# Preparation of a Crosslinking Cassava Starch Adhesive and its Application in Coating Paper

Songlin Wang,[a,*] Fangfang Zhang,[a] Fushan Chen,[a] and Zhiqiang Pang [b]

A new starch-based adhesive with high solid content, high binding force, and low viscosity was prepared *via* hydrolysis of cassava starch with α-amylase using glycerol as a plasticizer and Ammonium Zirconium Carbonate (AZC) as a crosslinker. The adhesive was applied to coated paper as a partial substitute for SBR latex. The effects of α-amylase, glycerol, AZC, and temperature on the starch adhesive and its performance in application were investigated. The prepared crosslinking cassava starch adhesive showed a significant effect when the starch slurry concentration was 50% (w/w), the dosages of glycerol and α-amylase were 15% and 0.075%, respectively, and the enzymolysis starch was crosslinked with 12% AZC at 50 $^{o}$C. The modified starch improved the paper in terms of surface strength, gloss, whiteness, and smoothness when 20% SBR latex was substituted into the coating formulation. Statistical analysis indicated that the crosslinking temperature and AZC had significant effects on the performance of the paper, while glycerin and α-amylase had little effect on it. Spectral analysis of the product showed that the crosslinking reaction took place between AZC and cassava starch. The average particle size was 528.6 nm. Scanning Electron Microscope (SEM) images of the paper surface were consistent with the other measured surface properties.

*Keywords: Crosslinking cassava starch; Ammonium Zirconium Carbonate; Coating adhesive; Biolatex*

*Contact information: a: College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China; b: Key Laboratory of Pulp and Paper Science & Technology of Ministry of Education of China, Shandong Polytechnic University Institute of Light Industry, Jinan, 250353, China; *Corresponding author: wangsongl@126.com*

## INTRODUCTION

Adhesives play a decisive role in coating paper. They can adhere pigments to paper, thereby improving the paper's printing-related properties to meet consumer requirements. Starch-based adhesives (Emengo *et al*. 2002; Imam *et al*. 2001; Masumbu *et al*. 2003; Mostafa and El-Sababary 2003) have been widely used to partially replace non-renewable petroleum-based latex in order to protect the environment and to reduce costs. However, commercial starch has rarely been used as a coating adhesive in high-concentration coating formulation because of its viscosity, instability, and aging shortcomings. Thus, modifying starch to achieve a high solids content, a high binding force, and a low viscosity is an important goal. There are many mature starch modification methods, such as physical modification, chemical and biological treatment, or mixed modification. Products with high solids contents, stable qualities, high binding forces, and low viscosities have been prepared using these methods.

Ecosythetix Inc. (Bloembergen *et al*. 2008, 2010, 2011) has prepared a novel biolatex conjugate composition by co-extruding a starch feedstock, a plasticizer

(glycerol), a crosslinker (glyoxal), and other performance-enhancing additives under shear force. This process transforms starch granules into nanoparticles and maintains the starch's molecular chain length and strength. Lei *et al*. (2011) also developed biolatex with stable performance, high bond strength, narrow molecular weight distribution, and low viscosity by co-extruding starch, a plasticizer, a modification agent, a crosslinker, and other performance-enhancing additives under shear force. The product can be substituted for SBR latex either partially or completely to obtain an excellent adhesive effect. Even so, there are few mature examples of a biolatex in the market that can be substituted for a petroleum-based latex, so it is necessary to find new ways to transform various bioresources into biolatex.

In this paper, starch adhesive was prepared *via* hydrolysis of cassava starch with α-amylase, using glycerol as plasticizer and AZC as crosslinker. Cassava is one of the world's three largest tuber crops. The plant is highly regarded for its biomass-to-energy conversion capacity due to its drought resistance, tolerance of unfertile soil conditions, and wide adaptability. Cassava can contain 25 to 35% starch, and the ratio of amylopectin to amylose can be as high as 80:20. Cassava has a high viscosity even at low concentrations because of its high amylopectin content, so it is necessary to reduce its viscosity by use of α-amylase, thereby obtaining good liquidity and applicability at higher solid levels. However, the hydrolysis process also decreases the bond strength.

Ammonium Zirconium Carbonate (AZC) is an eco-friendly crosslinking agent that has seen promising results in the current market and has the characteristics of both wide applicability and rapid aging. The agent is unstable in the air, and its aqueous solution can rapidly break down to anionic hydroxy zirconium polymer at 60 $^{o}$C. When suitably formulated, AZC (as shown in Fig. 1) can form hydrogen bonds (Wang 2007; Song *et al.* 2011) with polymers, such as starch, containing -OH groups. The mechanism of the reaction between AZC and starch is shown in Fig. 2. Ammonium ions in AZC solutions can react with starch *via* hydrogen bonding, which can link with basic zirconium carbonate ions *via* ionic attractions (Fig. 2a). During drying, $NH_3$ and $CO_2$ are released, and new hydrogen bonds are formed between the -OH of starch and the reactive sites of AZC (Fig. 2b). AZC can be applied to coated paper with starch as an adhesive system, whereby it can have a great effect when the pH value is 8. In the present work AZC was used to prepare a starch adhesive with high solid content, low viscosity, and good adhesive performance and was applied to coated paper to partially substitute for SBR latex. By varying the plasticizer dosage, AZC dosage, starch concentration, and temperature, the extent of crosslinking could be controlled. The optimum reaction condition was determined experimentally, and the product was characterized by means of Infrared Spectroscopy (FTIR), Scanning Electronic Microscopy (SEM), particle size distribution, and energy-dispersive X-ray spectroscopy (EDS).

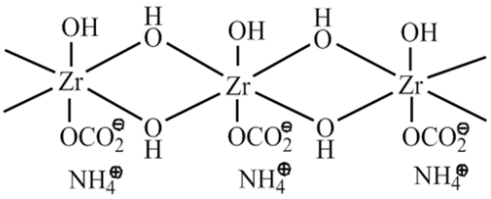


**Fig. 1.** Chemical structure of AZC

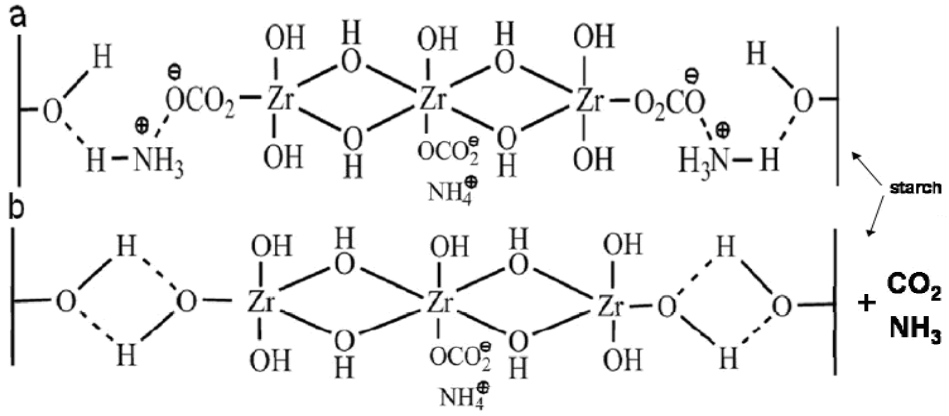


**Fig. 2.** The reaction of AZC with starch. a: $NH_4^+$ in AZC reacts with starch *via* hydrogen bonding, linking to basic zirconium carbonate ions *via* ionic attractions; b: $NH_3$ and $CO_2$ are released during drying, and form new hydrogen bonds between starch and AZC.

## EXPERIMENTAL

### Materials and Instruments

The cassava starch used for the testing of a 10% slurry treated at 95 $^oC$ for 0.5 h at a pH value of 7.0, was of industrial grade, having a fineness of 98% smaller than 150 μm, a whiteness of 89.1%, a moisture content of 11.03 wt%, and a viscosity of 3540 mPa·s. The materials were purchased from the following sources: starch (Guangxi Mingyang Biochemical Technology Limited Company); glycerin (AR, Laiyang Fine Chemicals Factory); alpha amylase (AR, Tianjin Fuchen Chemical Reagent Factory); AZC (Industrial-grade, Zibo Xinlvyuan Biological Chemical Co., LTD); GCC 60K, SBR latex 2606, thickening agent, water-resistance agent, and PVA1788 (industrial-grade, Shandong Chenming Paper Group).

The instruments used included AA-GWR Water Retention Meters (Kaltec Scientific, Inc.); XM60 moisture analyzer (Precisa); DH-f T.K. Homodisper (Tokushu Kika Kogyo. LTC); DV-10 Hercules Hi-Shear Viscometer (Kaltec Scientific, Inc.); Brookfield LVT cone-plate viscometer (Brookfield); K303Multi coater (RK); SE224 Gloss Tester (L&W); Elrepho (L&W); 58-05-00-0001 smoothness tester (The TMI Group of Companies); RNA-52 printability tester (Research North America, Inc); Bruker Tensor 27 FT-IR (Bruker); JSM-6700F SEM (Hitachi); and Nano-ZS90 Zeta Sizer (Malvern).

### Experimental Methods

*Preparation of starch adhesive*

Cassava starch and glycerin were added into a round-bottom flask, and water was added until the mixtured reached specified concentrations. The mixture was heated to 60 $^oC$ under continuous agitation and was then treated with α-amylase for 30 min. The slurry was heated to 90 $^oC$ and stirred for 30 min, then cooled to obtain enzyme-hydrolyzed starch. The mixture was treated with AZC at a certain temperature for 30 min under continuous agitation to obtain crosslinking starch adhesive.

*Preparation of coating formulation*

GCC 60K (100 in dry parts) was dispersed with a high-shear dispersion homogenizer at high speed for 20 min, then 10% (w/w) NaOH (0.06 in dry parts per hundred, the following are the same) was added to adjust its pH value within the range of 8 to 10. SBR latex (9.2), starch adhesive (2.3), and PVA (0.3) were added in sequence at 1200 rpm, then the water-resistance agent (0.6) was added at 300 rpm, and subsequently water was added into the mixture until it reached a target solids. The dosage of the thickener was adjusted according to the viscosity and was dispersed at 600 rpm for 5 min in order to obtain the coating formulation. The coating was applied to 70 $g \cdot m^{-2}$ culture paper, and the coating weight was 13±1 $g \cdot m^{-2}$. The coated paper was dried in an oven at 105 $^{o}C$ for 2 min.

*Performance tests for paper*

The coated paper was exposed to 0.5 MPa line pressure at 50 $^{o}C$ and then held under constant temperature and humidity for 24 h. The paper's smoothness (GB/T 456), gloss (GB/T 8941), whiteness (GB/T 7974), K&N ink absorption (GB/T 12911), and dry pick velocity (GB/T 2679.16) were analyzed.

*Characterization*

The solid content and viscosity of the starch adhesive were measured using an XM60 moisture analyzer and a Brookfield LVT cone-plate viscometer. The high-shear viscosity and Water Loss Value (WLV) of the coating formulations were measured using a DV-10 Hercules Hi-Shear Viscometer and an AA-GWR Water Retention Meters.

The starch sample was decanted and washed with ethanol/water (75:25) three times, then dried at 60 $^{o}C$ in an oven until it had achieved constant weight. The JSM-6700F EDS test was used to determine the elemental content of the crosslinking starch sample. The particle size distribution was measured using a Malvern Nano-ZS90 Zeta Sizer. A Bruker Tensor 27 FT-IR instrument was used to analyze the crosslinking starch adhesive sample. The starch and coating layer were characterized with a JSM-6700F SEM to obtain their morphologies, and the samples were coated with gold before observation.

## RESULTS AND DISCUSSION

The solids content of SBR latex can be as high as 50%, which makes it capable of meeting the requirements for high-concentration coating formulas. Accordingly, the solids content of the starch-based adhesive to be partially substituted for the SBR latex was set at 50%. The coating formulation properties such as viscosity, high-shear viscosity, and water loss value can be affected by the different preparation conditions of the starch adhesive, and these properties can influence the distribution of the pigments onto paper and subsequently affect paper performance. All the tables are arranged according to the sequence of adhesives, coating formulations, and paper performance indicators. For the adhesive and coated paper, dry pick velocity may be considered the most important indicator of performance. High quality paper is generally associated with higher surface strength, a low degree of linting, a low frequency of pull-up or other delamination of the coating as a result of printing, and a vivid color of the printed image. The smoothness and gloss are also very important factors for coated paper and can improve the paper's

printing properties. The K&N ink absorption value also influences the print color and clarity of paper.

## Influence of α-Amylase on Starch Adhesive

The effect of α-amylase (at dosages of 5%, 2%, 0.10%, 0.075%, 0.05%, and 0.01%, respectively) on the starch adhesive was investigated. The concentration of the starch slurry was 50% in each formulation, along with 15% glycerin and 12% AZC. The crosslinking temperature was 50 $^{o}$C. The results showed that the viscosity was reduced with the increase in α-amylase. When the dosage of α-amylase was higher than 0.1%, the phenomenon of sedimentation was apparent. This was attributed to the action of α-amylase, which cleaves the starch macromolecules into soluble maltoses and decomposes amylopectin into maltose and glucose. Another effect of the enzyme is the generation of insoluble α-limit dextrin. Under the combined effect of these factors, the sedimentation occurred. However, with α-amylase in a dosage less than 0.05%, the starch chain was not broken down sufficiently and was not suitable for the adhesive due to its excessively high viscosity (higher than 1864 mPa·s). When the dosage of α-amylase was 0.1% to 0.075%, the viscosity ranged from 280 to 490 mPa·s (the viscosity of SBR latex was 334 mPa·s), which met the requirements of an adhesive with good stability and low viscosity.

## Influence of Glycerin on Adhesive and Coated Paper

In the conventional coating process, paper can absorb moisture through capillary effect and pressure filtration, leading to dehydration of the coating formulation. The migration of adhesives, which is caused by moisture migration and the evaporation processes during drying, can affect the binding ability of the starch and the surface strength of the coated paper. To improve the coating formula's leveling property in blade coating and to eliminate scratches, it is necessary to control its water retention value (WRV) within an appropriate limit (Engstrom *et al*. 1991; Bernada and Bruneau 1996). Poor water retention properties result in the deterioration of the rheological properties and can lead to a sharp rise in solids content at the tip of the coating blade, resulting in a coating problem. The addition of glycerol can increase the high-shear viscosity and the WRV of a coating formulation and improve its liquidity in blade coating, making it possible to achieve superior surface performance.

Table 1 shows that with an increase in enzyme, the starch chain can be cleaved, resulting in a reduction of the coating formula's high-shear viscosity, which was helpful for achieving good flow properties during the high-speed blade coating process and for obtaining a smooth surface. The molecular structures in the adhesive were small enough to fill the gaps between GCC particles, thus improving the gloss and smoothness of the paper (Chinga and Helle 2003; Lee *et al*. 2004; Santos and Velho 2002). The WRV of the coating formulation was reduced due to the breakdown of the starch chain's reticular structure. The surface strength and the whiteness of the paper also declined.

**Table 1.** Influence of Glycerin on Adhesive and Coated Paper

| | Dosage of glycerin (%) | 10% | | 15% | | 20% | |
|---|---|---|---|---|---|---|---|
| | Dosage of α-amylase (%) | 0.075% | 0.10% | 0.075% | 0.10% | 0.075% | 0.1% |
| Properties of biolatex | Viscosity (mPa·s) | 312 | 215 | 490 | 280 | 548 | 358 |
| | Solid content (%) | 52.66 | 52.11 | 52.11 | 52.12 | 51.06 | 51.71 |
| Properties of coating formula | Final solids (%) | 67.75 | 67.77 | 68.35 | 67.49 | 67.53 | 67.96 |
| | Brookfield Viscosity (mPa·s) | 864 | 860 | 970 | 955 | 1014 | 964 |
| | Hercules Viscosity (mPa·s) | 11.2 | 11.0 | 12.0 | 11.4 | 12.1 | 11.5 |
| | Water Loss Value ($g \cdot m^{-2}$) | 114.1 | 116.5 | 113.5 | 115.2 | 108.6 | 112.5 |
| Properties of coated paper | Gloss (%) | 29.5 | 30.7 | 31.5 | 33.4 | 31.4 | 34.7 |
| | Smoothness (s) | 942 | 982 | 1112 | 1371 | 1150 | 1371 |
| | Whiteness (%) | 80.44 | 80.32 | 80.48 | 80.4 | 80.59 | 80.44 |
| | K&N ink absorption (%) | 27.71 | 28.02 | 29.03 | 29.9 | 29.1 | 30.07 |
| | Dry pick velocity ($m \cdot s^{-1}$) | 1.1 | 1.06 | 1.16 | 1.12 | 1.14 | 1.11 |

Note: The concentration of the starch slurry was 50%; 12% AZC was added; and the crosslinking temperature was 50 $^{o}$C.

Table 1 also shows that the starch viscosity increased with the increase in glycerol, and both the high-shear viscosity and the WRV of the coating formulation rose due to the high viscosity and hydrophilism of glycerol. The gloss and smoothness rose with the increase in glycerol.

As a plasticizer, glycerol was found to be helpful in forming a plastic coating layer and in achieving a smoother surface, but it had little influence on the coated paper's whiteness. The addition of glycerol also improved the high-shear viscosity and the WRV of the coating formulation, leading to a more orderly distribution of the pigments and the porosity of coating, and increased the K&N ink absorption finally. A higher K&N ink absorption value may lead to print-through, induce low print gloss, and influence the print color and clarity on the back of paper, causing economic losses due to spoilage. On the other hand, in this study, a low level of ink absorption caused weak attachment of the printing ink layer, affected the print drying rate, and caused printing to transfer to the back of the adjacent paper when drying, influencing the print quality. The appropriate range was therefore determined to be 20 to 40%.

When the dosage of glycerol was 15%, the starch had a good adhesive effect. The adhesive forms hydrogen bonds with cellulose when it is within 0.5 nm of the surface of fiber. Due to the evaporation and the permeation of water during drying, the starch molecules are brought closer together, forming a continuous membrane that improves the surface strength of the paper.

When the dosages of glycerol and α-amylase were 15% and 0.075%, respectively, the product displayed good adhesive performance, the dry pick velocity was better, and paper whiteness, gloss, and smoothness were improved. The following experiments were conducted under the above conditions.

### Influence of Crosslinking Temperature on Adhesive and Coated Paper

Table 2 shows that with the increase in crosslinking temperature lower than 60 $^{o}$C, the viscosity of the starch adhesive and WRV of coating formulation rose, and the high-shear viscosity of coating formula was first decreased, then increased. The AZC solution, which can be rapidly broken down into anionic hydroxy zirconium polymer at 60 $^{o}$C, demonstrates a strong combination with -OH in starch, which increases the average molecular weight and viscosity. The rising temperature can also accelerate molecular motion and reaction speed, increase the collision probability, and enhance crosslinking structure to raise the WRV of the coating formulation. The macromolecules of the starch adhesive were small enough to fill the gaps between pigments and acted as a moving bearing lubrication for pigments, leading to a decrease in high-shear viscosity. When the temperature was 60 $^{o}$C, the crosslinking structure was enhanced and the high-shear viscosity was increased.

**Table 2.** The Influence of Crosslinking Temperature on Adhesive and Coated Paper

| | Temperature ($^{o}$C) | 30 | 40 | 50 | 60 | 70 | 80 |
|---|---|---|---|---|---|---|---|
| Properties of biolatex | Viscosity (mPa·s) | 359 | 413 | 490 | 494 | 482 | 488 |
| | Solid content (%) | 52.47 | 52.09 | 52.11 | 52.57 | 52.97 | 52.86 |
| Properties of coating formula | Final solids (%) | 67.58 | 67.18 | 67.38 | 67.47 | 67.60 | 67.53 |
| | Brookfield Viscosity (mPa·s) | 1044 | 1080 | 1070 | 1040 | 1028 | 1118 |
| | Hercules Viscosity (mPa·s) | 12.8 | 12.4 | 12.1 | 11.5 | 12.1 | 12.2 |
| | Water Loss Value ($g \cdot m^{-2}$) | 118.15 | 116.2 | 114.2 | 112 | 110 | 108.63 |
| Properties of coated paper | Gloss (%) | 28.3 | 29.6 | 30.5 | 30.3 | 28.8 | 28.6 |
| | Smoothness (s) | 960 | 964 | 1015 | 1007 | 980 | 972 |
| | Whiteness (%) | 81.43 | 81.31 | 80.48 | 80.41 | 80.3 | 80.1 |
| | K&N ink absorption (%) | 30.89 | 30.07 | 29.07 | 30.59 | 30.99 | 29.38 |
| | Dry pick velocity ($m \cdot s^{-1}$) | 1.04 | 1.07 | 1.16 | 1.10 | 1.08 | 1.06 |

Note: The concentration of the starch slurry was 50%; the dosage of α-amylase was 0.075%; and 12% AZC and 15% glycerin were added.

With the increase in crosslinking temperature below 50 $^{o}$C, gloss, smoothness, and surface strength of the paper increased. This crosslinking effect was enhanced with the increase in temperature, thus improving the adhesive's stability and binding force. The WRV of the coating formulation also increased, making the coating layer smoother after application of pressure. The appropriate high-shear viscosity and WRV also gave the coating formulation flow characteristics for blade coating that were suitable for providing a smooth surface. The adhesive effect was enhanced due to the the crosslinked structure of the starch chains. However, over-crosslinking or gelation may have occurred at a higher temperatures, causing a decrease in the gloss and smoothenss of the paper. The binding capacity between the fiber and the pigments was decreased. The whiteness of the paper declined because the whiteness of the starch adhesive decreased with the increase in temperature. Poor gloss and smoothness can also affect the light scattering,

thus reducing whiteness. The ink absorption also increased due to large porosity on rough surface.

When the crosslinking temperature was 50 $^{o}$C, the product showed better adhesive performance, and the dry pick velocity, whiteness, gloss, and smoothness were better. The subsequent experiments were carried out under the conditions just described.

## Influence of AZC on Adhesive and Coated Paper

Table 3 shows that the starch viscosity and WRV of the coating increased with the increase in AZC. The increasing AZC resulted in a strong combination with the –OH groups of the starch, increasing the average molecular weight and viscosity and enhancing the reticular structure, thus achieving a better water retention effect.

**Table 3.** Influence of AZC on Adhesive and Coated Paper

| | Dosage of AZC (%) | 6 | 9 | 12 | 15 | 18 | 21 |
|---|---|---|---|---|---|---|---|
| Properties of biolatex | Viscosity (mPa·s) | 370 | 386 | 490 | 600 | 710 | 1081 |
| | Solid content (%) | 52.82 | 52.14 | 52.11 | 53.55 | 54.59 | 52.66 |
| Properties of coating formula | Final solids (%) | 67.43 | 67.47 | 67.42 | 66.93 | 66.99 | 67.75 |
| | Brookfield Viscosity (mPa·s) | 1002 | 1108 | 1100 | 1106 | 910 | 864 |
| | Hercules Viscosity (mPa·s) | 11.5 | 11.9 | 12.1 | 12.4 | 12.0 | 11 |
| | Water Loss Value ($g \cdot m^{-2}$) | 124.4 | 121 | 120.6 | 119.6 | 116.4 | 106.1 |
| Properties of coated paper | Gloss (%) | 30.82 | 30.98 | 31.18 | 30.18 | 30.03 | 29.4 |
| | Smoothness (s) | 962 | 1070 | 1103 | 1062 | 985 | 940 |
| | Whiteness (%) | 80.27 | 81.1 | 81.02 | 80.98 | 80.5 | 80.5 |
| | K&N ink absorption (%) | 29.34 | 29.15 | 29.03 | 29.28 | 29.32 | 30.02 |
| | Dry pick velocity ($m \cdot s^{-1}$) | 1.05 | 1.12 | 1.16 | 1.15 | 1.10 | 0.97 |

Note: The concentration of the starch slurry was 50%; 0.075% α-amylase and 15% glycerin were added; and the crosslinking temperature was 50.

The addition of AZC improved paper gloss, smoothness, whiteness, and surface strength until an additional level of 12% AZC had been reached. The crosslinking effect was enhanced with the increase in AZC. A partly crosslinked structure was helpful to the stability and adhesive effect of starch adhesive, allowing it to obtain a smoother surface after application of pressure. The ink absorption was decreased. The appropriate high-shear viscosity and WRV also endowed the coating formulation with better high-shear flow characteristics in blade coating, producing a smoother surface. However, gelation, which was caused by over-crosslinking, occurred at a higher dosage of AZC. The resulting starch was unevenly distributed in the coating formula, causing a decrease in gloss and smoothness of the coating layer and affecting ink absorption. The decrease in free hydroxyl groups also reduced the binding capacity between the fiber and pigments. The whiteness of the paper showed a similar trend towards gloss and smoothness, indicating that a smoother surface can enhance the light reflection, thus improving whiteness.

From above, when the dosage of AZC was 12% and the temperature was 50 $^{o}$C, the product obtained had good adhesive performance. The gloss, smoothness, and whiteness of the coated paper were better.

## Influence of the Biolatex-to-SBR Latex Ratio on Coated Paper

A complex latex mixture consisting of starch adhesive and SBR latex was applied to the paper in a further coating experiment. The effect of the starch adhesive-to-SBR latex ratio on coated paper was studied. The dosage of the complex latex was 11.5% in the coating formulation.

**Table 4.** Influence of the Starch Adhesive-to-SBR Latex Ratio on Coating Formulation and Paper

| The dosage of starch adhesive (%) | 0 | 10 | 20 | 30 | 40 |
|---|---|---|---|---|---|
| Final solids (%) | 67.83 | 67.73 | 68.65 | 67.70 | 68.20 |
| Brookfield Viscosity (mPa·s) | 920 | 1020 | 1102 | 1160 | 1280 |
| Hercules Viscosity (mPa·s) | 11.3 | 10.6 | 10.5 | 12.3 | 12.4 |
| Water Loss Value ($g \cdot m^{-2}$) | 111.38 | 104.5 | 103.88 | 110.88 | 110.90 |
| Gloss (%) | 30.83 | 30.85 | 31.23 | 31.29 | 31.38 |
| Smoothness (s) | 930 | 1048 | 1169 | 1149 | 1133 |
| Whiteness (%) | 79.42 | 79.94 | 80.18 | 80.48 | 80.56 |
| K&N ink absorption (%) | 26.48 | 28.83 | 29.03 | 29.56 | 30.9 |
| Dry pick velocity ($m \cdot s^{-1}$) | 1.16 | 1.17 | 1.16 | 1.09 | 1.01 |

Table 4 shows that the gloss, whiteness, and K&N ink absorption of paper increased with the increase of the percentage of starch-based biolatex in the complex latex. The viscosity and size of the starch adhesive were greater than that of the SBR latex. As a consequence, the crosslinked starch, when used to partially replace SBR latex, was of a suitable size to fill the gaps between GCC particles and to increase the viscosity of the coating formulation. When the dosage of the starch-based biolatex was 20%, the low Hercules viscosity and the high WRV may lead to good liquidity in blade coating, wich helps achieve a smooth surface. With the increase in starch adhesive, the adhesive can wrap the GCC particles, improve the rheological properties of the coating formula, obtain a smoother surface, and increase the gloss and whiteness of the paper. The superior whiteness can be attributed to the fact that the the starch adhesive contributed to the formation of a smoother surface, thereby enhancing light reflection and improving the whiteness of the paper.

The surface strength of the starch adhesive coating layer was inferior to that of SBR latex due to its higher surface tension and poor wetting effect. Thus, surface strength decreased with the increase in the starch adhesive, but when the adhesive was used to replace 20% of the SBR latex, the coating layer obtained showed better gloss, smoothness, whiteness, and dry pick velocity.

## Data Analysis by Software SPSS

The data obtained from the experiments were analyzed using the statistical analysis software SPSS in order to determine the factors significance to paper performance.

**Table 5.** Interaction Effects of Factor A (glycerin) and B (α-amylase)

| | | Value | N |
|---|---|---|---|
| Level A | 1 | 10% | 4 |
| | 2 | 15% | 4 |
| | 3 | 20% | 4 |
| Level B | 1 | 0.075% | 6 |
| | 2 | 0.10% | 6 |

The results shown in Table 6 indicate F-test values of 0.406 and 0.995, which, obviously larger than the significance level 0.05, showed that glycerin and α-amylase had little effect on paper gloss.

**Table 6.** Examination of the Interaction Effects

| Variable: Gloss | Type III sum of squares | Df | Mean square | F | Significance |
|---|---|---|---|---|---|
| Correcting model | 9.182a | 5 | 1.836 | 0.420 | 0.820 |
| Intercept | 12182.627 | 1 | 12182.627 | 2788.270 | 0.000 |
| Level C | 9.179 | 2 | 4.589 | 1.050 | 0.406 |
| Level D | 0.000 | 1 | 0.000 | 0.000 | 0.995 |
| Level C * Level D | 0.003 | 2 | 0.001 | 0.000 | 1.000 |
| Error | 26.215 | 6 | 4.369 | | |
| Total dispersion square sum | 12218.024 | 12 | | | |
| Correction of the total | 35.397 | 11 | | | |

Note: a. $R^2$ = 0.259 (adjusting $R^2$ = 0.358)

Tables 7 and 8 demonstrate that the F-test values (0.000) were obviously lower than the significance level 0.05, which showed that both crosslinking temperature and AZC had very important effects on paper performance.

**Table 7.** Analysis of Variance (ANOVA) of Crosslinking Temperature

| | | Sum of squares | Df | Mean square | F | Significance |
|---|---|---|---|---|---|---|
| Gloss | Factor C | 9.544 | 5 | 1.909 | 78.986 | 0.000 |
| | Error | 0.145 | 6 | 0.024 | | |
| | Total dispersion square sum | 9.689 | 11 | | | |
| Smoothness | Factor C | 4353.417 | 5 | 870.683 | 94.128 | 0.000 |
| | Error | 55.500 | 6 | 9.250 | | |
| | Total dispersion square sum | 4408.917 | 11 | | | |
| K&N ink absorption | Factor C | 6.114 | 5 | 1.223 | 282.194 | 0.000 |
| | Error | 0.026 | 6 | 0.004 | | |
| | Total dispersion square sum | 6.140 | 11 | | | |
| Dry pick velocity | Factor C | 0.018 | 5 | 0.004 | 71.067 | 0.000 |
| | Error | 0.000 | 6 | 0.000 | | |
| | Total dispersion square sum | 0.018 | 11 | | | |
| Whiteness | Factor C | 3.032 | 5 | 0.606 | 77.574 | 0.000 |
| | Error | 0.047 | 6 | 0.008 | | |
| | Total dispersion square sum | 3.079 | 11 | | | |

**Table 8.** Analysis of Variance (ANOVA) of AZC

| | | Sum of squares | Df | Mean square | F | Significance |
|---|---|---|---|---|---|---|
| Gloss | Factor D | 4.461 | 5 | 0.892 | 2433.000 | 0.000 |
| | Error | 0.002 | 6 | 0.000 | | |
| | Total dispersion square sum | 4.463 | 11 | | | |
| Smoothness | Factor D | 43788.000 | 5 | 8757.600 | 17515.200 | 0.000 |
| | Error | 3.000 | 6 | 0.500 | | |
| | Total dispersion square sum | 43791.000 | 11 | | | |
| K&N ink absorption | Factor D | 1.172 | 5 | 0.234 | 1172.267 | 0.000 |
| | Error | 0.001 | 6 | 0.000 | | |
| | Total dispersion square sum | 1.173 | 11 | | | |
| Dry pick velocity | Factor D | 0.058 | 5 | 0.012 | 116.733 | 0.000 |
| | Error | 0.001 | 6 | 0.000 | | |
| | Total dispersion square sum | 0.059 | 11 | | | |
| Whiteness | Factor D | 1.236 | 5 | 0.247 | 593.088 | 0.000 |
| | Error | 0.003 | 6 | 0.000 | | |
| | Total dispersion square sum | 1.238 | 11 | | | |

## Characterization of the Starch and Paper Coating Surface

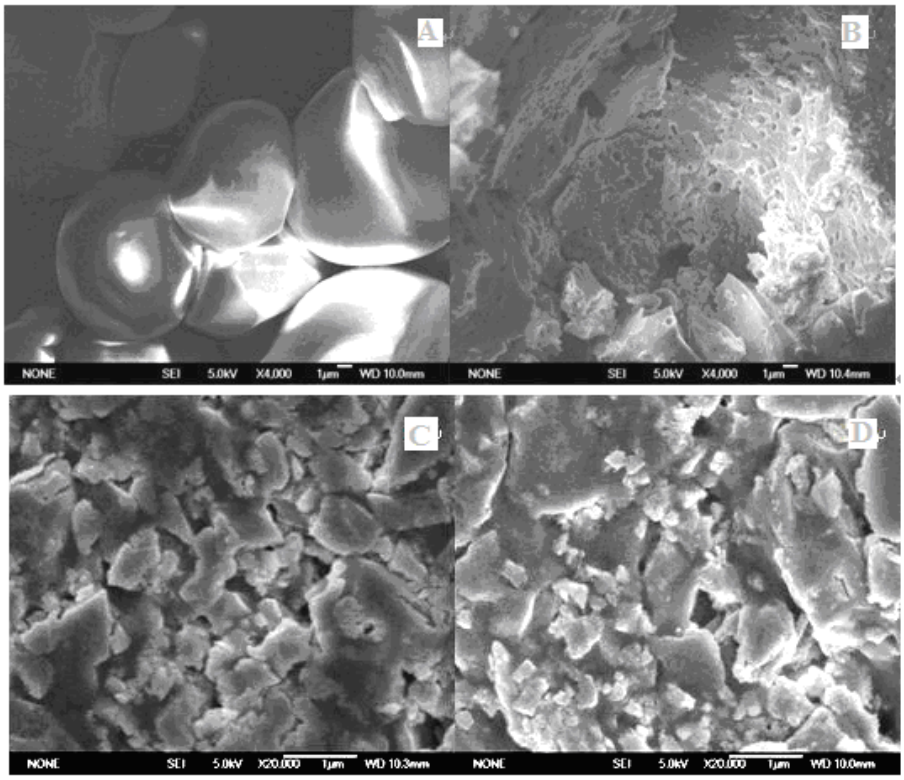


**Fig. 3.** SEM graphs of starch and paper surface: A and B are the SEM graph of cassava starch and crosslinked cassava starch, respectively; C and D are the SEM graph of the coated paper surface with the complex adhesive and SBR latex adhesive, respectively.

Figure 3 (A and B) shows the SEM micrographs of untreated cassava starch and crosslinking cassava starch. Cassava starch has spherical granules with a spherical surface and a central concave multi-trapezium undersurface. However, the crosslinking cassava starch completely lost its granular structure and formed a porous structure, probably because enzymatic hydrolysis had cleaved the starch molecular chains, while gelatinization had caused the starch chains to be fully extended, which was helpful to a crosslinking reaction between starch and AZC. The addition of the crosslinker gave the starch dimensional and porous structure.

The irregular particles in the SEM graphs of the coated paper (Fig. 3C and D) were pigment particles. The distribution of pigments on the coating layer was uniform. There were a large number of small particles in the paper coated with SBR latex that enhanced light scattering and reduced whiteness. The distribution of pigments in the case of the 20% starch adhesive was more uniform, and the paper showed a smoother surface as a result.

The FTIR spectra of cassava starch and crosslinking starch obtained in this work are shown in Fig. 4. The figure shows that the absorption peaks for each component were basically the same, indicating that there was no new group brought in after crosslinking. However, the strengths of the peaks appearing at 3393 $cm^{-1}$ in the spectra corresponding to the -OH stretching vibration absorption, intramolecular hydrogen bond absorption at

1639 $cm^{-1}$, -$CH_2OH$ stretching vibration absorption at 1242 $cm^{-1}$, and C-O bending vibration of primary alcohol at 1024 $cm^{-1}$ had changed greatly.

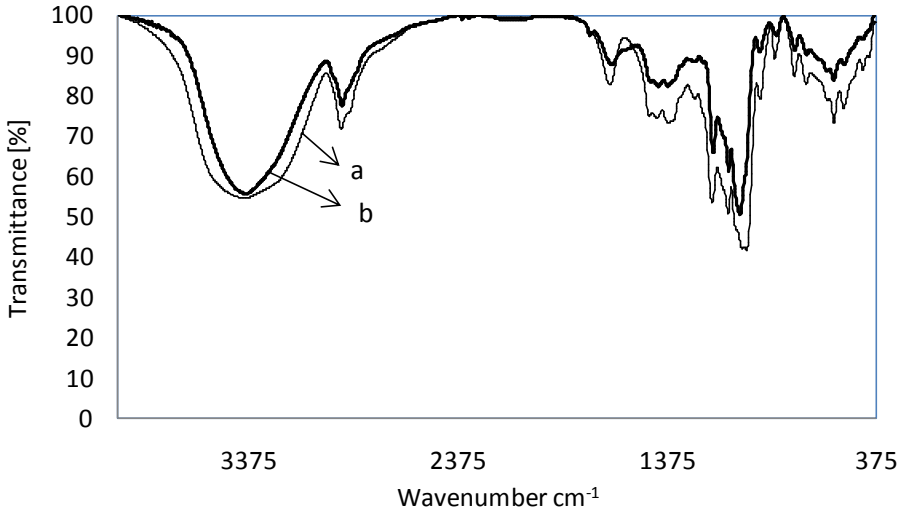


**Fig. 4.** IR spectrums of (a) cassava starch and (b) crosslinking cassava starch

Fig. 5 shows a narrow size distribution, and the average particle size of the crosslinking starch adhesive was 528.6 nm in normal distribution.

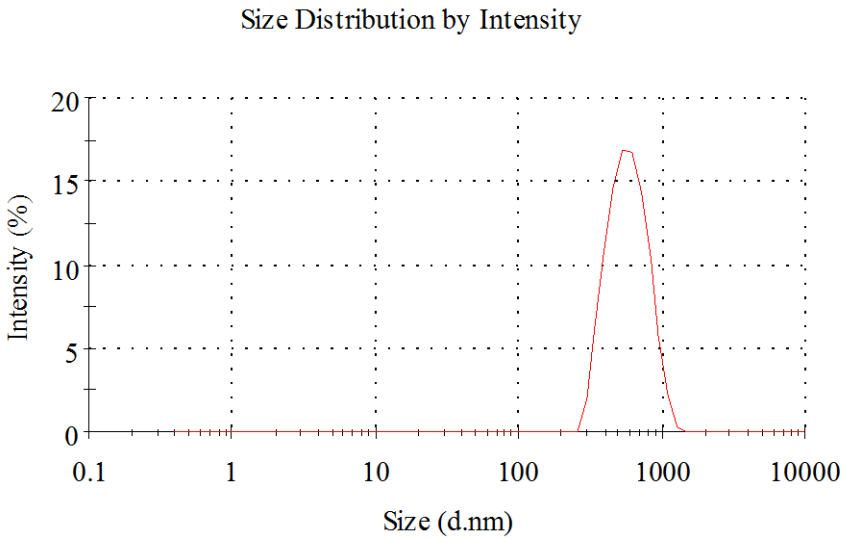


**Fig. 5.** Particle size distribution of crosslinking starch adhesive

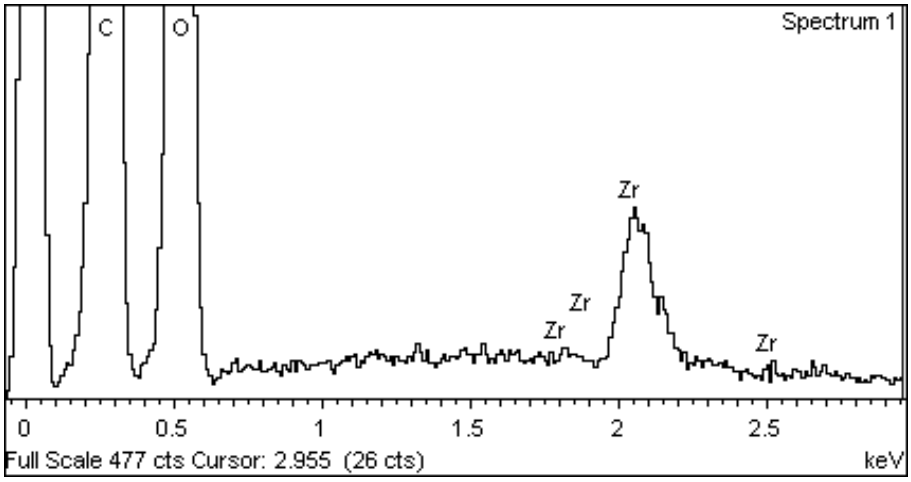


**Fig. 6.** The Energy Diffraction Spectrum of crosslinking cassava starch

A JSM-6700F EDS image (Fig. 6) shows the content of each element. As shown, the element Zr was present in the crosslinked starch, which is consistent with a crosslinking reaction between AZC and starch.

## CONCLUSIONS

1. The prepared crosslinking cassava starch adhesive showed great binding effect when the starch slurry concentration was 50% (w/w), the dosages of glycerol and α-amylase were 15% and 0.075%, respectively, and the enzymolysis starch was crosslinked with 12% AZC at 50 $^{o}$C. The average particle size was 528.6 nm.
2. When it was substituted for 20% of the SBR latex, the complex adhesive showed an excellent adhesive effect. The paper surface under this condition showed superior gloss, smoothness, whiteness, and dry pick velocity.
3. Statistical analysis of the data indicated that the crosslinking temperature and AZC had very important effects on paper performance, whereas glycerin and α-amylase had little effect on performance. An EDS spectrum of the product revealed the presence of Zr in the coating, which is consistent with its role in a crosslinking reaction between AZC and cassava starch. SEM images of the surface of the coated paper showed features that were consistent with a reasonable explanation of its surface properties.

## ACKNOWLEDGMENTS

The project was supported by an open fund of the Key Laboratory of Pulp and Paper Science & Technology of Ministry of Education of China (Grant No. KF2011004) and a Special fund for the Doctoral innovation program of Shandong Province (Grant No. 201203014).

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Article submitted: February 7, 2013; Peer review completed: April 3, 2013; Revised version accepted: May 14, 2013; Published: May 20, 2013.