Synthesized Silica from Rice Husk for Anti-slip Overprint Coating

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Abstract
Thailand is among the top ten rice exporters that have produced more than 30 million tons of rice in order to serve domestic and worldwide consumption. In a process of rice milling, more than 10 million tons of rice husk as agricultural waste are disposed. Since rice husk is enriched with abundant silica (SiO_2), this study aims to reflux silica from rice husk by 2M hydrochloric acid (HCl) for 120 min. The results yielded refluxed silica whose purity was 98.7% and had an amorphous structure. The silica powder was measured the color by a spectrophotometer according to printing standard (ISO12647-1), the color measurement (CIE L*a*b*) indicated 94.79+0.48+1.24 (white color), whiteness and color difference (ΔE) were 84.85, 3.28, respectively. Particle size of silica was analyzed by "Image Plus Pro" and exhibited a uniform size of 3-5 μm. The synthesized silica from rice husk was used as a anti-slip coating material for the improvement friction and smoothness on white kraft papers. The coating was prepared by a water-based varnish of acrylic resin mixed with the synthesized silica from rice husk at different ratios of 0%, 0.5%, 1.0%, and 1.5% on the weight basis. The varnished with 1.0% silica from rice husk displayed the highest friction and printing quality wasn't changed.

Keywords: Rice husk/Silica/Anti-slip/Overprint varnished

Introduction

Nowadays, Thailand is the top ten rice producer in the world. In 2016, 28 million tons of rice was produced for domestic consumption and worldwide export. Consequently, rice milling process disposed approximately 9 million tons rice husk as agricultural waste (Agricultural statistics, 2016). However, rice husk can be used as heating fuel in the production of bricks and electicity. It is also utilized for animal feed and fertilization. Due to energy crisis, rice husk is also made for biomass in combustion process for electricity generation and heating boiler in industries. However, burning rice husk causes air pollution such as CO_2, acid rain and greenhouse effect. So, alternative methods for rice husk ash removal have been continuously studied. Generally, rice husk consists of 30% by weight of silica. After acid extraction, silica content increases up to 95% by weight (Chiarakorn S., 2003). So, rice husk and rice husk ash can be used as a natural silica source to synthesize silicate materials such as zeolite and MCM–41 (Zhao, *et al*, 1996).

About 90% paper packaging were coated with overprint varnish. Anti-slip Overprint Coating is the most offten use for coating on package, which it‘s made from resin mixed silica (E.W. Flick, 1999). The silica in coating is served to increase friction on paper surface (A.A. Tracton, 2005) Anti-slip properties are important for packaging in packing and transport process. This research aimed to get silica as a raw material from agricultural waste to produce Anti-slip Overprint Coating.

Experimental

Rice husks by product from rice milling in Pathum Thani Province, Thailand was used in this research. They were washed with distilled water to remove soils and dirt before drying in the oven at 105 °C for 24 h. The dried rice husks were treated chemically by a solution of hydrochloric acid (HCl) that was previously prepared at different concentrations of 1, 2, and 3 M. The rice husks were mixed with different molarities of HCl and boiled in a hood at reaction temperature of 80±5 °C at difference time for 60 and 120 min (Yalcin, N., and Sevinc, V., 2001). The solution was filtered and the rice husks were washed with distilled water several times until they were acid-free. The acid-leached rice husks were dried in an oven heat at 105 °C. They were roasted at 650–700 °C in furnaces for 240 min (Chiarakorn S., 2003). The characteristics of the obtained silica powder were then measured. Analysis of their characteristics were performed by means of X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscope (SEM), particle size, color and color difference (ISO 12647-1/TIS2260-1, (2004). Selective silica powder with suitable properties in color and particle size (A.A. Tracton, 2005) was then used for Anti-slip Overprint Coating.

Varnished coating (Lloyd M. Smith, 1994) was made from 60% acrylic resin mixed with synthesized silica that had suitable properties at different ratio 0%, 0.5%, 1%, 1.5% and had additive that containing of anti-foam/wax/leveling agent at 2:3:5 in quantity of 1% and added water until got 100%. Analyzing properties of coated varnish on white kraft papers by printed test form 4 colors (Anthony P.Stanton, 1988) through inkjet printing at resolution of 4,800 dpi × 1,200 dpi for test transparency by trans-densitometer (N. Tipsotnaiyana, *et al*, 2012) and test coefficient of friction by slip-meter (George Wypych, 2005).

Results and Discussion

Analysis purities and organic elements of Rice Husk silica

The amounts of ingredients present in the ash at various concentration of HCl and times are shown in figure 1. All the ash samples contain Silicon dioxide, Potassium oxide, Calcium oxide, Phosphorus pentoxide, Aluminums oxide and Iron (III) oxide; of which the concentration of Silicon dioxide is greatest. The impurity content is significantly reduced by the acid-leached and thermal decomposition process (Yalcin, N., and Sevinc, V., 2001). The resulting purity of silica (Silicon dioxide) is better than 98% after burning the rice husk.

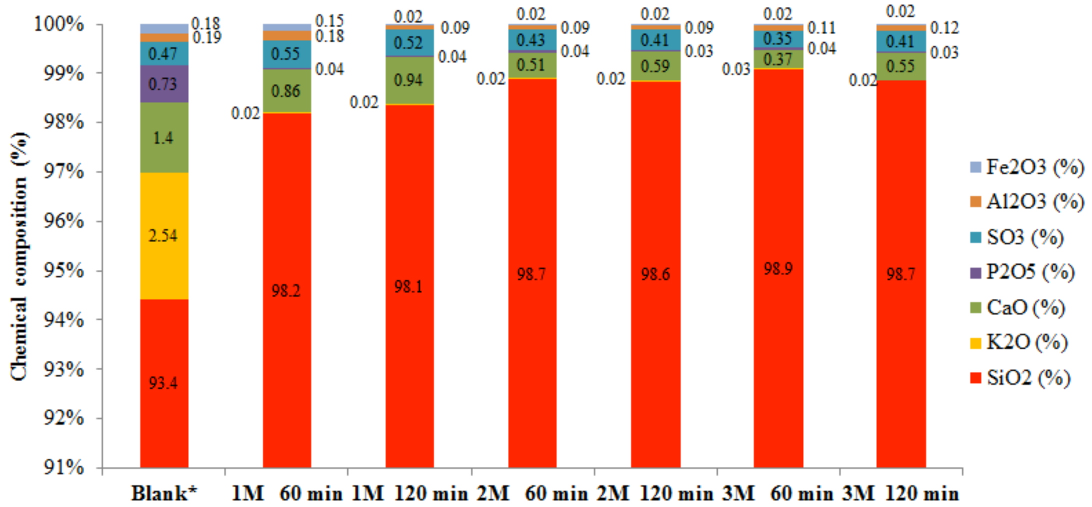

Figure 1: The purity of Rice Husk silica was determined by XRF techniques

Analysis of physical properties

In figure 2 shows X-ray diffraction analysis of rice husk at various concentration of HCl and times. All samples are amorphous. However, in the ash samples (fig. 2, A–G), the typical silica characteristic was observed at a broad peak centered at $2\theta = 22°$.

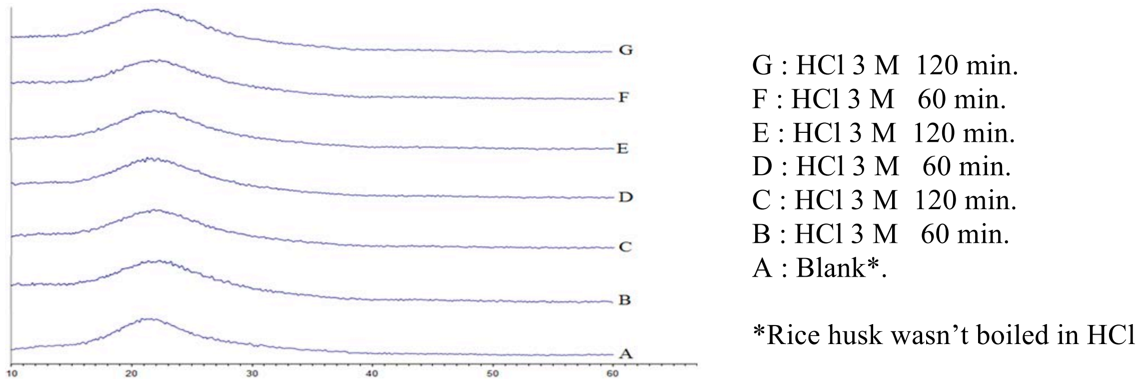

Figure 2: X-ray diffractogram of rice husk.

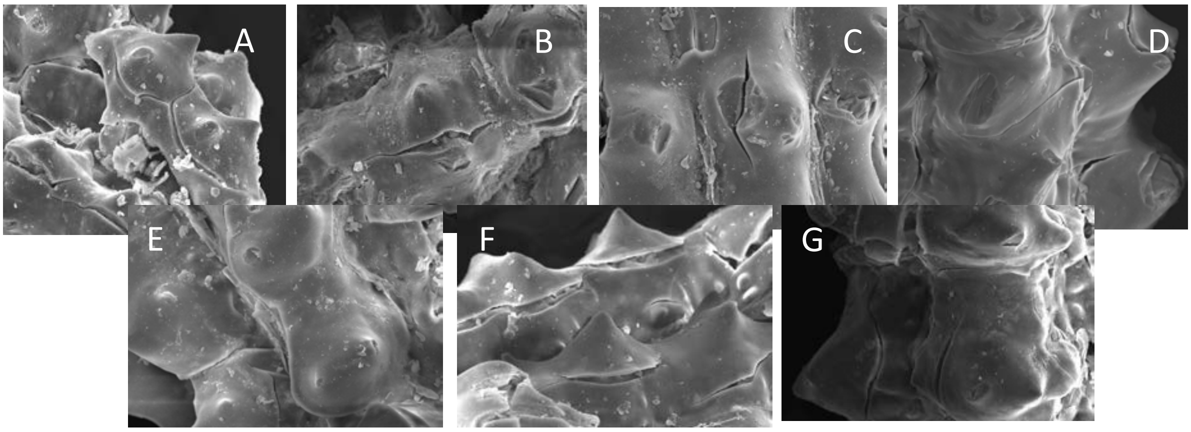

Figure 3: Scanning electron micrographs of rice husk: (1,000X @ 132 μm); (A) Blank; (B) 1M 60 min; (C) 1M 120 min; (D) 2M 60 min; (E) 2M 120 min; (F) 3M 60 min; (G) 3M 120 min

In figure 3 shows SEM micrographs 1,000X @ 132 μm of rice husk silica that made from rice husk calcined in a muffle furnace at 650 °C for 240 min. fig. (A-G) shows the inner epidermis of rice husk silica, which has a lamella structure. The morphology og all figure weren't different but figure 3A showed that the surface of ground rice husk silica powder was covered with flakes. Figure 3B, 3C and 3D shows that a less pores were distributed in silica powder. Fig. 3E, 3F and 3G that the silica is a highly porous material with a large internal surface area. The particle size of silica was analyzed by "Image Plus Pro" and exhibited a uniform size of 3-5 μm.

Analysis Optical properties of Rice Husk silica

The CIE and Delta E (ΔE, Color difference.) of Rice Husk silica powder was determined by color measurement techniques were shown in Table 1. Raw material that is suitable for producing anti-slip coating should have high whiteness and color which are similar to standards of white kraft paper (ISO 12647-1/TIS2260-1, 2004). Silica powder was made from refluxing of rice husk with HCl 2 M 120 min has a minimum Delta E = 3.28 and has maximum whiteness = 84.85

Table 1 Color CIE, Delta E and Whiteness of Rice Husk silica.

Sample	CIE L**	CIE a**	CIE b**	Delta E (ISO 12647)	Whiteness*
White paper	95.00	0.00	-2.00	-	80.00 ± 5
Blank	85.42	+3.90	+1.71	10.99	39.28
1M 60 min	94.48	+0.46	+1.39	3.46	80.17
1M 120 min	93.78	+0.45	+1.31	3.55	80.27
2M 60 min	94.54	+0.49	+1.47	3.53	80.27
2M 120 min	94.79	+0.48	+1.24	3.28	84.85
3M 60 min	93.24	+0.73	+2.08	4.51	79.00
3M 120 min	94.47	+0.39	+1.24	3.31	83.88

** Color CIE = color spaces of International Commission on Illumination

Analyze properties and printing quality of anti-slip coating on white kraft paper (printed-test chart 4 Colors).

Varnished coating were made from acrylic resin mixed with a highest purity synthesized silica that refluxing by HCl 2 M 120 min at different ratio and the additives type anti foaming, wax and leveling agent. The coefficient of friction and transparency of coating were shown in Table 2. The friction of anti-slip coating was increased when the ratio of synthesized silica was increased from about 0.11 to 0.58. When measured transparency of anti-slip coating found that it was decreased because density of dried-layer coating was increased from 0.10 to 0.70 respectively.

Table 2 The viscosity and transparency of water base coating.

Sample	Coefficient of friction : (COF)	Transparency : Density
Coating : silica 0.0 %	0.11 $\pm$ 0.02	0.10
Coating : silica 0.5 %	0.25 $\pm$ 0.08	0.19
Coating : silica 1.0 %	0.44 $\pm$ 0.03	0.21
Coating : silica 1.5 %	0.58 $\pm$ 0.05	0.70

After coated anti-slip coating on picture and test form that printed through inkjet printer (Canon Pixma 3000: 4,800 dpi x 1,200 dpi) on white Kraft paper. The printing quality was measured by spectrophotometer and analyze picture and color gamut of printing that were shown in figure 4-5.

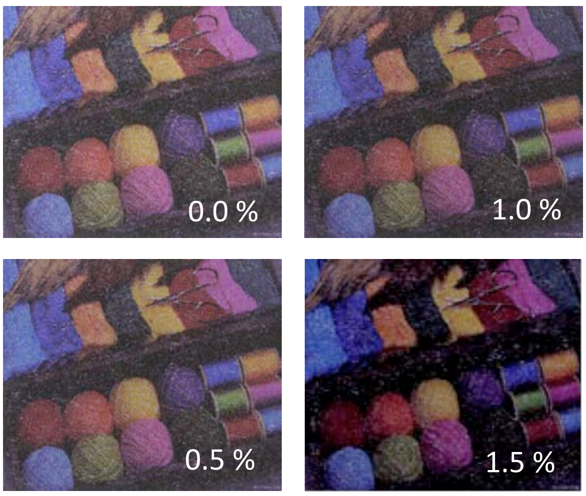

Figure 4: Picture after coated anti-slip coating

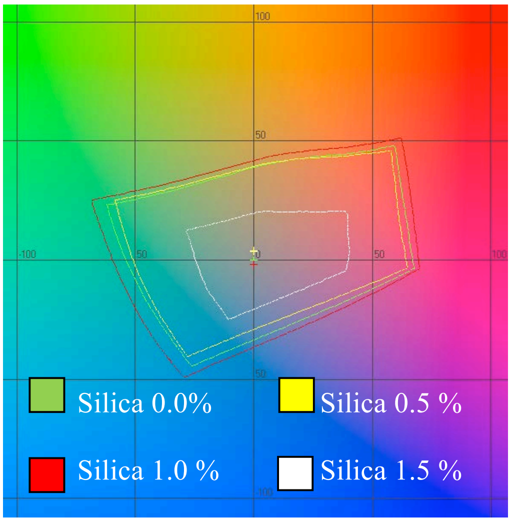

Figure 5: Color gamut of printing after (silica 0%,0.5%,1.0% &1.5%) coated anti-slip coating (silica 0%,0.5%,1.0% &1.5%)

From Figure 4 the picture that coated by anti-slip coating containing synthesized silica 1.5% is the highest density but picture has low details in shadows tone. The printing that coated anti-slip with synthesized silica 1.0% have color density close to the synthesized silica 0.5% but detail in shadows tone is better. Figure 5 showed the color gamut of printing that coated anti-slip containing synthesized silica 0%, 0.5%, 1.0% and 1.5%. The anti-slip mixed with silica coating 1.0% have a color gamut wider scope than color gamut of printing coated anti-slip silica coating 0.0%, 0.5% and 1.5%, respectively.

Conclusions

Silica particles can be obtained from the hydrolysis reaction of silicon alkoxide. The resulting particle size and morphology depended strongly on the hydrolysis condition and reaction time. The reaction continues until the solution is super saturated. To investigate a possibility of tailoring the particle size and the particle size distribution, the X-ray diffraction indicated that the silica particles were amorphous, according to the broad peak centered at $2\Theta = 22°$. This demonstrated that the particles had a higher percentage of amorphous than crystalline structures. The effect of different molar ratios of acidic reagents on the structure and morphology of silica particles was observed. The impurity content was significantly reduced by the acid-leached and thermal decomposition process. The resulting purity of silica was greater than 98%. The silica powder was made by refluxing the rice husk with 2-M HCl for 120 min, that was a suitable condition for raw material to produce Anti-slip coating.

The anti-slip coatings that made from acrylic resin mixed with synthesized silica 2 M HCl for 120 min in ratios is not over 1.0% have a similar transparency. Silica had ratios more than 1.0% were precipitated and reduce transparency. When coated more synthesized silica on top the printing was impact to detail and tone of picture. The coating that mixed synthesized silica from rice husk 1.0% is suitable for produce an anti-slip coating because it provided a high detail in print quality especially in shadow tone with wider color gamut.

Acknowledgement

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