

## Effects of Crosslinking Degree on the Coating Properties of Arabinoxylan

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Arabinoxylan (AX) was extracted from sugarcane bagasse and modified through crosslinking with glutaraldehyde (GA). The effects of crosslinking degree on the rheological and coating properties of glutaraldehyde crosslinked arabinoxylan (GAX) were investigated. To better evaluate the degree of crosslinking, the crosslink index was used to represent the degree of crosslinking for the GAX in this study. The viscosity of the GAX solution increased when the degree of crosslinking increased, and the solution demonstrated non-Newtonian flow behavior. A high degree of crosslinking was detrimental to the film and coating properties of the GAX. At an optimum degree of crosslinking, the tensile strength of the GAX films increased by approximately 170% and 60% compared with that of the AX and GAX with the highest degree of crosslinking, respectively; the tensile strength of the GAX-coated paper increased by approximately 15% compared with that of the GAX with the highest degree of crosslinking. When calcium carbonate was mixed with the paper coating adhesives, the GAX showed comparable coating properties to that of polyvinyl alcohol, demonstrating its potential to substitute petroleum-based paper coating adhesives.

*Keywords:* Arabinoxylan; Degree of crosslinking; Glutaraldehyde; Film; Paper coating

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### INTRODUCTION

To expand the applications of paper, coatings are usually applied to improve paper surface properties, such as glossiness, smoothness, printability, and water resistance (Barhoum *et al.* 2014; Anthony *et al.* 2015; Xiang and Runge 2016; Xiang *et al.* 2016). Traditional coating formulations consist of pigments and adhesives. Some commonly used pigments include calcium carbonate, titanium dioxide, silicon dioxide, and talc (Laudone *et al.* 2006; Barhoum *et al.* 2014). These are inorganic materials and they need adhesives to bind them together and onto the paper surface (Laudone *et al.* 2006; Aulin and Lindström 2011). Polyvinyl alcohol (PVOH) is one of the most widely used adhesives in paper coating. PVA is a non-toxic and water-soluble polymer with a good film formation ability and high strength, which has potential in packaging and coating applications (Ren *et al.* 2015). However, PVOH mostly comes from petroleum resources and thus raise problems for sustainability and the environment (Fardim 2002; Aulin and Lindström 2011). Therefore, there is an increasing interest in finding sustainable polymers for paper coating applications.

Bio-polymers have drawn increasing attention in recent years because of its non-toxicity, low-cost, abundance, and sustainability (Vieira *et al.* 2011; Xiang and Runge 2016). The food application of bio-polymers has been investigated for over a century, and applications of bio-polymers as films and coatings in paper have recently received increased interest (Aulin and Lindström 2011; Barhoum *et al.* 2014; Anthony *et al.* 2015). The bio-polymers that are widely used for films and coatings can be divided into three major categories: polysaccharides, proteins, and lipids (Aulin and Lindström 2011). Polysaccharides are widely used in films and coatings because of their natural abundance and sustainability (Aulin and Lindström 2011; Vieira *et al.* 2011). Major polysaccharides include cellulose, hemicellulose, starch, and chitosan (Vieira *et al.* 2011). Cellulose, starch, chitosan, and their derivatives have been widely studied and used in the film and coating industries (Mikkonen *et al.* 2009; Xiang and Runge 2016). However, unlike cellulose and starch, hemicellulose, which is widely distributed in plant biomass, is still utilized at a low level. A large amount of waste hemicellulose produced from pulping or other bio-refinery industries is used as low-value fuels or animal feed (Xing *et al.* 2011; Xiang *et al.* 2014; Xiang and Runge 2016). Achieving a high-value conversion of hemicellulose has gained interest in recent years.

Hemicelluloses are complex branched hetero-polysaccharides that consist of different sugar units and uronic acids (Mikkonen *et al.* 2009; Egüés *et al.* 2013). Their structures depend on the plant species and extraction conditions. Arabinoxylan (AX) is the dominant type of hemicellulose found in annual plants and agro-industrial residues (Egüés *et al.* 2013). The structure of AX is based on a linear backbone that consists of  $\beta$ -1,4-linked D-xylopyranose, and branches that contain acetyl, arabinosyl, and glucuronosyl residues (Mikkonen *et al.* 2009). Arabinoxylan consists of many hydroxyl groups, which can form strong hydrogen bonds that lead to a good film-formation ability (Egüés *et al.* 2013; Zhong *et al.* 2013). However, films made from AX demonstrate limitations in material applications because of its brittleness, low mechanical properties, and hygroscopic properties (Goksu *et al.* 2007; Escalante *et al.* 2012). Therefore, chemical modification is necessary to enhance the material application range of AX (Kayserilioğlu *et al.* 2003; Escalante *et al.* 2012). The esterification of hemicellulose can be achieved in homogeneous or heterogeneous solutions (Sun *et al.* 1999, 2002, 2003). Carboxymethyl hemicellulose can be synthesized by reaction with sodium chloroacetate in a slurry media (Petzold *et al.* 2006). Etherification of hemicellulose can be achieved in an alkaline solution by reaction with propylene oxide (Jain *et al.* 2000; Laine *et al.* 2013). However, these modifications are still not able to tackle all of the disadvantages that arise when utilizing hemicelluloses (Gröndahl *et al.* 2003; Hansen and Plackett 2008). Consequently, hemicelluloses can be used as coating or coating binder materials, which could minimize its material disadvantages, such as brittleness and low strength (Xiang *et al.* 2014; Anthony *et al.* 2015).

Crosslinking may be a modification method that can help better utilize hemicellulose as a paper coating binder material because a network structure can bind the coating surface and inorganic pigments. Furthermore, the molecular mass of hemicellulose is lower, so some improvements might be needed for the formation of a strong film. Crosslinking is an effective method that can effectively increase the molecular mass of hemicellulose. Glutaraldehyde (GA) is a dialdehyde compound that is widely used as a crosslinking agent in the modification of starch (El-Tahlawy *et al.* 2007), protein (Matsuda *et al.* 1999), guar gum (Sandolo *et al.* 2009), and chitosan (Monteiro Jr. and Airoidi 1999). The previous study by the authors showed that crosslinking hemicelluloses with GA

produced a paper coating binder that had a comparable performance to that of PVOH (Xiang *et al.* 2016). In this previous work, the effects of the amount of GA on the film properties and the effects of the degree of substitution (DS) on the coating properties were investigated (Xiang *et al.* 2016). The AX that had been crosslinked at a low DS with GA showed better coating properties compared with that of GA crosslinked with AX at a high DS. However, the viscosity of the low DS AX solution/suspension was higher than that of the high DS AX solution/suspension (Xiang *et al.* 2016). High viscous coatings are difficult to disperse evenly, and the addition of more solvent may result in wasting solvent. It also requires more time and energy to dry the coatings. Therefore, it is essential and useful to reduce the viscosity of crosslinked AX and still maintain its enhanced coating properties.

Two different types of crosslinking can take place during polymer crosslinking (Gebben *et al.* 1985). One type is intermolecular crosslinking, which leads to an increase in the viscosity because of the increase in the radius of gyration (Cherian *et al.* 2007; Foster *et al.* 2009). The other one is crosslinking within a single molecule, called intramolecular crosslinking, which leads to a decrease in the viscosity because of the volume contraction of the polymer coils (Fordyce and Ferry 1951). At high monomer concentration (>0.1%), intermolecular crosslinking is dominant (Fordyce and Ferry 1951; Tuteja *et al.* 2010). To induce intramolecular crosslinking, the use of ultra-dilute solutions with concentrations as low as 0.1% has been proposed (Fordyce and Ferry 1951). Therefore, it is feasible to reduce the viscosities of a crosslinked AX solution/suspension by reacting it in a dilute solution. However, even in a diluted solution intermolecular crosslinking is still evident (Wang *et al.* 2011). Furthermore, if the reaction is completed in a dilute solution, the production efficiency is low. In order to overcome these difficulties, a continuous dropwise addition strategy was proposed (Harth *et al.* 2002). Consequently, crosslinking with a continuous method has been developed (Harth *et al.* 2002).

In this work, the possibility of obtaining low-viscosity GA-modified AX (GAX) that still maintains its enhanced coating properties was investigated. The AX concentration and amount of GA were the two variables used to control the degree of crosslinking. During crosslinking, under acidic condition or high concentration, GA may polymerize with itself through forming hemihydrate multimers or an aldol condensation reaction forming  $\alpha,\beta$ -unsaturated aldehydes (Walt and Agayn 1994; Matsuda *et al.* 1999; Monteiro Jr. and Airoidi 1999). Therefore, it is not explicit enough to express the degree of crosslinking using the DS. As such, the crosslink index (CI) represented the degree of crosslinking for the GAX. The viscosity of the GAX was controlled or reduced by varying the degree of intermolecular crosslinking or even possibly inducing intramolecular crosslinking. The AX solution was added dropwise to the dilute GA solution to control the degree of crosslinking. The effects of crosslinking degree on the film and coating properties of the GAX were also investigated.

## EXPERIMENTAL

### Materials

Sugarcane bagasse was obtained from Guangxi Laibin Donta Paper Co., Ltd (Nanning, China). Sodium hydroxide, ethanol, and hydrogen peroxide were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ethylenediamine-tetraacetic acid disodium salt dihydrate (EDTA), GA (50% in water), acetic acid, calcium carbonate, sodium hydroxide, hydroxylamine hydrochloride, and polyvinyl alcohol

(PVOH) ( $M_w=27000$ ) were purchased from Shanghai Macklin Biochemical Co. Ltd. (Shanghai, China). Hydrochloric acid was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China).

Arabinoxylan was extracted from sugarcane bagasse using an alkaline peroxide solution. Briefly, sugarcane bagasse was pre-extracted with 95% ethanol for 16 h in a Soxhlet extractor to remove any waxy compounds. Prior to extraction, the sugarcane bagasse was washed with 0.2% (w/v) EDTA for 1 h at 90 °C to remove metal cations, as these ions promote decomposition of hydrogen peroxide and reduce its delignification performance. The sugarcane bagasse was then reacted in a 2% (w/v) NaOH solution with 4% (w/v) H<sub>2</sub>O<sub>2</sub> at 50 °C and a 1:10 solid to liquid ratio (w/v) for 3 h. Then, the pH of the alkali-soluble part was adjusted to 5.5 and slowly poured into three volumes of 95% ethanol before being stirred. The precipitated solid was then washed with 70% ethanol several times before being freeze-dried.

The extracted AX was in a brown powder form and consisted of 85.1% xylose, 7.0% arabinose, 4.6% glucose, 0.32% galactose, 1.14% glucuronic acid, and 0.72% galacturonic acid (relative % dry weight of hemicelluloses, w/w).

## Methods

### *Crosslinking of arabinoxylan*

Arabinoxylan was dissolved in deionized water to make a 10% (w/v) solution. Different amounts of GA (GA/AXU mole ratios = 0.1, 0.3, 0.5, and 1.0) were then dissolved in deionized water. The AX mono sugar unit has a molar mass of 132 g/mol and was referred to as AXU. Afterward, the pH of the GA solution was adjusted to 3.0 by acetic acid. Then, the GA solution was diluted to a certain concentration to reach final AX concentrations of 0.1%, 0.25%, 0.5%, and 1.0%. The AX solution was added to the GA solution dropwise (1 mL/3 min) for 150 min at 25 °C. After the reaction, the pH was adjusted to 6.0 with a 1% NaOH solution. The modified AX was precipitated by pouring the mixture into three volumes of 95% (v/v) ethanol and washed three times with 70% (v/v) ethanol. Three samples were made for each modification.

### *Film preparation*

All of the films were prepared by a casting method. Glutaraldehyde-modified AX (0.48 g) and PVA (0.12 g) were dissolved in deionized water and stirred at 300 rpm for 40 min at 80 °C to make a 7.5% (w/v) suspension. Then, the solution was poured onto a polytetrafluoroethylene dish (60 mm × 45 mm) and allowed to dry at 23 °C and a relative humidity of 50%. The film thickness was measured by a micrometer (precision = 1 μm). Measurements were taken at 10 different locations on each film, and the mean values were used in the calculations to determine the mechanical test measurement. The thickness of the films was approximately 0.17 mm.

### *Paper coated by modified arabinoxylan*

For paper coated with only AX or GAX, 20% (w/w) coating suspensions were prepared with a pH of approximately 3. When GAX or AX were used as paper coating adhesives, 40% (w/w) coating suspensions were prepared, which contained 10% (w/w) GAX or AX and 90% (w/w) calcium carbonate. The same amount of PVA was also added to calcium carbonate as a control.

Prior to coating, printing paper (70 mm × 210 mm) was dried in a drying oven at 105 °C for 8 h and kept in a desiccator for 24 h. The paper was coated with a manual

coating machine to control the coating weight, which was approximately 6 g/m<sup>2</sup>. The coated paper was dried at 170 °C for 5 min, and further dried at 105 °C for 60 min. The coated paper was kept in a desiccator for 24 h. After that, the weight of the paper samples was measured to determine the weight of the coating. Two sheets of coated paper were prepared for each modification.

#### *Characterization of the crosslinked arabinoxylan*

The DS of the modified AX was the moles of the GA reacted per mole of AXU. The free aldehyde content of the modified AX samples was determined by following the method using hydroxylamine hydrochloride (Yu *et al.* 2010) with some modifications. 0.15 g sample was added in 25 mL hydroxylamine hydrochloride solution (0.25 M). The pH was adjusted to 5.0 by using NaOH solution (0.1 M). The conversion of aldehydes into oximes continues at 50 °C for 2 h. The mixture was then titrated back to pH 5.0 using 0.1 M NaOH. The aldehyde content was calculated with Eq. 1,

$$\text{CHO (\%)} = 0.1 \times (V_{\text{sample}} - V_{\text{blank}}) / m \quad (1)$$

where  $V_{\text{sample}}$  and  $V_{\text{blank}}$  represent the consumption of NaOH by the sample and the blank, 0.1 is the molar concentration of NaOH solution, and  $m$  is the weight of the sample.

The aldehyde content in the GAX filtrate was also measured to determine the unreacted GA content. The reacted GA was calculated by subtracting the amount of unreacted GA from the amount of GA added, and then the DS values of the GAX samples were determined. The samples were labelled as GAX<sub>N</sub>, where N is the CI.

The Fourier transform infrared (FT-IR) spectroscopy analysis was performed in an absorbance range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> using a Bruker TENSOR27 FT-IR spectrometer (Karlsruhe, Germany).

The suspension viscosities of the AX and GAX were measured with a rotary viscometer (DV-II HE, Brookfield, USA). The viscosity of the 20% (w/w) AX and GAX suspension was measured at different rotational speeds.

#### *Characterization of the crosslinked arabinoxylan films and coatings*

Films from each modification were cut into five rectangular specimens with a 40-mm length and 10-mm width. The tensile strength of the specimens was measured using a tensile strength machine (Universal Testing Machine 5565, Instron, Canton, USA) at 23 °C and a 50% relative humidity. The initial length of the grips was 25 mm and the testing speed was 5 mm/min with a preload of 0.5 N.

The contact angle of the films was measured with an OCA40 contact angle system apparatus (Dataphysics, Filderstadt, Germany). Five measurements were conducted randomly on the tested surface.

Each coated paper was cut into six specimens with a 120-mm length and 15-mm width. The dried tensile strength was measured with a tensile strength machine (L&WCE062, L&W, Kista, Sweden). The wet tensile strength was measured after soaking the middle of the coated paper in water for 6 s. The brightness, whiteness, and opacity of the coated paper was measured with a whiteness tester (Color Touch PC CTP-ISO, Technidyne, New Albany, IN, USA).

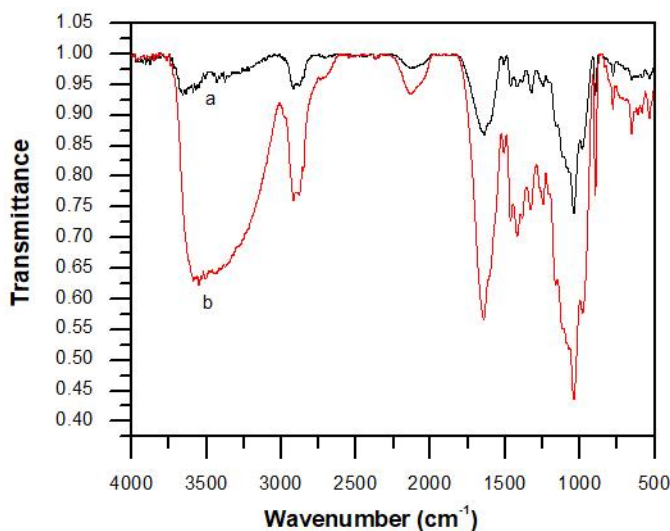
Scanning electron microscopy (SEM) (EVO-18, Zeiss, Oberkochen, Germany) was used to investigate the surface structure of the film and coated paper.

## RESULTS AND DISCUSSION

### Characterization of the Crosslinked Arabinoxylan

Glutaraldehyde forms crosslinks between AX by reacting its aldehyde groups with the hydroxyl groups of the AX. Aldehyde can react with hydroxyl groups under acidic conditions to form acetals or hemiacetals. Glutaraldehyde crosslinking may lead to several possible results (Matsuda *et al.* 1999; Monteiro Jr. and Airoidi 1999). The GA is a dialdehyde compound, so during the process of crosslinking, the aldehyde groups of GA can have one aldehyde group react with the AX hydroxyl groups or have both aldehydes react with hydroxyl groups (Xiang *et al.* 2016). Under an acidic condition or high GA concentration, GA molecules may also polymerize with themselves through aldol condensation to form unsaturated aldehydes (Walt and Agayn 1994; Matsuda *et al.* 1999; Monteiro Jr. and Airoidi 1999).

The FT-IR spectra of the AX and GAX were quantitatively analyzed (Fig. 1). The FT-IR spectra of the AX and GAX showed a strong peak at  $1720\text{ cm}^{-1}$  that corresponded to C=O in the free aldehyde groups. Such groups likely resulted from the reaction of uncrosslinked GA at only one end with AX. The strong peak at  $1520\text{ cm}^{-1}$  was ascribed to C=C in the unsaturated aldehyde from the GA polymerizing with itself. The peak at  $1258\text{ cm}^{-1}$  was evidence of C-O in the acetals (Tipson *et al.* 1959; Kast and Funke 1979).



**Fig. 1.** FT-IR spectra for the GAX films: (a) AX and (b) GAX

After modification, the DS of the GAX samples increased from 0.012 to 0.35 (Table 1). At the same AX concentration (0.25%), the DS increased from 0.023 to 0.35 when the GA/AXU ratio increased from 0.1 to 1.0. Furthermore, at the same GA/AXU ratio (0.3), the DS increased from 0.043 to 0.260 when the AX concentration increased from 0.1% to 1.0%. These results indicated that the reaction activity between the AX and GA was affected by both the AX concentration and GA/AXU ratio. This was explained by the fact that both the AX concentration and GA/AXU molar ratio can facilitate collision between the GA and AX molecules, which would promote reaction between the two.

The number-average molecular weights ( $M_n$ ) of the GAX are shown in Table 1. After crosslinking, the molecular weight of the AX increased by up to 180%, which was because of the larger molecules and increase in the radius of gyration. With the same

crosslinking agents and substrates, larger molecular weights should lead to higher degrees of crosslinking (Aharoni 1977).

**Table 1.** Properties of the GAX

Sample	Label	Concentration (%)	GA/AXU Ratio	DS	$M_n$	CI
1	GAX1.79	0.1	0.3	0.043	15698	1.79
2	GAX0.98	0.25	0.3	0.095	8565	0.98
3	GAX1.34	0.5	0.3	0.180	11751	1.34
4	GAX1.64	1.0	0.3	0.260	14356	1.64
5	GAX1.25	0.25	0.1	0.023	10949	1.25
6	GAX1.33	0.25	0.5	0.141	11614	1.33
7	GAX1.19	0.25	1.0	0.350	10443	1.19
8	GAX1.51	0.1	0.1	0.012	13256	1.51
AX	AX	-	-	-	8754	-

To better evaluate the degree of crosslinking, the CI was used to represent the degree of crosslinking for the GAX. The CI was calculated with Eq. 2,

$$CI = M_{n0} / M_n \quad (2)$$

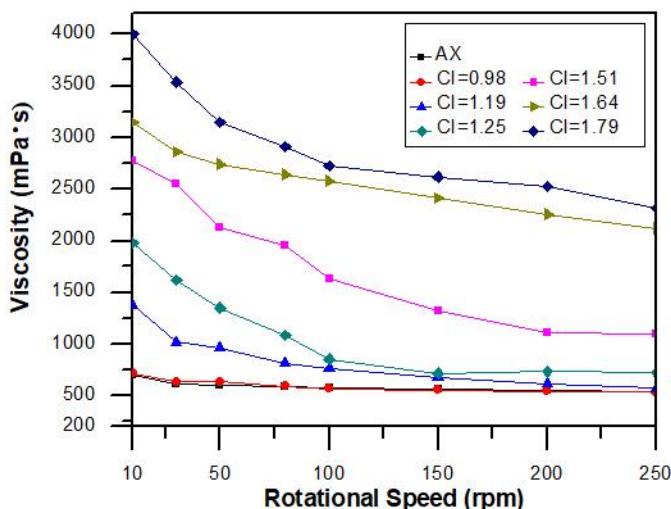
where  $CI$  is the crosslink index, and  $M_{n0}$  and  $M_n$  are the number-average molecular weights of the GAX and AX, respectively.

The CI is usually greater than 1. When CI is less than 1, it possibly suggests that intramolecular crosslinking is dominant because intramolecular crosslinking reduces the radius of gyration (Fordyce and Ferry 1951).

As the amount of molecules changed after crosslinking, the degree of crosslinking could be speculated from the changes in the CI. The CI values of the GAX are given in Table 1. The CI ranged from 0.98 to 1.79 when the AX concentration ranged from 0.1% to 1% at a GA/AXU ratio of 0.3. The CI had a minimum value of 0.98 when the AX concentration was 0.25%. At the same AX concentration (0.25%), the CI changed from 0.98 to 1.33 when the GA/AXU molar ratio increased from 0.1 to 1.0. The minimum CI value was found at a GA/AXU molar ratio of 0.3. The AX concentration and GA/AXU ratios were the two variables that affected the degree of crosslinking. Previous studies have found that intramolecular crosslinking occurred preferentially in dilute polymer solutions (Fordyce and Ferry 1951). When intramolecular crosslinking was the dominate-type of crosslinking, crosslinking mainly occurred in one molecule, which led to the coiling and aggregation of the other molecule. This led to a decrease in the radius of gyration. The decrease in the radius of gyration represented the decrease in the molecular weights. Consequently, the degree of intramolecular crosslinking also contributed to the variation in the CI for the other GAX samples.

The viscosity of the AX and GAX suspensions were also affected by the degree of crosslinking as the radius of gyration changed. The dynamic viscosity of the AX and GAX coating suspensions of 20% (w/w) are shown in Fig. 2. The AX suspension showed Newtonian fluid properties, in that its viscosity remained almost constant (~700 mPa·s) when the rotational speed was increased. The GAX suspension at a lower CI (CI = 0.98) also showed Newtonian fluid properties. However, when the CI was greater than 1, the GAX suspensions behaved similarly to non-Newtonian fluids, in that their viscosities decreased when the rotational speed increased. The reason for this was that the GAX molecules with a high CI were highly entangled and thus had more chances to induce Van

der Waals forces and hydrogen bonds. The Van der Waals forces and hydrogen bonds were easily destroyed at high shear forces. The GAX samples with a high CI had a higher dynamic viscosity than that of GAX samples with a low CI, which indicated that the degree of crosslinking can also be indicated by the viscosity. The dynamic viscosity of the GAX suspension at different rotational speeds was similar to the dynamic viscosity of the AX suspension because the CI was close to 1 (CI = 0.98). This was explained by the fact that intramolecular crosslinking might have occurred to a low degree and did not affect the viscosity remarkably.



**Fig. 2.** Dynamic viscosity of the AX and GAX solutions at different rotational speeds and 20% concentration

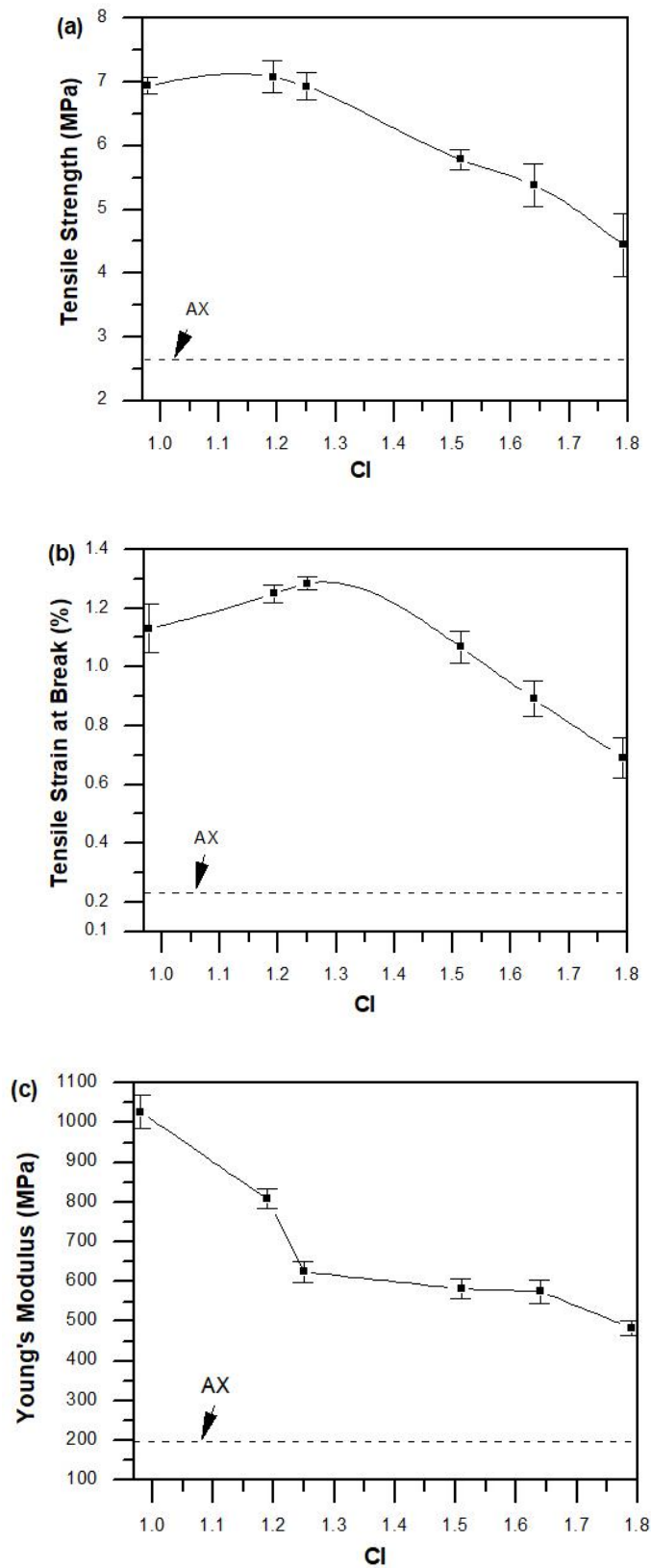
### Film Properties of the Crosslinked Arabinosylan

Evaluation of the GAX film properties is important to investigate and optimize its coating properties. The tensile strength, tensile strain at break, and Young's modulus are presented in Fig. 3. The AX films had a tensile strength of 2.69 MPa, tensile strain at break of 0.24%, and Young's modulus of 198.2 MPa. After GA crosslinking, the mechanical properties of the AX films improved remarkably (Fig. 3). The tensile strength increased from 4.5 MPa to 7 MPa, the tensile strain at break increased from 0.7% to 1.3%, and the Young's modulus increased from 500 MPa to 1000 MPa. These results indicated that GA crosslinking on the AX had a positive impact on the mechanical properties.

The CI represented the degree of crosslinking. With an increasing CI, the tensile strength and tensile strain at break of the GAX films first increased to approximately 7.1 MPa and 1.3%, and then decreased to approximately 4.5 MPa and 0.7% at a CI of 1.79, respectively. Additionally, with an increasing CI, the Young's modulus of the GAX films decreased from approximately 1000 MPa at a CI of 0.98 to approximately 500 MPa at a CI of 1.79.

The effects of different CI values on the mechanical properties of the GAX films indicated that after crosslinking, the film mechanical properties improved. However, a high degree of crosslinking did not necessarily result in a high mechanical property. The maximum value of the tensile strength and tensile strain at break appeared at a medium CI value, while the maximum Young's modulus appeared at the lowest CI in this study.





**Fig. 3.** (a) Tensile strength, (b) tensile strain at break, and (c) Young's modulus with standard error bars of the GAX films at different CI values

The changes in the Young's modulus indicated that, with an increasing degree of crosslinking, the stiffness of the GAX films increased, which was explained by the highly entangled reticular structure that formed after covalent bond crosslinking. These results suggested that GAX films at low and medium CI values had better mechanical properties than the GAX films at a high CI. Furthermore, the GAX at low and medium CI values had a relatively low viscosity compared with that of the GAX at a high CI (Fig. 2), which was more suitable for coatings and films.

The contact angles of the AX and GAX film surfaces are presented in Fig. 4. The contact angle of the AX films was approximately 50°, while the contact angles of the GAX films were higher (~75°). Previous studies have shown that the unmodified AX film from other sources (e.g. bamboo and corncob) had low contact angles of 31.0° (bamboo) and 59° (corncob) (Egüés *et al.* 2013; Zhong *et al.* 2014). The low contact angles of AX films indicated a high hydrophilicity of AX chains. The contact angles of the GAX films at lower CI values were still relatively higher than that at a high CI.

The changes in the contact angles of the GAX films at high CI values was explained by the higher levels of intermolecular crosslinking at high CI values making the hydroxyl groups more exposed, which facilitated the interaction between the GAX molecules and water. Furthermore, at high levels of crosslinking, some free GA oligomers might have been wrapped in polymer chains (Xiang *et al.* 2016). When water was on the surface of the GAX films, these oligomers could be dissolved in water (Xiang *et al.* 2016). At low CI values, intramolecular crosslinking took place, which led to molecular chains coiling and the hydroxy groups becoming less exposed. Consequently, it became more difficult for water to contact with hydroxyl groups, which resulted in a higher contact angle.

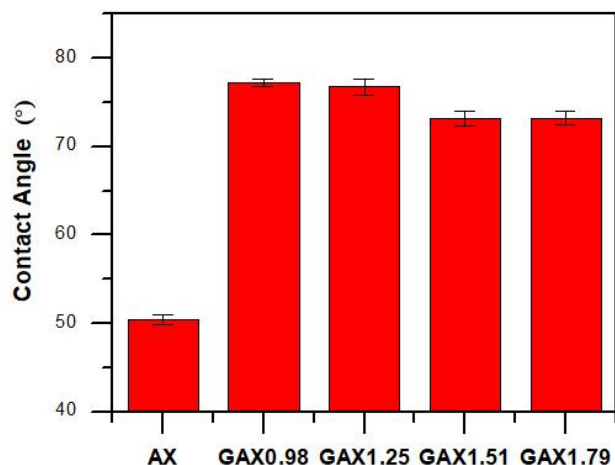


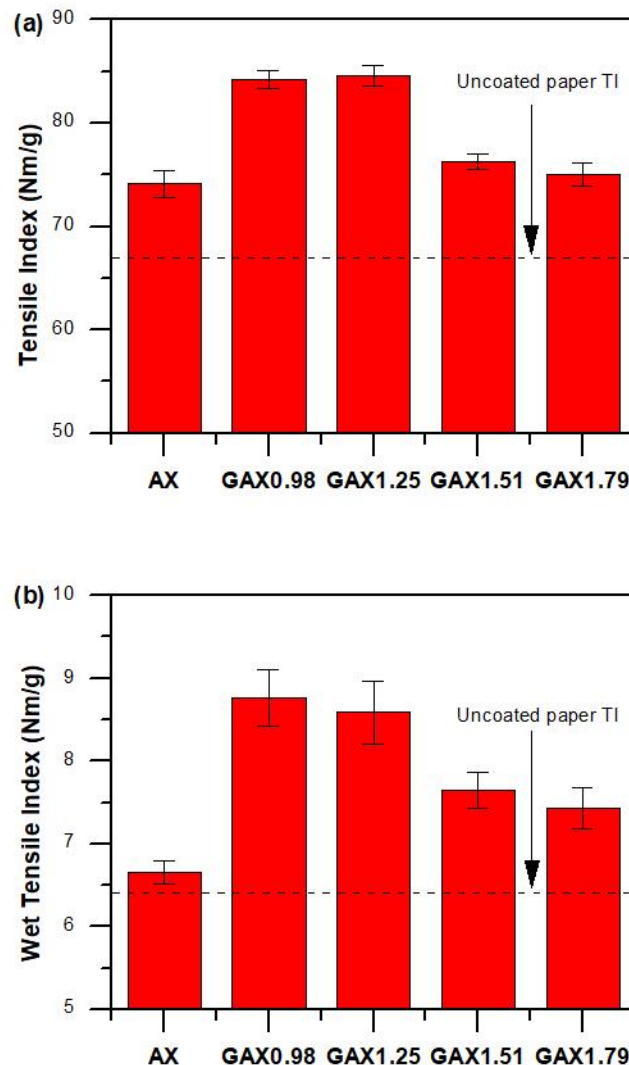
Fig. 4. Contact angles of the AX and GAX films

In summary, to obtain suitable films with good mechanical properties and a good hydrophobicity, AX crosslinking should be kept at a low degree, while a relatively low viscosity can still be maintained.

### Coating Properties of the Crosslinked Arabinosylan

As was previously discussed, paper coatings are a mixture of coating pigment and adhesives (Barhoum *et al.* 2014). However, to investigate the potential of GAX as an adhesive, it was necessary to investigate its properties without pigments.

Both the dry and wet tensile index (TI) of the coated paper are presented in Fig. 5. These results indicated that the AX- and GAX-coated papers had a higher dry TI than the uncoated paper (Fig. 5a). This result suggested that all of the AX and GAX samples had interactions with the paper fibers. The AX-coated paper had a dry TI of approximately 74 Nm/g and a wet TI of 6.6 Nm/g. All of the GAX-coated papers had higher dry and wet TI values than that of the AX-coated paper. Among them, the GAX with low CI values of 0.98 and 1.25 had the highest dry and wet TI values of approximately 85 Nm/g and 8.5 Nm/g, respectively.

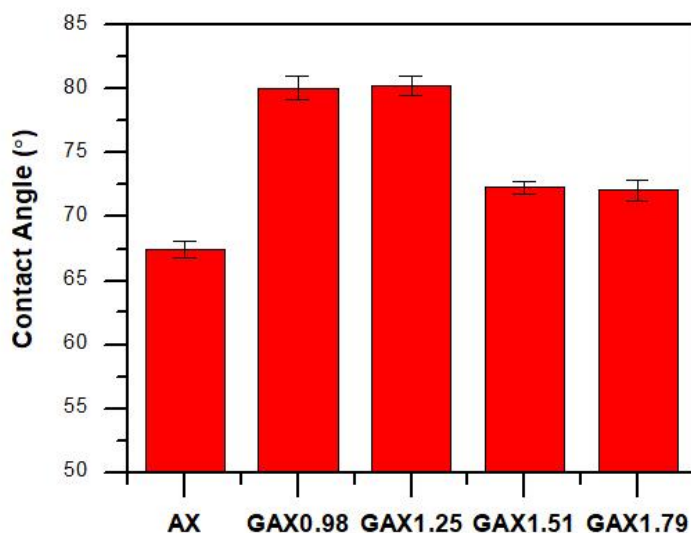


**Fig. 5** (a) Dry TI and (b) wet TI for the paper coated with AX and GAX

It was speculated from these results that the GAX coatings might have some covalent bonding or hydrogen bonding connections with the paper fibers that contributed to the high dry and wet TI values. Furthermore, the unreacted aldehyde groups in the GAX can also react with the paper fibers to form acetals and/or hemiacetals at a pH of 3.0 (Xiang *et al.* 2016), which results in a highly entangled matrix between the coating and fibers. At a low CI, the corresponding high TI was explained by the low degree of crosslinking

resulting in more free hydroxyl and aldehyde groups, which had more chances to further interact or crosslink with the plant fibers.

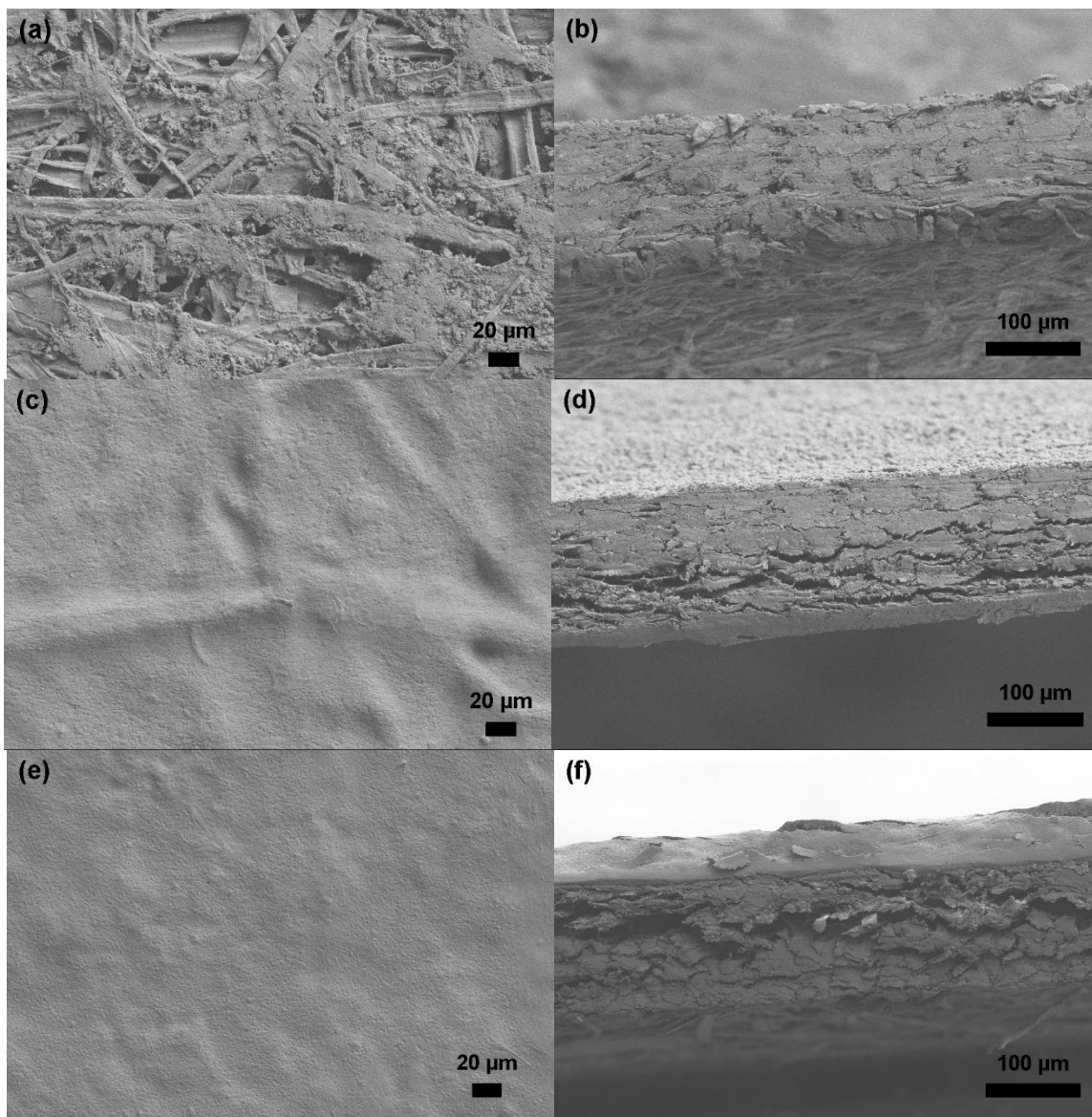
The contact angles of the AX- and GAX-coated papers are presented in Fig. 6. These contact angles increased compared with the corresponding contact angles of the AX and GAX films (Fig. 4). This further showed that the AX and GAX coatings had interactions with the plant fibers, including hydrogen bonds and acetals/hemiacetals, which decreased the amounts of hydrophilic hydroxyl groups on the paper and coating surface. The papers coated with the GAX with low CI values of 0.98 and 1.25 had the highest contact angle of approximately 80°, which was because of the high hydrophobicity of its corresponding films. A high hydrophobicity can prevent the ink from spreading too fast over the coated paper, which could improve the paper printing properties.



**Fig. 6.** Contact angles of the AX- and GAX-coated paper

The coating structure on the coated paper was investigated with SEM (Fig. 7). The SEM images showed that both the AX and GAX coatings improved the paper surface structure. The GAX coating surface had a better covering ability compared with that of the AX coating at the same coating weight (6 g/m<sup>2</sup>). The cross-sectional area of the paper in the SEM images suggested that the GAX coating had a better interaction with the paper fibers than the AX coating. The boundary between the AX coating and paper can be seen clearly, while the boundary between the GAX coating and paper was not evident. Additionally, the SEM images showed that the AX and GAX coatings did not permeate into the paper. This suggested that the effects of coating permeation on the paper mechanical properties can be ignored (Xiang *et al.* 2016).

In summary, it was again postulated from the coating property of the GAX-coated paper that AX crosslinking should be controlled at a low degree to enhance the mechanical properties and hydrophobicity of the coated paper, while a relatively low viscosity can still be maintained. Crosslinking between the GAX and paper fibers, induced by the free hydroxyls and aldehydes, is important for mechanical strength enhancement of the coated paper.



**Fig. 7.** SEM images of the paper surface (a, c, and e) and cross-sections (b, d, and f): (a and b) uncoated paper; (c and d) AX-coated paper; and (e and f) GAX0.98-coated paper

### Modified Arabinosyl as Paper Coating Adhesive

As was discussed, GAX0.98 had the highest hydrophobicity and dry TI among the GAX samples. Therefore, GAX0.98 was selected to be the coating adhesive, was mixed with calcium carbonate, and compared with PVOH. The formulation of the paper coating was 4% (w/w) coating adhesive and 36% (w/w) calcium carbonate, which is a typical paper coating with PVOH (Barhoum *et al.* 2014). The coating weight of the GAX coating was similar to that of the PVOH coating, which suggested that the GAX coating had a similar paper adhesion compared with the adhesion of the PVOH coating. The dry TI of the GAX coatings was lower than that of the PVOH coating. The GAX-coated paper had a more hydrophobic surface, which could have improved its printing properties. The brightness and whiteness of the GAX-coated paper was lower than that of the PVOH-coated paper. However, this can be improved easily by bleaching the AX. The opacities of the GAX- and PVOH-coated papers were close. In general, the GAX-coated paper had comparable

properties to that of the PVOH-coated paper. This suggested that the GAX has the potential to substitute petroleum-based paper coating adhesives.

**Table 2.** Mechanical and Optical Properties of the Paper with GAX or PVOH as a Coating Adhesive

Adhesive Type	Coating Weight (g/m <sup>2</sup> )	Dry Tensile Index (Nm/g)	Contact Angle (°)	Brightness (%)	Opacity (%)	Whiteness (%)
GAX	23.91 ± 0.2	57.92 ± 0.3	45.2 ± 0.9	75.02 ± 0.1	87.2 ± 0.1	82.1 ± 0.1
PVA	23.38 ± 0.3	63.64 ± 0.2	39.8 ± 1.1	88.35 ± 0.1	90.2 ± 0.2	91.5 ± 0.1

## CONCLUSIONS

1. Glutaraldehyde was used to crosslink AX. The effects of crosslinking degree on the rheological and coating properties of the GAX were investigated. The film and coating properties of the GAX samples indicated that AX crosslinking should be controlled at a low degree.
2. The GAX samples with low crosslinking degrees demonstrated lower viscosity values than the GAX samples with high crosslinking degrees. At low crosslinking degrees, the GAX films and its coated paper had a better strength enhancement and better hydrophobicity than that at a high crosslinking degree. The type of crosslinking and forming of the highly entangled matrix between the coating and paper fibers was the major reason for the better mechanical strength enhancement of the paper coated by GAX with a low degree of crosslinking.
3. When keeping the degree of crosslinking low, the GAX showed the potential to substitute petroleum-based paper coating adhesives.

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