## Surface Modification of Cellulose Fibers by Starch Grafting with Crosslinkers

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**ABSTRACT:** Polymer grafting is a widely used technique in modifying the properties of cellulose fibers. Many methods, such as free radical, esterification reactions and layer-by-layer adsorption, have been applied for grafting polymer on different substrates. In this study, a facile method to graft biodegradable starch on fiber surface through the hydrogen bond formation among cellulose, starch, and ammonium zirconium (IV) carbonate (AZC) was developed. The effects of grafting conditions, including pH, temperature, fiber consistency, crosslinker, starch dosage, and mechanical agitation on the grafting yield were systematically investigated. Optical and electron microscopes clearly revealed that, after grafting, the fiber surface was covered by hydrogel of starch. The significant improvements of water retention value (WRV) of fibers with starch grafting were also demonstrated in this study. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3019–3026, 2009

**Key words:** biodegradable; crosslinking; fibers; hydrogels; viscosity

## INTRODUCTION

As a polysaccharide, cellulose is the most abundant organic polymer on Earth. Because of the low cost, high-strength property, good processability, and biodegradability, cellulose and cellulose fibers have been widely used in various applications, including support materials for water absorbent,<sup>1</sup> raw materials for textile and paper industry,<sup>2</sup> and reinforcing materials for composites.<sup>3</sup> The chemical and physical properties of cellulose fibers may be modified so that some desired properties such as water absorbency,<sup>1</sup> strength,<sup>2</sup> hydrophobicity,<sup>4</sup> thermal resistance,<sup>1</sup> and antimicrobial activity<sup>5</sup> can be improved.

Modification of cellulose fibers is a very active research area, and numerous methods, including physical, physico-chemical, and chemical treatments, have been studied in the past decades.<sup>3,6</sup> The chemical methods for fiber modification mainly include fiber wall crosslinking,<sup>7,8</sup> layer-by-layer (LbL) nano-coating technology<sup>9,10</sup> and grafting of polymers onto fibers.<sup>1,3,5,11–17</sup>

Graft copolymerization of cellulose fibers with monomers has been intensively investigated by many researchers. By using appropriate initiation techniques, such as UV irradiation, plasma irradia-

tion, gamma ray irradiation, and redox initiation with manganese or ceric (IV) ion, free radicals can be generated on the cellulose molecules, and then monomers can be grafted onto cellulose fibers. Various monomers, such as methyl acrylate,<sup>1,11</sup> ethyl acacrylic acid,<sup>13</sup> methyl methacrylate,<sup>14</sup> rylate,<sup>12</sup> acrylamide,<sup>15</sup> styrene,<sup>16</sup> vinyl acetate, and methacrylamide,<sup>17</sup> have been used for grafting of polymers onto cellulose fibers. However, there are some drawbacks related to free-radical polymerization technique, such as complex and rigorous reaction conditions, long reaction time, high cost of chemicals, and environmental concerns.<sup>18</sup> Normally, the obtained products from free-radical polymerization grafting are a mixture of grafted polymers, ungrafted homopolymers, and unreacted monomers. Nonwater solvent is commonly involved in free-radical polymerization process. The unreacted monomer residues are usually toxic. The purification of the products is a difficult and energy cost process. To remove the monomers and ungrafted homopolymers, the grafted products are often washed with large amount of water or extracted with solvents for more than 24 h. Consequently, the final products after extraction are completely denatured and become nonfibrous cellulose.<sup>18</sup> Furthermore, the reaction time for graft copolymerization is normally very long, requiring several hours, which is not suitable for some industry applications, such as papermaking.

Instead of free-radical polymerization with monomers, directly grafting commercial available polymers

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**Figure 1** Chemical structure of AZC [(a) AZC structure; (b) polymerized AZC chain in aqueous solution].

onto cellulose fibers by simply adsorption or layerby-layer self-assembly has also been reported.<sup>18</sup> For example, cationic polymers can be physically grafted onto fiber surface via electrostatic adsorption, because cellulose fibers have a negative surface charge. By adsorbing cationic polyacrylamide with fibers, Roche<sup>18</sup> prepared a polycation grafted cellulose fibers, which could be used as a retention aid. On the other hand, anionic or nonionic polymers may be chemically grafted onto cellulose fibers by using appropriate crosslinkers or couple agents. Although simple adsorption method can physically graft polymer on fibers, the maximum adsorption amount is limited by the saturation of adsorption. The low amount of polymer grafting sometimes cannot satisfy certain applications. For example, grafting of superabsorbent on wood fibers is a technique that has been widely used in diaper industry. For this application, large amount of polymers need to be grafted on fiber surface.

Starch is a low-cost abundant natural polymer that has been widely used in many industrial applications. To effectively adsorb on negatively charged fibers, raw starch must be modified by introducing either cationic or anionic charges to the starch backbones. The charge modification of starch results in a significantly increase of the cost of final products. Furthermore, because of the saturation of the adsorption, the amount of charged starch on fiber surface is low. Therefore, a simple, economic, and effective technique for grafting raw starch directly on fibers should be developed. To chemically crosslink a polymer that contains hydroxyl groups on the backbones, such as starch, the crosslinkers must have capability to react with at least two hydroxyl groups in the polymer molecule or in adjacent molecules.<sup>19</sup> It has been reported that ammonium zirconium carbonate (AZC) can crosslink hydroxyl or carboxyl groups in water. Because of the low cost, nontoxic characteristics of AZC, it is commonly used as insolubilizers or crosslinkers in paper coating to

crosslink starch molecules in the coating film<sup>20–25</sup> or surface sizing application.<sup>26</sup> AZC is a water-soluble salt as shown in Figure 1(a). In water solution, zirconium atoms in AZC are bridged by hydroxyl groups as shown in Figure 1(b).<sup>22</sup> Although it is accepted that AZC can form such polymer chains in aqueous solution, the degrees of polymerization is hard to be measured due to the sensitivity of the species to their environment.<sup>27</sup>

Farnworth et al.<sup>28</sup> proposed a possible mechanism of reaction between AZC and starch: the ammonium ions in AZC solution could interact with starch by hydrogen bond to form a pseudocationic starch, which can link with basic zirconium carbonate ions via ionic attraction (Fig. 2a). During drying, ammonia and carbon dioxide are released, and then new hydrogen bonds are formed between the hydroxyl groups of starch and the reactive sites of AZC (Fig. 2b). Similarly, AZC can also react with cellulose by forming hydrogen bonds.

One benefit of using AZC as a crosslinker is that the crosslinking reaction between cellulose and starch can occur in water and no high-temperature drying–curing is required although heat can speed the crosslinking process. In addition, unlike aldehyde and other organic crosslinkers, AZC is not considered as a toxic chemical and can be used for some products such as food packages.<sup>22</sup>

In this study, a simple technique using AZC as crosslinker to graft raw starch on wood pulp fibers was reported. The effects of grafting conditions, such as pH, temperature, fiber consistency, crosslinker, and starch dosages, on grafting yield were systematically investigated. The morphology of starch-grafted fiber was revealed by optical microscope and SEM images. The bonding strength of starch hydrogel on fiber surface was studied by applying different shear forces. The water retention value (WRV) of modified fibers was also evaluated.



Figure 2 AZC interaction with hydroxylated polymers.

### **EXPERIMENTAL**

#### Materials

Commercial pulp (bleached softwood kraft pulp) with an initial Canadian standard freeness (CSF) of 750 mL was received from Georgia Pacific, USA. The raw corn starch (B200) was provided by Grain Process (Muscatine, Iowa). The starch was cooked for 40 min using a rotary evaporator at 95°C. Ammonium zirconium (IV) carbonate solution (contains 1–2% tartaric acid as stabilizer) was purchased from Aldrich, USA.

#### Viscosity measurement

The rheological property of starch was characterized by measuring the viscosity of starch before and after AZC addition with a M3500 viscometer (Grace Instrument, Houston, TX) at different temperatures.

#### Fiber modification procedure

The basic process of grafting was to add AZC crosslinker into fiber slurry to react with fibers for a few minutes, followed by addition of precooked starch. To accurately determine the grafted amount of starch on fibers, the wood fines in the pulp was preremoved using a Bauer-McNett Fiber Classifier, and only the long fibers retained on 150 mesh wire was collected and used.

Certain amount of fiber (2g o.d. weight in this study) was put into a 300 mL glass beaker, and appropriate amount of deionized water was added to prepare fiber slurry at a designed consistency (1-4%). Then fiber was soaked at least 2 h and well dispersed in water with mechanical stirring before use. The beaker was put in a water bath at 80°C or a higher temperature, and a moderate mechanical stirring was applied by using a food mixer at 200 rpm. The required amount of AZC solution was slowly added into the fiber slurry, and the pH of the fiber slurry was adjusted by using 5% NaOH or 5% HCl. After mixing for 2-3 minutes, the required amount of precooked starch solution was added slowly into the fiber slurry. After reaction for 5 min, the beaker was cooled with cold water to stop the grafting reaction.

# Amount of grafting and grafting yield determination

The starch-grafted fiber sample was thoroughly washed with a large amount of water (about 4 L of water for 2 g oven-dried fiber) by using a dynamic drainage jar with a 200 mesh screen under moderate agitation at 400 rpm, aiming to remove the ungrafted starch. The samples collected on the screen were transferred to a preweighted filter paper and dried in 105°C. Then the amount of grafting on fibers and grafting yield were determined by using the following equations:

Amount of grafting (%) =

$$\frac{Mass_{final} - Mass_{AZC} - Mass_{fiber}}{Mass_{fiber}} \times 100$$

Grafting yield (%) =

 $\frac{Mass_{final} -}{Mass_{AZC} - Mass_{fiber}}_{Mass_{starch \ added}} \times 100$ 

#### Morphology of fiber surface

Optical microscope and scanning electron microscope (Hitachi S-800 FE-SEM) images were taken to reveal the morphology of fiber surface.

#### Water retention value test

The WRV of fiber was determined according to TAPPI UM 256. Fiber samples (0.5 g oven dried) were diluted to a consistency of 0.2%, and then drained onto a fine mesh screen at the bottom of a centrifuge cup. The samples in the centrifuge cups were centrifuged at 900 G for 30 min. The obtained fiber pad was weighted and dried in an oven at 105°C for 3 h. After drying, the mass of fiber samples was determined. The WRV was defined as the ratio of water mass in the wet fiber pad after centrifuging to the oven-dried mass of fiber.

#### **RESULTS AND DISCUSSION**

# Reaction between AZC and starch—Characterized by viscosity changes

It was proposed that AZC reacts with starch/cellulose via hydrogen bonding.27 However, direct evidence about the formation of such hydrogen bonds has not been reported in literatures due to the difficulty in experimental measurement. The viscosity measurement is the most common way to study the gelation of polymer solution although it does not provide the information about the bonding mechanism of the polymer. Floyd and Boss<sup>29</sup> suggested that the increase of viscosity under low-shear rate was an indirect evidence for the hydrogen bonding interaction for AZC-starch system. Comyn<sup>27,30</sup> found that the interaction between zirconium propionate and nitrocellulose was a moderately strong one. He argued that the polymer would be crosslinked and form a gel if covalent bonds were formed. To test Figure 3 Viscosity change of starch under different shear rates (starch concentration: 3%; pH: 9; AZC: starch = 1 : 3; temperature:  $40^{\circ}$ C). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

the strength of starch-AZC network formed during the crosslinking, the viscosity of starch under different shear rates was measured. Figure 3 shows that at a given shear rate, the viscosity of starch with AZC was higher than that without AZC, which indicates a certain network formed between starch and AZC. At the low-shear rates, such as  $100-200 \text{ s}^{-1}$ , the increase of viscosity after adding AZC was significant, more than 20 cp. However, at a high-shear rate of 1000  $s^{-1}$ , the viscosity of starch only increased 8 cp. That means the bonds formed between AZC and starch is relatively weak, and sensitive to shear force. When the shear rate was switched back to smaller values, the viscosity of starch resumed to high values, suggesting some bonds were reformed, and the breakage of the bonds was reversible. These results from the viscosity measurements agreed well with literatures.<sup>21,23,29,31</sup> Theoretically, the viscosity change of starch results from the synergy between hydrogen bonding and charge association. However, the contribution of the charge association is very small due to the very low charge density of raw corn starch (less than  $-2 \mu eq/$ g measured in our laboratory). Therefore, the system can be considered as a neutral charge condition. The increase in the viscosity of the starch solution is mainly attributed to the formation of crosslinking through AZC-starch hydrogen bonding.

It was reported that when AZC reacts with hydroxyl group contained polymers, such as starch and cellulose, no high-temperature curing is needed.<sup>29</sup> However, because heating the system even in the present of water can cause dehydration of hydrogel, it is expected that the crosslinking process can be speeded up by heating. To verify the

effect of heating on reaction between AZC and starch, the viscosity change of starch solution over reaction time at different temperatures was investigated. From Figure 4, it can be seen that before adding AZC the initial viscosities of starch at all three temperatures were relatively low, at the range of 20–27 cp. After adding AZC, the viscosity of starch at 23°C increased very slowly over time, and the slope of the curve is very small, indicating a very low-reaction rate of crosslinking. However, at the higher temperatures, i.e., 65°C and 90°C, the viscosity of the solution significantly increased over time, suggesting that the crosslinking of starch occurred quickly.

#### Morphology of modified fibers

As AZC can directly form chemical or hydrogen bonds with the hydroxyl groups on cellulose, it is expected that an AZC layer can form on fiber surface by mixing it with fibers at desired temperature and pH. However, because of the multireactive sites of an AZC polymer chain, there must be some unreacted sites on the AZC polymer chains. When starch is added, unreacted sites of AZC will further react with hydroxyl groups of starch via hydrogen bonding. As a result, starch could be grafted onto the fiber surface through the bridging of AZC. Moles<sup>32</sup> proposed a similar process to use zirconium-based coupling agents as adhesion promoters in ink industry.

Figure 5 is a comparison of unmodified fibers and starch-grafted fibers. The fibers in the left beaker are unmodified fibers dispersed in water. After starch grafting treatment, the wood fibers formed large flocs by crosslinking the fibers and starch, and left a









**Figure 5** Comparison of fiber slurry before (left) and after (right) starch grafting. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

clear water layer on the top (the right beaker in Fig. 5). Generally speaking, the more the starch added, the bigger the flocs were formed. The optical microscope pictures [Fig. 6(a,b)] illustrates a remarkable change of fiber surface before and after starch grafting. It can be seen that the fiber surface [Fig. 6(b)] was covered by large amount of starch aggregates and "starch fibrils" after starch grafting. It is believed that with such "starch fibrils," the WRV and bonding capability of fiber would be significantly improved.

The SEM pictures of unmodified fibers and starchgrafted fibers were also taken in this study [Fig. 6(c,d)]. More clear change of morphology of fiber surface before and after starch grafting can be clearly seen. Compared with the unmodified fibers, the surface of grafted fibers became rougher. Furthermore, both the optical microscope pictures and SEM images indicate that the grafted starch was not uniformly distributed but formed some aggregates on fiber surface, resulting in the increase of roughness of fiber surface. The morphology change of fiber is different from that by simple polymer adsorption, such as cationic starch and cationic polyacrylamide, in which the fiber is covered only by a thin film of polymer and no significant aggregates or fibrils can be observed.<sup>18</sup>

#### Effects of grafting conditions on grafting yield

There are several possible crosslinking reactions, such as fiber-AZC-starch, fiber-AZC-fiber, and starch-AZCstarch interaction in the system studied here. As a crosslinker, AZC would have different reactivity at different reaction conditions, such as pH, temperature, fiber consistency, AZC dosage, stirring speed.



**Figure 6** Microscope pictures of fibers: (a) optical microscope picture of unmodified fibers; (b) optical microscope picture of starch-grafted fibers; (c) SEM picture of unmodified fibers; and (d) SEM picture of starch-grafted fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



**Figure 7** Effect of pH on grafting yield (fiber consistency: 3%; starch dosage: 10% based on fiber; AZC : starch = 1 : 2; temperature:  $95^{\circ}$ C). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Consequently, the grafting performance would be highly dependent on these conditions.

The grafting yield at different pH was determined and illustrated in Figure 7. It can be seen that the grafting yield increased up to pH of 9, and then decreased with further increase of pH. The lowgrafting yield at low pH is mainly attributed to the decomposition of AZC at acid condition.<sup>29</sup> Wolff et al.<sup>20</sup> reported that the active pH range of AZC in surface sizing is around 5.5–10.

As showed in the starch viscosity measurement part, the crosslinking process can be speeded up by increasing the reaction temperature. It is likely that the fast reaction rate may also result in a high-grafting degree of starch on fibers. In this study, the grafting yield at different temperatures for a fixed reaction time (5 min) was investigated. Figure 8 indicates that the higher the reaction temperature, the higher the grafting yield. One of the reasons for the high-grafting yield is probably due to the fast dehydrates at a high temperature and more bond formation, resulting in the shrinking of starch hydrogel to form a hard gel, which can bond to fiber surface stronger than the soft gel formed at a low temperature. From the reaction between AZC and starch (Fig. 4) at 90°C, it took around 83 min to accomplish the crosslinking reaction. In this part of study, 80-90% of grafting yield could be achieved only after 5 min. Theoretically, a higher grafting yield, and even 100% yield could be achieved if more reaction time was chosen.

Fiber consistency is also an important parameter for the grafting reaction system. It can be seen from Figure 9 that there is an optimal fiber consistency, i.e., at around 3%. At a lower fiber consistency, fibers could not provide enough surface area for AZC and starch to graft on fiber surface so that large amount of starch would form homo-crosslinked



**Figure 8** Effect of temperature on grafting yield (pH: 9; fiber consistency: 3%; starch dosage: 10% based on fiber; AZC : starch = 1 : 2). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

hydrogel particles. However, when fiber consistency was too high (higher than 3%), the fibers formed large fiber flocs and could not be well dispersed in water. The poor mixing of the system at a high-fiber consistency might end up with some unreacted AZC or starch, resulting in a low-grafting yield.

It is expected that AZC functions as a crosslinker or a coupling agent between cellulose fibers and starch during the reaction. Figure 10 shows that at a starch addition of 5% (based on fiber), the grafting yield first increased with AZC dosages and then leveled off at AZC dosage of 3% based on fibers. At this condition, the grafting yield reached around 98%. When 10% starch was used, the grating yield was also increased with the AZC dosage. However, after reaching a peak value, the grafting yield deceased when more AZC was added. The reason



**Figure 9** Effect of fiber consistency on grafting yield (pH: 9; starch dosage: 10% based on fiber; AZC : starch = 1 : 2; temperature: 95°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com.]



**Figure 10** Effect of crosslinker dosage on grafting yield (pH: 9; fiber consistency: 3%; Temperature: 95°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for the decrease of the grafting yield at the high AZC dosage is the formation of homocrosslinked starch gel. It can be concluded that from both a high-grafting yield and a low-cost point of view, too high AZC to starch ratio should be avoided in a practical application.

The effect of starch dosage on the grafting performance was also determined (Fig. 11). The results indicate that the more starch added, the higher the amount of starch grafted on fibers. However, the grafting yield, i.e., starch retention rate, was decreased with the increase of starch dosage, suggesting more ungrafted portion of starch in the system. It can also be seen that a highest grafting yield could be achieved at 5% starch addition level at current grafting condition (i.e. pH 9, temperature 95°C, AZC : starch = 1 :2).

To achieve a good mixing, appropriate stirring must be applied either during the grafting process or postgrafting process. The effect of stirring speed



**Figure 11** Effect of starch dosage on grafting amount and grafting yield (pH: 9; fiber consistency: 3%; temperature:  $95^{\circ}$ C, AZC : starch = 1 : 2). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]



**Figure 12** Effect of stirring speed on grafting yield (fiber consistency: 3%; pH: 9; temperature:  $95^{\circ}$ C; starch dosage: 10% based on fiber; AZC : starch = 1 : 2). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

on grafting yield was also studied. During the starch grafting process, moderate stirring speeds at the range of 50–400 rpm were chosen in this study. Figure 12 indicates that applying agitation at 100 rpm during grafting process, an optimal grafting yield was obtained. When a higher stirring speed was applied, the grafting yield was decreased. This is because the hydrogel aggregates formed on the fibers (i.e. grafted starch) is soft and high-shear force can easily break the hydrogel resulting in a falloff starch hydrogel from the wood fibers. It was noted that if the stirring speed was too low, AZC and starch would form ungrafted hydrogel particles, resulting in a lower grafting yield.

From the microscope pictures, we can see that the surface of modified fibers was covered by starch hydrogel aggregates. The bonding stability of starch hydrogel on wet fibers is an important property, which should be considered when setting up the condition of postprocessing, such as pumping and stirring in a real manufacture. In this part of study, fibers with 9.5% starch grafting on the surface were used to test the starch bonding stability. After exposing to different shear force, the remaining amount of starch on fibers was evaluated. From Figure 12 (postgrafting), it can be seen that the grafting yield was remarkably decreased with the increase of stirring speeds. Before drying, the grafted starch is soft hydrogel with weak strength. Therefore, when processing the slurry of modified fibers, high-shear force should be avoided.

## Water retention value of modified fibers

In many applications, such as drug delivery and dapper, the water retention capability is important. The WRV of fibers is an indication of fibers' ability



**Figure 13** The water retention value (WRV) of fiber vs. starch grafted amount (23°C). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

to take up water. The WRV of fiber can be improved by different ways, such as refining and grafting hydrophilic polymers. The improvement of WRV of fibers by refining is mainly attributed to the increased surface area of fibers. Starch is a typical hydrophilic polymer that can form hydrogel by crosslinking the starch molecules. The starch gel itself is a swellable hydrophilic polymer network, which can hold more water than wood cellulose fibers. In this study, the WRVs of starch-grafted fibers were measured at 23°C. Figure 13 shows that WRV of modified fibers was significantly increased with the increase of grafted starch amount on fiber surface.

It is reported that WRV is highly correlated to the bonding ability of fibers during paper formation.<sup>2</sup> From the results of WRV test, it can be expected that the bonding ability of starch-grafted fibers should be significantly increased, and consequently, the paper strength should be improved. In our research, the significant improvements of paper properties, such as tensile strength and stiffness have been demonstrated, and it will be reported separately.

#### CONCLUSIONS

In this study, a simple and practical technique of fiber modification via starch grafting was developed by crosslinking starch with wood fibers using AZC as the crosslinker. It could be concluded that

- Starch can form a hydrogel with AZC, and high temperature can speed up the hydrogel formation.
- Reasonable amount of starch could be grafted on fiber surface to form "starch fibrils" by hydrogen bond formation between fibers and starch molecules.
- The effects of grafting conditions, including pH, temperature, fiber consistency, AZC and starch dosage, stirring speed, on the grafting yield were systematically investigated. An optimal

reaction conditions were obtained (pH: 9; temperature: >80°C; fiber consistency: 3%; starch dosage: 5%; AZC dosage: 2.5%).

- The soft starch hydrogel grafted on fibers surface is sensitive to shear force. High shear forces should be avoided during postprocessing.
- Starch grafting treatment on fibers could significantly improve the WRV of fibers.

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