UNIVERSITI PUTRA MALAYSIA

# SAGO STARCH AND ITS ACRYLAMIDE MODIFIED PRODUCTS AS COATING MATERIAL IN RECYCLED PAPER

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**Chairman : Dr. Paridah Md. Tahir**

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Starches are usually used in recycled paper to improve the paper strength properties. Apart from the common starches available in the market, sago starch offers another alternative since it is cheaper. This study was carried out to determine the suitability of sago starch as paper additive. The basic properties i.e., pH, viscosity and solid content, of the unmodified (4%, 5% and 6% w/v basis) and modified sago starch [sago starch blended with acrylamide (38.5% grafting efficiency), sago starch grafted with acrylamide in an acidic condition and sago starch grafted with acrylamide in an alkaline condition] were determined. The starches were then used to coat laboratory made recycled papers. Various effects were studied, namely, starch concentrations, methods of sago starch modification, addition of different types of initiator and further curing at different temperatures.

Increasing the concentration of the unmodified sago starch solutions from 4% to 6% caused significant reduction in their pH values and increased both the viscosity and solid content of the solutions. The unmodified sago starch solution was very viscous

(>447 mPa.s) and were susceptible to biological attack after two days at ambient. The incorporation of acrylamide into sago starch through blending or grafting significantly reduced the viscosity of the solutions. All the modified starches remained biologically resistant even after 14 days of exposure to ambient.

Coating the paper with unmodified sago starch, generally improved both the physical and mechanical properties of the paper significantly as compared to the uncoated paper. Paper coated with unmodified sago starch at 5% concentration (US5) gave higher burst index (2.64 $kPa.m^2/g$), better smoothness (950 ml/min) and lower porosity (35 ml/min) than those coated at 4% (US4) and 6% (US6). Amongst the three types of sago starch modification methods (blending, grafting in acidic condition and grafting in alkaline condition), blending gave superior performance when coated on the recycled paper, producing papers with very high folding endurance (110 times) and crush strength (128 N). Nevertheless, the smoothness and porosity of these papers were unsatisfactory due to insufficient curing shown by the micrographs. Fourier Transform Infrared Spectroscopy (FTIR) spectra show that the interaction between the blended acrylamide-starch solutions and the fibre was weak. The use of ceric ammonium nitrate (CAN) as initiator and further curing at $50^0C$ however, had able to improve these properties. Amongst the five types of paper produced (uncoated, coated with unmodified sago starch, coated with sago starch blended with acrylamide, coated with sago starch grafted with acrylamide in acidic and alkaline condition), paper coated with blended acrylamide- sago starch gave the most desirable physical and mechanical properties as well as resistant towards biodegradation.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**KANJI SAGU DAN PRODUK UBAHSUAIANNYA DENGAN AKRILAMIDA SEBAGAI BAHAN PENYALUT DALAM KERTAS KITAR SEMULA**

Oleh

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Kanji biasanya digunakan dalam kertas kitar semula bagi memperbaiki kekuatan kertas. Selain daripada kanji-kanji yang biasa didapati di pasaran, kanji sagu menawarkan satu lagi sumber alternatif. Kajian ini telah dijalankan untuk menentukan kesesuaian kanji sagu sebagai additif kertas. Ciri-ciri asas (pH, kepekatan dan kandungan pepejal) untuk larutan kanji sagu yang tidak diubahsuai (4%, 5% dan 6% w/v basis) dan larutan kanji sagu yang telah diubahsuai (kanji sagu dicampur dengan akrilamida, pempolimeran cangkuk kanji sagu dengan akrilamida di dalam larutan asid dan alkali) telah ditentukan. Seterusnya, larutan kanji sagu akan disalut ke atas kertas kitar semula yang dihasilkan di dalam makmal. Pelbagai kesan-kesan telah dikaji seperti kepekatan kanji sagu, kaedah pengubahsuaian untunk kanji sagu, penambahan 'initiator' dan suhu kematangan di suhu-suhu yang berbeza.

Penambahan kepekatan kanji sagu yang tidak diubahsuai menyebabkan pengurangan nilai pH, dan penambahan daam kedua-dua kepekatan dan kandungan pepejalnya. Larutan kanji sagu yang tidak diubahsuai mempunyai kepekatan yang tinggi (> 447

mPa.s) dan mudah diserangi kulat. Penambahan akrilamida ke dalam kanji sagu secara pencampuran atau pempolimeran cangkuk telah mengurangkan kepekatan larutan dengan bererti. Kesemua kanji sagu yang telah diubahsuai tahan ke atas serangan biologikal walaupun didedahkan selama 14 hari.

Penyalutan kertas dengan kanji sagu yang tidak diubahsuai, secara amnya, dapat mempertingkatkan sifat-sifat fizikal dan mekanikal kertas dibandingkan dengan kertas yang tidak disalut. Kertas yang disalut dengan kanji yang tidak diubahsuai pada kepekatan 5% (US5) memberi indeks ketembusan (2.64 kPa.$m^2$/g), kelicinan (950 ml/min) dan ketelusan (35 ml/min) yang lebih baik dibandingkan dengan kertas yang dilitupi kanji sagu yang tidak diubahsuai pada tahap kepekatan 4% (US4) dan 6% (US6). Di antara tiga jenis kaedah pengubahsuaian kanji (pencampuran terus, pempolimeran cangkuk di dalam acid dan alkali). Pencampuran terus memberi keputusan yang lebih baik dengan keupayan lipatan (110 kali) dan 'crush' (128 N) yang sangat tinggi. Akan tetapi, pencampuran terus memberi sifat kelicinan dan ketelusan yang kurang memuaskan. seperti yang dilihat di dalam mikrograf. Spektra 'Fourier Transform Infrared Spectroscopy (FTIR) menunjukkan hubungan yang lemah di antara larutan pencampuran terus akrilamida- kanji sagu dengan gentian. Walaubagaimanapun, melalui penggunaan 'ceric ammonium nitrate' (CAN) sebagai 'initiator' dan suhu kematangan pada 50$^0$C, sifat- sifat ini telah dapat dipertingkatkan. Di antara lima jenis kertas yang dihasilkan (tidak disalut, disalut dengan kanji sagu yang tidak diubahsuai, disalut dengan kanji sagu yang dicampurkan terus dengan akrilamida, disalut dengan pempolimeran cangkuk kanji sagu dengan akrilamida di dalam acid dan alkali), kertas yang dilitup menggunakan

pencampuran terus memberi sifat fizikal dan mekanikal yang lebih baik serta sifat ketahanan terhadap kulat.

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# INTRODUCTION

## 1.1 General Review

Utilisation of recycled fibre 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 (Howard, 1991). Today, paper recyclability is the main issue in pulp and paper industries (Capps, 1994; Mouyal, 1994; Uutela and Black, 1990). There are four important driving forces for recycled paper utilisation. The first being the environmental issues such as the growing shortage of landfill sites, the limited/prohibition of burning of paper waste and the saving of energy resources (Mouyal, 1994; Virtanen and Nilsson, 1993). The second is the economic factor, especially in countries or regions where forest resource is scarce. Recycled fibre in such countries is very often cheaper than virgin pulp. The third is the increase in quality of recycled fibre due to the latest developments in recycling technology which has enabled recycling mills to produce a very high quality recycled pulp with properties similar to that of virgin pulp (McCool, 1991). Finally, legislation has been passed in numerous countries which set minimum requirements for the recycled fibre content in certain products and mandatory collection schemes (Capps, 1994).

There are at present 18 paper mills including one integrated pulp and paper mill in operation in Malaysia. Out of this number, 16 mills use recycled paper either from

old newspaper, or magazine paper or corrugated liners. In 1999 alone, about 850,000 metric ton recycled paper was produced in Malaysia (Anon, 2000).

However, the use of recycled pulp has its limitation, particularly to the strength of the paper. Additive is thus used to strengthen the paper. In some cases it is not possible to add a chemical additive to the dilute pulp slurry and achieve the desired paper property. Hence, a number of functional additives are applied to the surface of preformed paper. Starch, one of the more popular additives, has become more important as strength additive, either applied internally or on the surface (Spence, 1990).

Starch is the principal food reserve polysaccharide in the plant kingdom. It forms the major source of carbohydrates in the human diet and is therefore of great economic importance. Since ancient times conversion of starch to a variety of products has been known to many populations. Breadmaking and fermented beverages are among the early technologies of human civilisation (Charles, 1953; Ralph, 1950; Jones, 1983). Starch, taken from grains, tubers and roots has been consumed as food and feed for centuries. Starches are also utilised in several other non-food sectors such as in paper industry which consumes a significant amount of starch annually. In North America alone, the total volume of industrial starches consumed in paper and papermills for the year of 1995 is over 3 billion pounds at industrial capacity. The total volume of the industrial starches in paper and boardmaking is USD400-USD425 million (Anon, 1995).

Although the current consumption of starch by the paper industry is high, many other synthetic materials are available that can substitute for starch are available. Recent advances in papermaking technology have made it easier to use such substitutes at a specific cost/performance basis. This is a serious challenge to the starch industry. At present, this challenge can be met by many advantages that starch provides. Starch is a natural polymer with high molecular weight that can be depolymerised with a great degree of control. It is a hydrophilic polymer that disperses in water and attaches to cellulose fibres 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 grafted to produce new materials with properties that combine the advantages of natural and synthetic polymer (BeMiller, 1997).

The principle material used for surface treatment in commercial paper mills is starch. Other materials for this purpose include strength additives [poly (vinyl alcohol), carboxymethylcellulose and natural gums] and sizing agent (wax emulsions or blends of these emulsions with rosin size, styrene-maleic anhydride copolymers, polyurethane resins and fluorochemical sizes). Because of its high amylose content, sago starch has some potential as additive (Anon, 1999). Nevertheless, sago starch is easily hydrated and swelled, lose viscosity and produce very cohesive pastes (Bujang and Ahmad, 2000). Thus it has to be modified prior to usage. Modified sago starch has improved properties such as viscosity, gelling time, and molecular weight which are vitally crucial for application as paper additive.

Since in its natural form sago starch has limited number of uses, chemical modification is crucial in meeting the certain requirements such as viscosity. Some of these modifications are blending and grafting of sago starch with other synthetic monomer to improve the viscosity, as well as the durability.

## 1.2 Justification of the Study

Synthetic paper additives were used commercially since the early 1940's. They are generally added at levels of 5 % or more and are used primarily for specialty paper grades (Alince et al., 1976.). Polymers of polyacrylamide were soon found to have many unique properties that made them especially effective as dry strength additives. Various other compositions have been reported as having dry strength-properties. Most of these can be classified as being cationic non-acrylamide-containing polymers such as polyethylenimine, vinyl pyridine, vinyl sulfonium, polyacrylic hydrazide and condensation polymers of polyamines, ketones and aldehydes (Allan and Reif, 1971; Quere and Guiroy, 1973; Humiston et al., 1964; Machida et al., 1965; Chan and Guitard, 1977).

Naturally occurring polysaccharides such as starches and gums were the first commercially used dry strength additives, and the products and their derivatives are still widely used today. However, the usage of these natural polymers is hindered by the preference and wide consumption for synthetic additives. Therefore, the modification of natural polymers such as sago starch is a promising method for the preparation of new materials. This enables one to introduce special properties and

broaden the field of the potential application of those abundance biopolymers. Two of such methods are through the incorporation of these types of biopolymers (starch) with synthetic monomers. Blending and grafting of sago starch with synthetic monomers such as styrene, methylmethacrylate and acrylamide have improved several properties of the sago starch. Harrizzeandi (1998), Pang (1999) and Puspamalar (1999) reported that incorporating sago starch with synthetic monomers reduces the swelling behaviour and increases the molecular weight of the starch.

It is hoped that this work could provide the impetus to use sago starch as a complimentary additive to the local paper industry. Through this study it is hoped that sago starch could establish another alternative usage that would help to accelerate development of sago industry in Malaysia.

### 1.3 Objectives of the Study

The main objectives of the study are:

- To investigate the suitability of sago starch as an additive to improve the mechanical and physical properties in recycled paper
- To determine the effects of modification with acrylamide on the properties of starch solutions and the paper coated with it
- To determine suitable curing methods for sago starch - coated paper