AN APPLICATION OF WAXY RICE AS THE PAPER COATING BINDER

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Abstract: Waxy rice is one of the major agricultural products in Asia. Its applications, however, have been limited only to the food products, and no literature reports could be found about its application to paper products. In view of its chemical composition containing almost all amylopectin, waxy rice starch should be applicable to the paper coatings. This report presents our research on the applicability of waxy rice as the paper coating binder. Experimental results indicate that waxy rice is applicable as the coating binder, since when applied using the same formulation, waxy rice provides similar paper coating properties as do corn starch and soy protein, the commonly used coating binders. The coating properties can even be enhanced using waxy rice after alkaline or acid treatment. Sodium hydroxide treatment results in improved picking resistance and gloss. And light hydrogen chloride treatment provides enhanced brightness and opacity. Three different types of waxy rice were studied, namely, long, short, and black waxy rice. Among them, short waxy rice performs the best as the coating binder. But after the alkaline treatment, long waxy rice yields better coating properties than either short or black waxy rice. Finally, the experimental results suggest that a critically diluted concentration should be practiced with the acid treatment in order to maintain the picking resistance.

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Introduction

The waxy rice

The annual rice production in Asia is over 140 million tons. Among this production rate, waxy rice has a significant share. It is about 12% of the rice production in China and is 2.5% in Taiwan (Lu, 1989). Its applications, however, have been limited only to the food products, and no literature reports could be found about its application to paper products.

Tables 1 and 2 show that although waxy rice are grown in different areas and have disparate types and compositions, they all have about 70% starch (DOH survey, 1994). In addition, while rice starch is composed of around 17% amylose and 83% amylopectin, waxy rice starch contains almost all amylopectin (Shan, 1936, Walter, 1993). Moreover, corn starch, which is commonly used as a coating binder, contains 28% amylose and 72% amylopectin and has an average particle size of 15 μm. The gelatinization temperature (5% solution) of corn starch is between 62 and 72 °C (Kearney and Maurer, 1990). Compared with corn starch, waxy rice starch containing no amylose and about 100% amylopectin has an average particle size of 3 μm and a gelatinization temperature of 72 °C (Shan, 1936). These characteristics suggest that waxy rice have a potential to be applied as the paper coating binder.

Table 1. Typical compositions of waxy rice in Asia.

Area	Moisture, %	Protein, %	Fat, %	Fiber, %	Ash, %	Starch, %
Chain	12.1	10.3	2.2	0.8	1.3	73.6
Japan	14.3	8.5	3.2	1.0	0.9	72.1
Taiwan	14.7	8.3	1.7	0.9	1.6	67.3

Table 2. Types and compositions of waxy rice grown in Taiwan.

Type	Moisture, %	Protein, %	Fat, %	Fiber, %	Ash, %	Starch, %
Black	15.8	9.3	3.3	1.4	1.5	68.7
Long	13.7	7.9	0.9	0.2	0.4	76.9
Short	13.5	8.2	1.1	0.1	0.4	76.7

Research objectives

Based on the previous discussion, the motivation of this research is from the fact that waxy rice starch has similar physical properties as corn starch does. Moreover, waxy rice starch containing almost 100% amylopectin should provide a higher paste viscosity, and thus a higher binding strength. Therefore, the objective of this research is to study the applicability of waxy rice as the paper coating binder. The applicability is evaluated by comparing the binder performance of waxy rice with the commonly used corn starch and soy protein under equivalent conditions. This research also compares the binder performance of different types of waxy rice which are available from the market. Finally, this research attempts to improve the binder performance of waxy rice through simple pre-treatments on the material by either alkaline or acid modification.

Experimental procedures

Binder performance comparison

Commercially available Xerox paper (70 g/m^2) was used as the basesheet for all experiments. It has an opacity of 86%, a brightness of 85%, and a gloss of 20% (all Tappi methods on Photovolt 577); its surface smoothness is 56 s measured on a Bekk smoothness tester.

The coating pigments were made down using the formulation shown in Table 3. Calcium carbonate pigment (Wet-ground variety, 0.85 μm) was

Table 3. The experimental formulation of the coating pigments.

Chemical	% Solids of chemical	Parts
Clay	100	20
Calcium carbonate	75	80
Dispersant	41	0.3
Defoamer	100	0.05

supplied as a 75% slurry. It was first metered and mixed in a plastic beaker (250 ml) with the dispersant and defoamer. Under continuous stirring, clay pigment (BetaCote, ECCI) was then slowly added to the pigment slurry. The solids content of the pigment slurry was next adjusted to 70%. A high-shear mixer was then used to disperse the pigment slurry at 6,000 rpm for 40 min, and then 1,500 rpm for 15 min. The pigment slurry was finally sealed with aluminum foil and stored for the subsequent coating color preparations.

For the coating binder preparation, the corn starch (69.48 g, 20% moisture, oxidized type) was first slowly added into a round bottom flask and mixed with water (312.66 g). The flask was then tightly sealed, transferred into a water bath, and continuously stirred (300 rpm) while bringing up the temperature. When the starch temperature reached 90 °C, the stirring was stopped. But the flask was remained in the water bath (90 °C) for another 15 min. Next, the starch paste was cooled down to room temperature. After taking its viscosity reading (Brookfield, DV-II, 100 rpm, No. 7 spindle, 20°C), the starch paste was sealed with aluminum foil and stored for the subsequent coating color preparations.

Tree different types of waxy rice (long, short, and black) were experimented. They were pulverized, screened (2-4 μm), and made into paste (16%) following the same procedure as in preparing the corn starch. The soy protein (PC-5,000, PTI) was used by direct addition into the pigment slurries.

To prepare the coating color, pigment slurry was first metered and mixed with water. Then, the starch binder was added, making the final coating color a 45% slurry with three different binder addition levels (10%, 15%, and 20%). Afterward, the coating color was continuously stirred (2,000 rpm) for another 15 min. A laboratory coater was next used to carry out the paper coating with a coating weight of 15 g/m^2. The coated paper (four duplicates) were air dried overnight and conditioned before testing their properties. The coating properties were tested following the Tappi Standard Methods and included opacity, brightness, gloss, smoothness, and Dennison wax.

When preparing the coating color with soy protein, pigment slurry with pre-determined amount was first stirred (1,300 rpm) in a beaker. The soy protein (dry powder) was then directly added (three different levels) into the pigment slurry at a very slow rate. Next, the solids content was adjusted (45%) and the coating color was stirred (2,000 rpm) for 15 min. After this step, the pH of the coating color was adjusted to 10 using ammonium water (38%). After another 15 min stirring (2,000 rpm), the coating color containing soy protein was applied to coat paper using a laboratory coater. Finally, the coated paper were tested following the same procedure as stated above.

Chemical modification

Both alkaline and acid treatments were practiced on the three types of waxy rice. Sodium hydroxide was used for alkaline treatment and hydrogen chloride was for acid treatment. The modification procedure started out by mixing the pulverized waxy rice with water in a round bottom flask and adequately shaken. The flask was then tightly sealed and transferred into a water bath. Next, the bath temperature was brought up to 90 °C while mixing (300 rpm) the waxy rice with water. After the temperature had reached 90 °C, the stirring was stopped, and the content of the flask was kept at 90 °C for 15 min.

Afterward, the flask was opened in the bath, and a pre-determined amount of sodium hydroxide (20 *N*) was pipetted into the flask to make the concentration of sodium hydroxide in the flask either 0.5, 1.0 or 2.0 *N*. The starting reaction time was immediately recorded. And the modification reactions were proceeded at 90 °C with mild mixing (450 rpm) for 1.0 h. When the reaction period was completed, the flask was removed from the bath and cooled down to room temperature. The modified waxy rice was then used as the coating binder following the same procedure stated before. The modification procedure for the acid treatment was the same as the alkaline treatment, except that hydrogen chloride (36%) was used in place of sodium hydroxide.

Results and discussion

Comparison with corn starch and soy protein

Figure 1 depicts that corn starch and soy protein provide a similar magnitudes of the coating color viscosity at all binder addition levels. But when waxy rice is used as the binder, the coating color viscosity is remarkably higher. This viscosity change has to do with the molecular composition of the waxy rice which contains almost all amylopectin. Amylopectin with a branched polymeric structure has an average molecular weight in the range of 50 to 500 million. And this is about 200 to 300 times greater than the molecular weight of amylose, a straight chain polymer (Kearney and Maurer, 1990). A high polymer such as amylopectin tends to have a more coiled molecular conformation in solutions and its molecules are usually tangled together. Thus, the waxy rice paste solutions are relatively harder to flow, rendering greater coating color viscosity. It should be mentioned that the waxy rice used in this phase of the research is the long type waxy rice, and the binder performance of other types of waxy rice is reported in a later discussion.

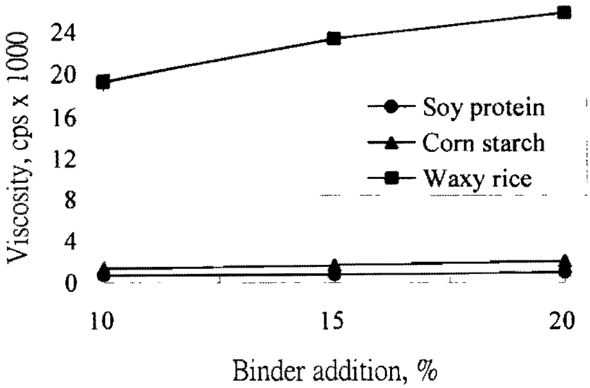

Figure 1. The coating color viscosity against binder addition level of soy protein, corn starch, and waxy rice.

Table 4 lists all the measured properties of the coated paper and is used to compare the binder performance of soy protein, corn starch, and waxy rice. Table 4 indicates that soy protein provides the greatest picking resistance (Dennison wax number). And the waxy rice produces lower picking resistance compared with both soy protein and corn starch. This is probably because soy protein has amino groups ($-NH_2$) on its molecules and can provide a structured coating layer. Amino groups with nitrogen atoms

Table 4. The measured properties of coated paper for the comparison among soy protein, corn starch, and waxy rice.

Binder type	Soy protein			Corn starch			Waxy rice		
Binder addition, %	10	15	20	10	15	20	10	15	20
Dennison wax, #	6	7	8	5	7	8	5	6	7
Opacity, %	96.0	93.6	91.2	91.8	91.0	90.5	96.9	95.7	94.6
Brightness, %	85.9	84.3	82.2	85.3	84.6	82.8	85.0	84.2	83.6
Gloss, %	10.1	8.0	6.0	10.2	6.9	6.0	10.3	7.0	6.0

can form stronger hydrogen bonds with the paper surface than the hydroxyl groups (-OH) associated with corn starch. The structured coating layer would provide better coating coverage on the paper surface, giving rise to an even binder distribution and thus greater picking resistance.

The plausible reason why waxy rice gives lower picking resistance than corn starch is again the molecular conformation. As discussed before waxy rice has a closed, coiled molecular conformation which can result in a reduced molecular surface area for forming hydrogen bonds. Moreover, because of the closed conformation, the paper surface would not be covered as evenly as the corn starch which contains 28% amylose and a more opened molecular conformation. Therefore, it may be concluded that it is the closed conformation which causes the waxy rice to yield lower picking resistance than corn starch.

With respect to the optical properties of the coated paper, Table 4 clearly denotes that all opacity, brightness, and gloss decrease as the binder addition level increases. Apparently, as the binder addition increases more flocculation among the pigment particles occurs. This increased flocculation in turn would decrease the quantity of air-particle interfaces, reducing the effect of light scattering, and thus lowered optical properties. Moreover, among the three optical properties, only opacity has a relatively more meaningful difference with waxy rice being the greatest, followed by soy protein then corn starch. This outcome might be related to the calcium carbonate pigments, because another experiment using 20% calcium carbonate and 80% clay did not display a meaningful difference in opacity. It is therefore assumed that there is some kind of "opacity dispersion" between calcium carbonate particles and waxy rice which can provide a higher opacity after the paper coating. On the other hand, the soy protein gives higher opacity than corn starch is possibly due to the structured coating layer with soy protein, augmenting the light scattering effect.

Hence, waxy rice is applicable as the paper coating binder, since it provides similar coating properties as do soy protein and corn starch. Additionally, even though waxy rice yields lower picking resistance, it can provide a higher opacity for the final coated paper.

Comparison among types of waxy rice

Figure 2 shows the coating color viscosity with the three different types of waxy rice studied in this work. And it indicates that the long

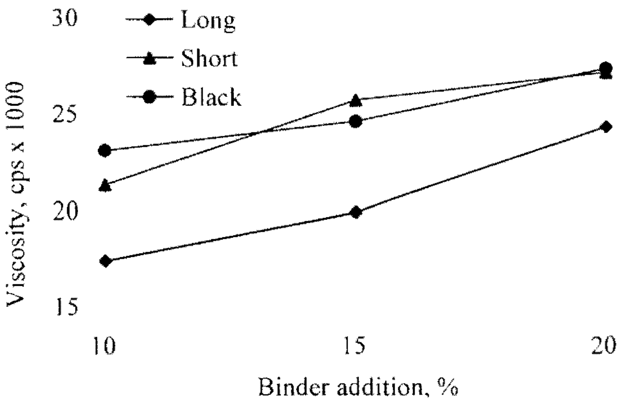

Figure 2. The coating color viscosity against binder addition level of the long, short, and black waxy rice.

waxy rice provides relatively lower coating color viscosity at all binder addition levels. However, the lower viscosity does not necessarily mean a better binder performance.

As can be seen from Table 5, the best coating properties are associated with the short type of waxy rice. It is possible that the short waxy rice has

Table 5. The measured properties of coated paper for the comparison among long, short, and black waxy rice.

Waxy rice type	Long			Short			Black		
Binder addition, %	10	15	20	10	15	20	10	15	20
Dennison wax, #	5	6	7	6	7	7	5	6	7
Opacity, %	95.8	95.0	93.5	97.0	96.6	93.3	96.9	95.7	94.6
Brightness, %	85.6	84.8	83.2	86.2	85.6	84.3	85.0	84.2	83.6
Gloss, %	10.0	9.0	6.0	11.2	9.0	5.7	10.3	7.0	6.0

comparatively shorter molecules, leading to better coating color dispersion and distribution on the paper surface. This would then provide better picking resistance and optical properties. In addition, the composition difference (Table 2) among the three types of waxy rice is probably another cause by which the short waxy rice outperforms the other two waxy rice. For instance, among the three waxy rice, the black type has the least starch content, yet has the highest content of protein, fat, fiber, and ash, resulting in decreased binder performance.

Moreover, compared with Table 4, Table 5 suggests that the short waxy rice can provide better binder performance than both corn starch and soy protein. Accordingly, waxy rice, particularly the short type, is probably a good alternative to be applied as the paper coating binder.

Alkaline modification

Although chemical modifications were performed at concentrations of 0.5, 1.0, and 2.0 *N*, only part of the experimental results (0.5 *N*) are presented in this report, and other information can be found elsewhere (Dong, 1996). Compared with Figure 2, Figure 3 illustrates that sodium hydroxide has a considerable effect on decreasing the solution viscosity of all types of waxy rice. This suggests that alkaline depolymerization reactions, including the chain breakage and the peeling reaction (Clayton, *et al.*, 1989), have occurred during the treatment and significantly modify the molecular composition and conformation of all waxy rice.

Applying the alkaline treated waxy rice to the coating color, Table 6 shows that in general alkaline treatment will increase the picking resistance of the coating color, as compared with Table 5. The possible reason is a more opened molecular conformation and a better coverage of the waxy rice on the paper surface. Moreover, the gloss is apparently higher after the alkaline modification, possibly due to an improved film forming ability of the waxy rice and then a smoother paper surface. However, the opacity and brightness have decreased after the alkaline treatment. These decreases might be caused by both an increased flocculation and the alkaline darkening reactions. An increased flocculation is seemingly due to the depolymerization reactions that makes the interactions between the pigment particles and the binder easier, giving rise to decreased opacity and brightness. Alkaline darkening reactions with starch and other components would also decrease the brightness of the binders themselves, and thus the coating color.

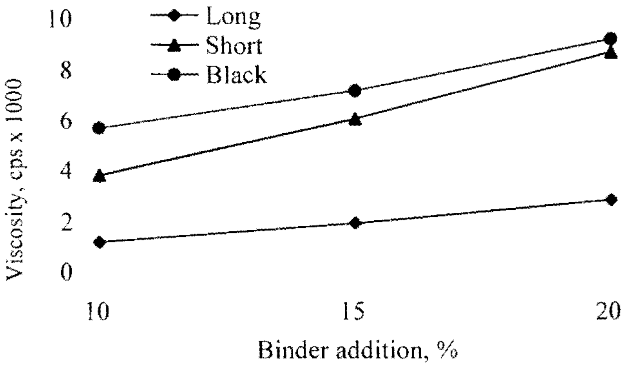

Figure 3. The coating color viscosity against binder addition level of the long, short, and black waxy rice after sodium hydroxide (0.5 *N*) treatment .

Among the waxy rice themselves, the long waxy rice generally performs the best as the coating binder, since it provides the higher picking resistance, brightness, and gloss. The only disadvantage is the opacity.

Table 6. The measured properties of coated paper for the comparison among long, short, and black waxy rice after sodium hydroxide (0.5 *N*) treatment.

Waxy rice type	Long			Short			Black		
Binder addition, %	10	15	20	10	15	20	10	15	20
Dennison wax, #	6	7	8	4	6	7	7	7	8
Opacity, %	91.1	90.3	89.2	92.8	92.3	89.7	94.1	93.4	91.6
Brightness, %	83.2	82.1	79.6	82.3	80.2	78.0	81.9	81.7	80.2
Gloss, %	12.0	8.7	7.5	12.3	8.5	6.6	9.7	8.4	6.0

This outcome can be interpreted by postulating that sodium hydroxide exerts different effects on different waxy rice. It is possible that sodium hydroxide might modify the long waxy rice to have a more suitable composition and conformation that would result in better picking resistance, brightness, and gloss. However, after the alkaline treatment, the "opacity dispersion" as mentioned before might decreased to a meaningful extent, leading to a lower opacity.

Thus, sodium hydroxide treatment (0.5 *N*) on waxy rice brings about increased picking resistance and gloss, but decreases the brightness and opacity. Moreover, the long waxy rice performs relatively better than the short and black types of waxy rice after the alkaline treatment.

Acid modification

Compared with sodium hydroxide at the equivalent treatment concentration, hydrogen chloride (0.5 *N*) brings about remarkable differences in the binder performance. First, the acid treatment decreases the binder viscosity to a greater extent than that by alkaline treatment, as Figures 3 and 4 illustrate. Secondly, acid treatment results in a shear

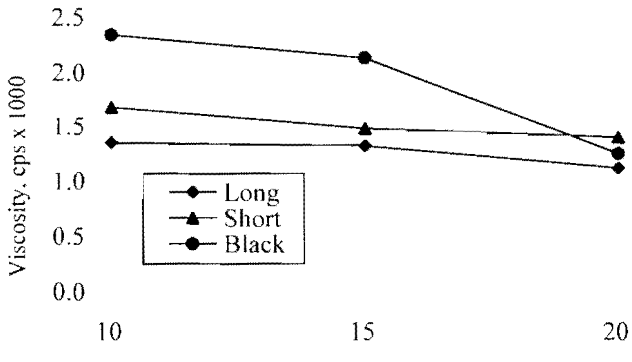

Figure 4. The coating color viscosity against binder addition level of the long, short, and black waxy rice after hydrogen chloride (0.5 *N*) treatment .

thinning effect, because as the binder addition increases, the coating color viscosity decreases (Figure 4). And this is found for all types of waxy rice. Thirdly, calcium carbonate must have reacted with hydrogen chloride to form calcium chloride (1) as the formation of bubbles (CO_2) suggests while

$$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + H_2O + CO_2 \qquad (1)$$

performing the experiment. The shear thinning is then possibly caused by both the chemical reaction which consumes calcium carbonate and the decrease in the binder viscosity.

Finally, Table 7 soundly indicates that the acid treatment could almost destroy the binding ability of waxy rice, since no picking resistance data could be obtained (Dennison wax No. less than 3) using the acid treated

Table 7. The measured properties of coated paper for the comparison among long, short, and black waxy rice after hydrogen chloride (0.5 *N*) treatment.

Waxy rice type	Long			Short			Black		
Binder addition, %	10	15	20	10	15	20	10	15	20
Dennison wax, #	--	--	--	--	--	--	--	--	--
Opacity, %	99.9	99.5	98.4	99.2	98.6	98.7	99.5	99.9	98.8
Brightness, %	87.5	87.0	86.8	87.0	86.8	86.6	87.1	86.9	86.5
Gloss, %	5.4	4.7	4.0	7.0	6.2	5.6	6.8	6.4	5.8

waxy rice. However, acid treatment can result in an extraordinary dispersion state of the pigment particles giving very high opacity and brightness, as shown in Table 7. Table 7 also suggests that since the polymeric nature has probably been destroyed after the acid treatment, the film forming ability of waxy rice no longer works, causing a great decrease in gloss. These results imply that to bring about coating advantages with acid modification, the treatment concentration has to be critically diluted for maintaining the picking resistance and gloss. Otherwise, calcium carbonate should be removed from the coating color formulation.

Conclusions

Waxy rice is applicable to paper coating and has a potential to be used as an alternative for the coating binder. This is because waxy rice provides similar coating properties as do corn starch and soy protein. Among the three types of waxy rice studied, namely, long, short and black waxy rice, the short type performs the best as the coating binder. It may also be concluded that alkaline treatment on waxy rice improves the picking resistance and gloss, but can decrease opacity and brightness. After the alkaline treatment, it is the long waxy rice which produces the best coating properties. On the other hand, although acid treatment on waxy rice yields high opacity and brightness, it decreases the picking resistance substantially. Therefore, it is implied that a critically diluted concentration should be practiced with the acid treatment.

Acknowledgments

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