C. To start the initiation, ceric (IV) ammonium nitrate (0.548 g) in 6.0 mL nitric acid (Aldrich, USA) (1.0M) was then added into the mixture. Nitrogen gas was introduced into the flask to seize any oxidation reactions in the mixture. Acrylamide (8 g) was added to the slurry after 10 min and allowed to polymerize for 1 h. The solution was then cooled to room temperature.

All the sago starch solutions prepared were analyzed for pH,³ viscosity,⁴ and solid content in three replicates each.

Handsheet making, coating, and evaluation of the coated handsheets

Recycled pulp fibers from Genting Sanyen Industrial Paper Sdn. Bhd., Banting, Selangor, Malaysia were used and made into laboratory scale handsheets. The handsheets were then coated with the different starch solutions prepared by using a P1-1210 Film Coater. The handsheets were conditioned for at least 48 h in a controlled atmosphere prior to testing. Conditioned handsheets were cut into test specimens for physical and mechanical evaluations and tested in a controlled temperature ($23 \pm 1^\circ\text{C}$) and humidity ($50 \pm 2\%$) room as stipulated in TAPPI T 402 om-88.⁵ The properties evaluated were folding endurance, bending stiffness, burst strength, tensile strength, ring crush, tear strength, smoothness, and air permeance.

A General Linear Model procedure from statistical package of Statistical Analysis System (SAS) was used

to evaluate the significant effects among the effects studied. The means were further analyzed by using a Duncan's Multiple Range Test (DMRT) method.

Scanning electron microscope (SEM) was done on the handsheets to observe surface bonding between the pulp fibers and the starch. FTIR work was also carried out to determine the functional groups in the handsheets coated with the sago starch.

RESULTS AND DISCUSSION

Effect of sago starch modification on their solutions' properties

The pH values for unmodified sago starch (US) and sago starch blended with acrylamide (B) sample were 4.16 and 4.49, respectively (Table I), whereas that of the grafted starch in acidic condition (AC) was 1.13. Because the AC starch was too acidic (acidic condition causes fibers in handsheets to degrade in long term as opposed to alkaline condition), the pH was adjusted to pH 8. This alkaline solution was referred to as AL. All the pH readings were significantly different ($\alpha = 0.05$).

Although having the same concentration at 5%, the viscosities of the solutions were significantly different ($\alpha = 0.05$), ranging from 473 to 1371 mPa s. It appeared that pH has great influence on viscosity: too alkaline or too acidic reduced the viscosity of the solutions prepared, and at pH near neutral, the viscosity was much lower at 473 mPa s. In both AC and AL solutions, the grafting process in acidic condition appeared to hydrolyze the solutions. It is believed that acid preferentially attacks the amorphous regions within the solutions.⁶

The solid contents for US, B, AC, and AL were 5.16, 5.09, 5.20, and 5.12%, respectively. However, these values were not significantly different. The appearance of the solution differs greatly where the US and B starch solutions were opaque, whereas AL and AC were much clearer. All the modified starches (B, AC, and AL) remained biologically resistant under observation even after 14 days of exposure to ambient.

TABLE II
Properties of Handsheet Coated With Different Methods of Sago Starch Modification

	US	B	AC	AL
Fold (times)	70 ^b	110 ^a	98 ^a	68 ^b
Stiffness (mNm)	2.40 ^{ab}	2.03 ^b	2.18 ^b	3.23 ^a
Burst index (kPa m ² /g)	2.64 ^{ab}	2.40 ^b	2.58 ^{ab}	2.75 ^a
Tensile index (N m/g)	33.81 ^{ns}	34.21 ^{ns}	36.55 ^{ns}	33.36 ^{ns}
Crush (N)	105 ^{ns}	128 ^{ns}	123 ^{ns}	122 ^{ns}
Tear index (mN m ² /g)	10.7 ^{ns}	9.9 ^{ns}	9.7 ^{ns}	10.4 ^{ns}
Smoothness (ml/min)	950 ^a	600 ^b	700 ^{ab}	825 ^{ab}
Air permeance (ml/min)	35 ^b	74 ^a	68 ^a	68 ^a

Note. Values are average of eight replicates; Means followed by the different letter (a,b) in each row for each handsheet property are significantly different ($\alpha = 0.05$) according to Duncan's Multiple Range Test (DMRT), where US is handsheet coated with unmodified sago starch; B is handsheet coated with sago starch blended with acrylamide; AC is handsheet coated with sago starch grafted with acrylamide in acidic condition; AL is handsheet coated with sago starch grafted with acrylamide and adjusted to alkaline condition; ns is not significant.

Effects of sago starch modification on the properties of coated handsheets

As shown in Table II, the investigated physical and mechanical properties of handsheets coated with modified sago starches were mostly improved as compared to those coated with unmodified sago starch. Sago starch blended with acrylamide (B) showed the highest folding endurance of 110 times for the coated handsheets, whereas the lowest can be seen for AL 68 times. Handsheets coated with AL gave the highest stiffness (3.23 mNm) and burst index (2.75 kPa m²/g), which were significant ($\alpha = 0.05$). The highest tensile index (36.55 Nm/g) was given by handsheets coated with AC. B gave the highest value for crush strength (128N) as compared to the other methods of sago starch modification. Conversely, the modification of sago starch with acrylamide through the various methods did not improve the tear index of the coated handsheets. It was also observed that blending the sago starch with acrylamide before being coated onto the handsheet did not give satisfactory surface air permeance and smoothness.

Blending did not provide sufficient interaction between the sago starch and acrylamide. As a result, the mixture became less homogeneous and lacked in the ability to flow [Fig. 1(b)]. This evidently suggests that there is a lack of bonding formation between sago starch with acrylamide and between recycled pulp fibers with the blended sago starch and acrylamide. In contrast, handsheets coated with AC have relatively smooth surfaces as a result of the higher stability at low pH where the starch was deposited onto the handsheets as individual particles that flowed easily and ideally covering the fiber surface as a monolayer. To produce a smooth surface handsheet, all spaces on the handsheet should be sufficiently filled with sago starch solutions and this is difficult to achieve if the mixture does not have sufficient flow as seen in the handsheet coated with B. Conversely, the unmodified

and both the acid- and the alkali-based acrylamide-sago starch had relatively good mixtures [Fig. 1(c, d)], resulting in a much smoother surface.

The FTIR absorption spectra of handsheets coated with US, B, AC, and AL were illustrated in Figure 2. Overall, the IR spectra for handsheets coated with modified sago starches resemble the IR spectra for handsheets coated with US solutions, which showed the characteristic absorption of starch at 3000–3800 cm⁻¹. For B, the FTIR spectra showed that there is N—H symmetric stretching at a frequency of 3442 cm⁻¹. Weaker absorption at 1380 cm⁻¹ may be due to the O—H band in the plane, whereas absorption at 1054 cm⁻¹ may be due to the C—O stretching in the CH₂OH. As for the AC and AL samples, the peaks appeared to resemble the peak in B except for a small frequency shift. The FTIR spectra indicate the absence of peak, which represents the characteristic of the double bond (C=C) at a frequency of ~ 1600 cm⁻¹, which can be observed from the IR spectrum of acrylamide. This might be due to the small amount of acrylamide added to the sago starch solution and the handsheet coated was not immersed in the solution. The lack of interaction could also be attributed to the insufficient curing of blended or grafted sago starch-acrylamide, thus, less bond formation between pulp fiber and the coating material. Because the coated handsheets were cured at ambient, an increase in temperature may provide better curing to the modified starch.

CONCLUSION

In the first part of the study, increasing the concentration of the unmodified sago starch solutions caused significant reduction in their pH value and an increase in viscosity property. The unmodified sago starch solutions appear to be of high viscosity and susceptible to biological attack. Blending or grafting process with acrylamide makes the sago starch resistant to biological attack, reduced in viscosity, and an appearance altered to their solutions.

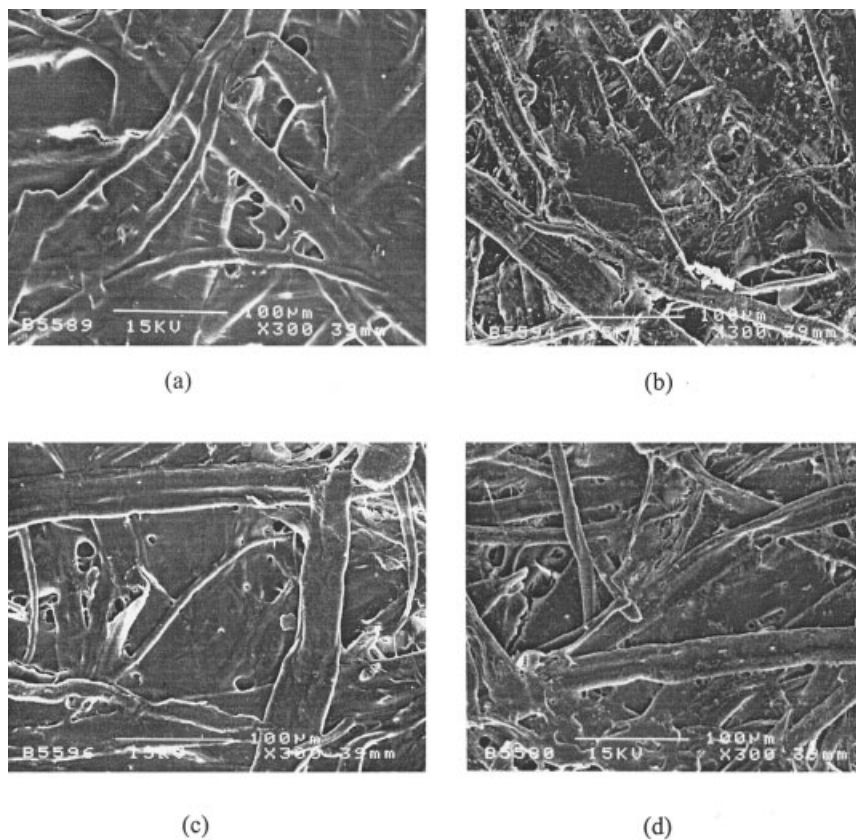


Figure 1 SEM micrographs of handsheets’ surfaces coated with (a) unmodified sago starch, (b) sago starch blended with acrylamide, (c) sago starch grafted with acrylamide in acidic condition, and (d) sago starch grafted with acrylamide and adjusted to alkaline condition. Magnification: ×300.

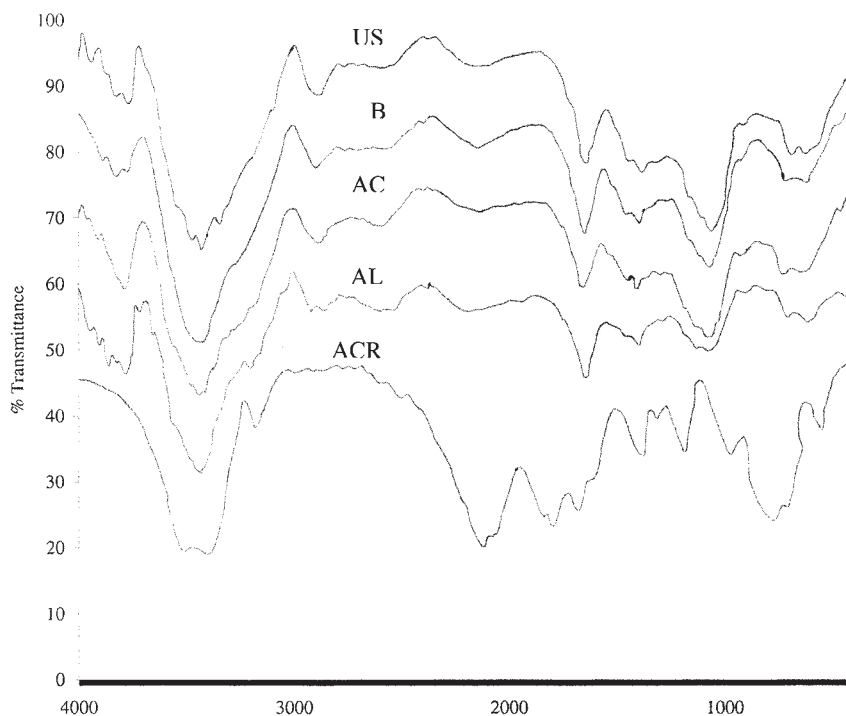


Figure 2 FTIR spectra of acrylamide (ACR) and handsheets coated with different methods of sago starch modification (US = unmodified sago starch, B = sago starch blended with acrylamide, AC = sago starch grafted with acrylamide in acidic condition, AL = sago starch grafted acrylamide and adjusted to alkaline condition).

In the second part of the study, generally, the addition of unmodified sago starch improved the physical and mechanical properties of the coated handsheets. However, the unmodified sago starch solutions are not resistant to biological attack. Therefore, the incorporation of acrylamide into the starch system through blending or grafting gave the needed biological resistance. The usage of the grafted sago starch with acrylamide on handsheets did not improve greatly the mechanical properties of the handsheets, but it did give equivalent smoothness and air permeance properties as compared to handsheets coated with unmodified sago starch solutions. Blending of sago starch with acrylamide did improve certain properties of the coated handsheets, although there is insufficient polymerization on the surface of the coated handsheets, as shown in the micrographs.

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