AJSTD Vol. 22 Issue 4 pp. 363-369 (2005)

SUITABILITY OF SAGO STARCH BLENDED WITH ACRYLAMIDE AS AN ADDITIVE ON HANDSHEETS MADE FROM RECYCLED PULP FIBERS

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Received 22 June 2005

ABSTRACT

This study was carried out to determine the suitability of sago starch blended with acrylamide as paper additive. Solutions of unmodified and blended sago starch with acrylamide, were prepared at 5% weight over volume (w/v) basis before the basic properties (i.e., pH, viscosity and solid content) were determined. The starches were then used to coat on laboratory made handsheets from recycled pulps. Various effects were studied, namely, modification of sago starch, addition of different types of initiator and further curing at different temperatures. The incorporation of acrylamide into sago starch through blending significantly increased the pH and viscosity of the solutions. All the blended starches remained biologically resistant even after 14 days of exposure to ambient temperature. Solution of sago starch blended with acrylamide, gave superior performance when coated on the handsheets, producing handsheets with high folding endurance (110 times) and crush strength (128 N) as compared to the handsheets coated with the unmodified sago starch. Nevertheless, the smoothness and air permeance of these papers were unsatisfactory due to insufficient curing shown by the micrographs. The use of ceric ammonium nitrate (CAN) as initiator and further curing at 50^{o}C however, were able to improve the smoothness and air permeance properties.

Keywords: starch; acrylamide; blending; handsheet properties

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1. INTRODUCTION

Utilization of recycled fibers in the paper industry is not new. Even though it has become commercial since 1800, serious investigation on this material had only started by late 1960's [1]. Today, paper recyclability is the main issue in pulp and paper industries [2 – 4]. At present, 18 paper mills including one integrated pulp and paper mill are in operation in Malaysia. Out of this number, 16 mills are using recycled paper, either from old newspaper, magazine paper or corrugated liners [5].

However, the use of recycled pulp has its own limitation, particularly to the strength of the paper produced. Additive is thus used to strengthen the paper. Starch, one of the more popular additives, has become more important as strength additive, either applied internally or on the surface [6].

Starch is a natural polymer with high molecular weight that can be depolymerized with a great degree of control. It is a hydrophilic polymer that dispersed in water and attached to cellulose fibers and pigments through hydrogen bonding. Starch has hydroxyl groups that allow a wide range of substitution or oxidation reactions to adjust its rheological characteristics and to eliminate retrogradation. Cationic, anionic, or amphoteric groups can be added to induce specific charges. Starch may be blended or grafted to produce new materials with properties that combine the advantages of natural and synthetic polymer [7]. In this paper, sago starch is used as an additive to coat handsheets. In its natural form, sago starch has limited properties. Therefore, modification is needed to be done by blending the sago starch with synthetic monomer such as acrylamide to improve such properties as well as the durability.

2. MATERIALS AND METHODS

2.1 Preparation of sago starch solutions

The sago starch sample in the form of commercial grade flour, was obtained from a sago starch processing factory in Mukah, Sarawak, Malaysia. Two types of sago starch solutions were prepared. They were (1) Unmodified sago starch and, (2) Sago starch blended with acrylamide. The concentration of all the mixtures was 5% (w/v). For unmodified sago starch solutions, sago starch was diluted with distilled water and gelatinised at 80^{o}C for 15 minutes. Meanwhile, in the blending part, sago starch which was gelatinised first at 80^{o}C for 15 minutes was blended with acrylamide at 1:1 ratio and further heated for one hour at 40^{o}C.

Different initiators were also added into the sago starch blended with acrylamide solutions prior to handsheet coating and stirred at constant rate for 15 minutes at room temperature. The initiators used were potassium persulfate and ceric ammonium nitrate at 2% concentration of the blended sago starch solutions.

2.2 Evaluation of sago starch solutions

All the sago starch solutions were analyzed for pH (TAPPI T638 hm, 1985 [8]), viscosity (TAPPI T676 hm, 1985 [9]) and solid content. Three replicates were done for each property.

2.3 Handsheet making, coating, curing and evaluation of the coated handsheets

Recycled pulp fibers obtained from a commercial papermaking plant was used. The pulp was soaked for 24 hrs and cleaned through running water to remove impurities or foreign materials. Cleaned pulp was later used to make laboratory handsheets of 120 g/m^2. The handsheets were

then coated with the prepared sago starch solutions using a P1-1210 Film Coater. The curing of the coated handsheets were done in four conditions: (i) room temperature for 24 hrs, (ii) oven at 50°C for 15 minutes, (iii) oven at 75°C for 15 minutes and (iv) oven at 90°C for 15 minutes.

The coated handsheets were conditioned for at least 48 hours in a controlled atmosphere prior to testing. The handsheets were later cut and prepared into test specimens for physical and mechanical evaluations. Tests were conducted in a controlled temperature (23 ± 1°C) and humidity (50% ± 2%) room as stipulated in TAPPI T 402 om (1983) for folding endurance, stiffness bending, burst strength, tensile strength, ring crush, tear strength, smoothness and air permeance. 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 unmodified and modified sago starch.

2.4 Statistical analysis

A General Linear Model procedure of Statistical Analysis System (SAS) was used to evaluate the significant effects among the variables studied. The means of significant effects were further analyzed using a Duncan's Multiple Range Test (DMRT) method at $p \leq 0.05$.

3. RESULTS AND DISCUSSION

3.1 Effects of modification of sago starch on their solution properties

Table 1: *Basic properties of sago starch solutions*

Content (%, g/l basis)	pH	Viscosity (mPa.s)	Solid Content (%)
US	4.16^{b}	1134^{b}	5.16^{ns}
B	4.49^{a}	1371^{a}	5.09^{ns}
Commercial Paper Resin	4.24	2438	15.92

Note: Each value is an average of three replicates; Means followed by the different letter (a,b) in each column are significantly different at $p \leq 0.05$ according to Duncan's Multiple Range Test (DMRT).

ns = not significant; US = unmodified sago starch; B = sago starch blended with acrylamide.

The pH values for unmodified sago starch (US) and sago starch blended with acrylamide (B) sample were 4.16 and 4.49 respectively as shown in Table 1 and were significantly different at $p \leq 0.05$. Although having the same concentration at 5%, the viscosities of the solutions were significantly different ($p \leq 0.05$) with 1134 and 1371 mPa.s respectively for US and B. The solid contents for US and B were not significantly different with the values of 5.16% and 5.09% respectively. As compared to commercial paper resin for coating, the viscosities and solid content of the solutions prepared were about two times lower, while the pH for B was higher than the pH of the commercial resin. After 14 days of visual observation, there was no biological degradation to the blended starch with acrylamide as compared to the unmodified sago starch solution. So it remained biologically resistant even after 14 days of exposure to ambient temperature.

3.2 Effects of modification of sago starch on the properties of coated handsheets

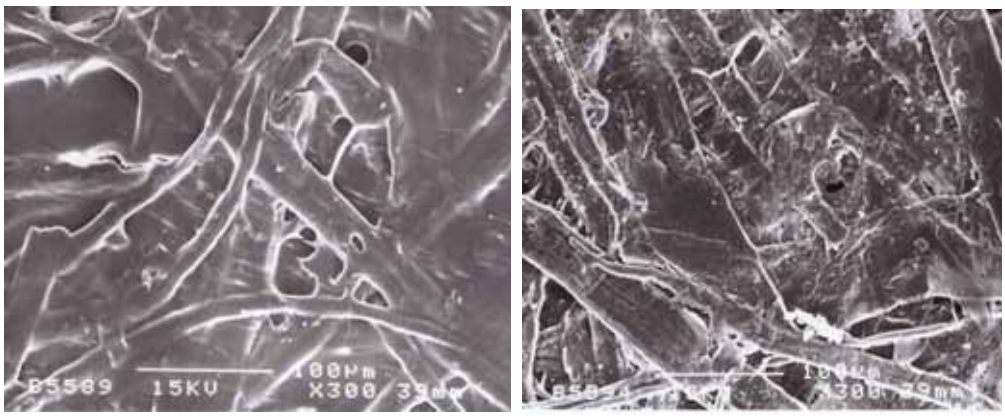
As shown in Table 2, the physical and mechanical properties of handsheets coated with the blended sago starch were generally improved compared to those coated with US. Coated handsheets with B, had significantly ($p \leq 0.05$) increased the folding endurance; the value being 110 times. It also gave higher value for crush strength of 128 N compared with 105 N for US coated handsheets.

Table 2: *Comparison of properties of handsheets coated with unmodified sago starch and sago starch blended with acrylamide solutions*

	US	B
Double fold (times)	70^{b}	110^{a}
Stiffness (mNm)	2.40^{a}	2.03^{b}
Burst index (kPa.m^2/g)	2.64^{ns}	2.40^{ns}
Tensile index (N.m/g)	33.81^{ns}	34.21^{ns}
Crush (N)	105^{ns}	128^{ns}
Tear index (mN.m^2/g)	10.7^{ns}	9.9^{ns}
Smoothness (ml/min)	950^{a}	600^{b}
Air permeance (ml/min)	35^{b}	74^{a}

Note: Each value is an average of eight replicates; Means followed by the different letter (a, b) in each row for each handsheet property are significantly different at $p \leq 0.05$ according to Duncan's Multiple Range Test (DMRT).

ns = not significant; US = unmodified sago starch; B = sago starch blended with acrylamide.



(a) (b)

Fig. 1: *Photomicrographs of handsheet surfaces coated with (a) unmodified sago starch, (b) sago starch blended with acrylamide. Magnification: 300X*

It was also observed that B coated handsheets did not give satisfactory surface air permeance (74 ml/min) and smoothness (600 ml/min) as compared to the handsheet coated with US. This is probably due to blending which did not provide sufficient interaction between the sago starch and acrylamide and as a result; the mixture became less homogeneous and lacking in flow ability. This can clearly be seen in Fig. 1(b) where, some of the handsheets coated with acrylamide blended sago starch showed the existence of unpolymerized acrylamide on it's surface. This evidently suggests that there is the lack of bonding formation between sago starch and acrylamide and between pulp fibers and the blended sago starch with acrylamide.

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 lack of bonding formation between sago starch with acrylamide and between recycled pulp fibers with the blended sago starch and acrylamide.

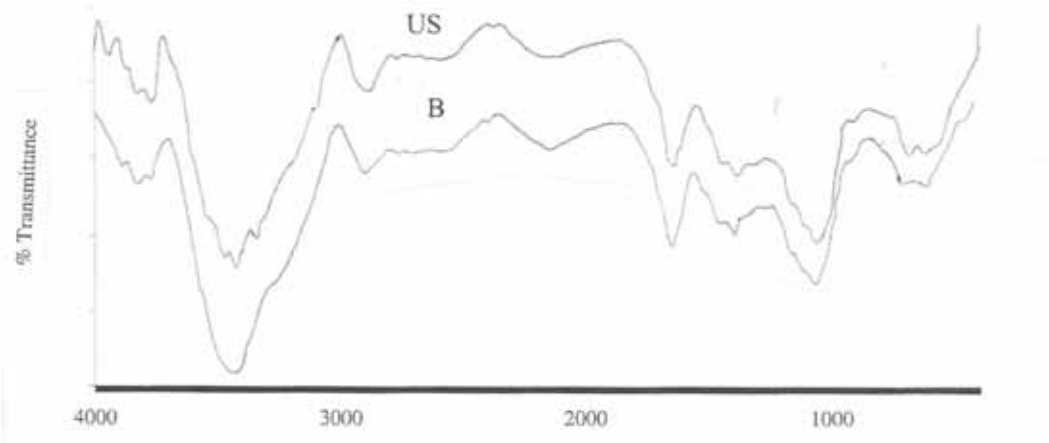


***Fig. 2*:** *FTIR spectra of acrylamide (ACR) and handsheets coated with unmodified sago starch (US) and modified sago starch (B)*

The FTIR absorption spectra of handsheets coated with US and B were illustrated in Fig. 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 cm^{-1} - 3800 cm^{-1}. For B, the FTIR spectra showed that there is N-H symmetric stretching at the frequency of 3442 cm^{-1}. Weaker absorption at 1380 cm^{-1} may be due to the O-H band in the plane where as absorption at 1054 cm^{-1} may be due to the C-O stretching in the CH_2OH.

3.3 Effects of initiators addition in the solution of blended sago starch with acrylamide on the properties of coated handsheets

Earlier investigation (Section 3.2), found that there was a lack of bonding formation between the cellulose fibers and the acrylamide which may be due to incomplete cure of the modified starch. Thus, in this section, initiators of ceric ammonium nitrate (CAN) and potassium persulfate (PP) were used to accelerate the curing of the blended sago starch with acrylamide.

The results in Table 3 indicate that, except for crush, smoothness and air permeance, generally all the properties of the coated handsheets were significantly improved ($p \leq 0.05$) with the use of initiators. This confirms the earlier observation where there was insufficient curing of the starch. The presence of initiators help to accelerate polymerization between the starch and the fibers, hence a better bridging was produced. Between the two initiators, CAN and PP, the former gave relatively better performance particularly in folding endurance.

Table 3: *Properties of handsheets coated with sago starch blended with acrylamide at different initiators*

	Without Initiator	CAN	PP
Double fold (times)	110^{ab}	124^{a}	94^{b}
Stiffness (mNm)	2.03^{b}	3.12^{a}	2.57^{ab}
Burst index (kPa.m^2/g)	2.40^{a}	2.18^{b}	2.18^{b}
Tensile index (N.m/g)	34.2^{a}	32.4^{b}	32.6^{b}
Crush (N)	128^{a}	107^{ab}	94^{b}
Tear index (mN.m^2/g)	9.9^{b}	12.9^{a}	13.1^{a}
Smoothness (ml/min)	775^{a}	378^{b}	536^{b}
Air permeance (ml/min)	68^{a}	19^{b}	24^{b}

Note: Each value is an average of eight replicates; Means followed by the different letter (a,b,c) in each row for each handsheet property are significantly different at p≤ 0.05 according to Duncan's Multiple Range Test (DMRT).
ns = not significant; CAN = ceric ammonium nitrate; PP = potassium persulfate.

3.4 Effects of further curing on the properties of coated handsheets

The poor results obtained in Section 3.2, suggest that the modified starch was not fully polymerized. Further curing of the handsheet was carried out using an oven at various temperatures. The results were then compared with handsheets coated with blended sago starch with acrylamide that did not undergo the further curing process. An initiator, PP was also added into the sago starch system. It was found, handsheets undergone further curing had increased in strength significantly.

Table 4: *Properties of handsheets coated with sago starch blended with acrylamide at different levels of curing*

	OVEN-0	0VEN-50	OVEN-75	OVEN-90
Double fold (times)	94^{b}	94^{b}	142^{a}	138^{a}
Stiffness (mNm)	2.57^{b}	2.97^{ab}	2.57^{b}	3.07^{a}
Burst index (kPa.m^2/g)	2.18^{a}	2.34^{a}	2.20^{ab}	2.26^{ab}
Tensile index (N.m/g)	32.6^{ns}	34.0^{ns}	32.8^{ns}	32.7^{ns}
Crush (N)	94^{ns}	91^{ns}	85^{ns}	90^{ns}
Tear index (mN.m^2/g)	13.1^{ns}	13.7^{ns}	13.3^{ns}	13.0^{ns}
Smoothness (ml/min)	536^{ns}	570^{ns}	547^{ns}	550^{ns}
Air permeance (ml/min)	24^{ns}	21^{ns}	26^{ns}	29^{ns}

Note: Each value is an average of eight replicates; Means followed by the different letter (a,b,c) in each row for each handsheet property are significantly different at p≤ 0.05 according to Duncan's Multiple Range Test (DMRT).

ns = not significant.

In Table 4, the folding endurance increased significantly ($p \leq 0.05$) from handsheets coated without any further curing (Oven-0) to handsheets coated and cured at 75^{o}C (Oven-75).

However, as the temperature rose to 90^{o}C (Oven-90), there was no further improvement in handsheet properties. There was however, no definite trend for stiffness strength where, Oven-90 gave the best stiffness value of 9.07 mNm. Handsheets cured at 50^{o}C (Oven-50) gave the highest burst index and tensile index of 2.34 kPa.m^2/g and 33.98 N.m/g. By further curing the coated handsheets, it did not significantly increase the crush value as with uncoated handsheets gave the highest value of 93.5 N. At 50^{o}C curing, the tear index (13.72 mN.m^2/g) was the highest. Further curing of the coated handsheets at 50^{o}C increased significantly the smoothness and air permeance property.

4. CONCLUSION

Blending of sago starch with acrylamide improved the viscosity. Coating the handsheets with the blended sago starch with acrylamide did improved certain properties, although, the micrographs of these surfaces indicate that there is insufficient polymerization. This confirmed the use of initiator and further curing were able to improve some of the handsheet properties. CAN is seen to react better as compared to PP. A temperature of 50^{o}C was suitable to cure sago blended with acrylamide.

REFERENCES

1. Howard, R.C. (1991), The effects of recycling on paper quality. Paper Technology, vol. 32 (4), pp. 20-25.
2. Capps, C. (1994), Environmental legislation, World Paper June, pp. 37-40.
3. Mouyal, P. (1994), Chemical treatment reduces stickiew buildup on machine fabric, Pulp and Paper, vol. 4, pp. 105-106.
4. Uutela, E. and Black, N.P. (1990), Recycled fiber use expected to grow by 41% and reached 130 million tons yearly by 2001, Tappi, vol. 73(7), pp. 50-52.
5. Anonymous (2000), The status and market information for pulp and paper industry in Malaysia, 1999, Malaysian Pulp and Paper Manufacturers Association.
6. Spence, G.G. (1990), Paper additives and resins. Concise Encyclopedia of Polymer Science and Engineering, Ed: Kroschioitz, J.J. John Wiley and Sons, Inc.
7. BeMiller, J.N. (1997), Starch modification: challenges and prospects. Starch=Stärke, vol. 49 (4), pp. 127-131.
8. T638 hm (1985), Analysis of starch and starch products. TAPPI Testing Procedures, Technical Association of the Pulp and Paper Industry, Atlanta.
9. T676 hm (1985), Viscosity of starch and starch products. TAPPI Testing Procedures. Technical Association of the Pulp and Paper Industry, Atlanta.
10. T402 om (1983), Standard conditioning and testing atmospheres for paper, board, pulp handsheets and related products, TAPPI Testing Procedures. Technical Association of the Pulp and Paper Industry, Atlanta.