

AN ABSTRACT OF THE THESIS OF

Dakai Ren for the degree of Master of Science in Wood Science presented  
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Title Development of Temporary Wet Strength Resins from Wheat Gluten

Abstract approved

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Kaichang Li

Many paper products like towel and tissue cannot serve their purposes without temporary wet strength. Glyoxal-polyacrylamide (GPA) resin is one of the widely used commercial wet strength additives that impart the temporary wet strength to paper and paperboard products. However, GPA resin is derived from petrochemicals and contributes to contaminants in the recycling of papers. Wheat gluten is one of the most abundant proteins in nature. Unique chemical composition of wheat gluten makes it an ideal raw material for temporary wet strength additives. This research investigated how to convert gliadin, one of key components of wheat gluten, to effective temporary wet strength additives. Gliadin was first modified with glycidyltrimethylammonium chloride (GTA) to generate

positively charged GTA-gliadin. Further reaction of GTA-gliadin with glyoxal provided GTA-gliadin-glyoxal resins. For enhancing the dry and wet strengths of GTA-gliadin-glyoxal-treated paper, the optimum reaction conditions for the reaction between GTA and gliadin were found to be 75 wt% GTA based on dry gliadin and 8 h reaction time at 70°C. Thirty percent of glyoxal based on dry weight of GTA-gliadin in the reaction between glyoxal and GTA-gliadin resulted in the highest dry and wet strengths. The GTA-gliadin-glyoxal resin was comparable to a commercial GPA resin in terms of enhancing the dry and wet strengths of the wet-strength-resin-treated paper.

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Development of Temporary Wet Strength Resins from Wheat Gluten

by

Dakai Ren

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Dakai Ren, Author

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# DEVELOPMENT OF TEMPORARY WET STRENGTH RESINS FROM WHEAT GLUTEN

## Chapter 1 Introduction

### 1.1 Wet-end paper chemicals

Since the invention of paper in 105 AD, the papermaking has already evolved tremendously from the original handicraft to today's highly computer-controlled processes and equipments. The first major evolution was probably the invention of Fourdrinier papermaking machine in France in the 18th century. Afterwards, the paper machines were continuously improved. The increases in web width and working speeds led to an enormous progress in production scale and efficiency. The second major evolution occurred as the use of wood fibers as raw materials. The third evolution was the introduction of kraft pulping and kraft recovery system in the early 20<sup>th</sup> century. The last but not the least evolution was the application of additives in the papermaking processes. The addition of chemicals improves both the papermaking processes and paper quality. These chemicals are called wet-end paper additives.

There are two categories of paper additives, the functional additives and the control additives [1]. The functional additives are used to change the properties of the paper such as the strength, opacity, etc. The control

additives are used to improve efficiency of the papermaking processes and help reduce the losses of fibers, fines and fillers

### 1.2 Dry and wet strength additives

Recycled fibers are generally cheaper than virgin fibers. The recycling of waste paper can reduce the municipal solids waste, extend the lifetime of landfill sites, and preserve the forest resources. Therefore, the use of recycled fibers has increased dramatically in the past two decades. In January 1999, President Clinton's 1993 executive order whereby recycled printing and writing papers purchased by the federal government must contain 30% post-consumer recycled materials went into effect [2]. Soon afterwards, the federal standards were adopted by many private sectors [2]. Therefore, the executive order has had a significant impact on increasing the recovery of paper products in U.S. The recovery goal of 50% set in 1995 has been achieved in 2003 and a new goal of a 55% recovery rate by 2012 has been announced by AF&PA (American Forest & Paper Association) (<http://www.tappi.org/index.asp?rc=1&pid=26773&ch=7&ip=>) [3]. The recovered fibers are shorter and weaker than the virgin pulp. The dry and wet strength additives are generally used to improve the strengths of recycled fiber-based paper products.

Dry strength resins can greatly increase fold endurance, burst index and tensile strength of the resulting paper products. The use of dry strength additives allows the reduction of the paper grammage and the paper thickness, thereby increasing the overall yield of paper from pulp. About 400,000 tons of dry strength additives are consumed each year in the US with the sales values of US \$320 million [2]. Commonly used dry strength additives include cationic starch and polyacrylamide copolymers.

In paper products, fibers are held together through intermolecular hydrogen bonds. Because water can easily disrupt the hydrogen bonds among fibers, the tensile strength of wet paper is only about 1~5% of that of dry paper [4]. However, the performance of many types of paper such as filter papers, hygienic papers, paper bags, beverage containers, etc requires adequate wet strength. The wet strength of paper is improved by the application of wet-strength resins. About 50,000 tons of wet-strength resins are consumed each year in the US with the sales values of about US \$160 million [2]. There are two kinds of wet strength resins, permanent wet strength resins and temporary wet strength resins. Permanent wet strength resins provide long-lasting wet strength and temporary wet strength resins give the wet strength for a short period of time. At present, the most commonly used wet strength resins include polyaminoamide-epichlorohydrin (PAE) resins and glyoxal-polyacrylamide (GPA) copolymers. PAE resins are permanent wet strength resins and GPA

copolymers are temporary wet strength resins. GPA copolymers are also used as dry strength resins in some paper mills.

There are some disadvantages of currently used dry and wet strength resins. First, PAE, GPA and polyacrylamide resins are derived from non-renewable petrochemicals and natural gas. Secondly, these additives contribute to stickies and contaminants in the recycling of treated papers, resulting in many problems such as an increased machine downtime, reduced product quality, increased replacement costs and so on [5, 6]. Instead of being recycled, most of these papers are burned. Finally, PAE resins contribute to the emission AOX (absorbable organic halide) that is suspected to be carcinogenic. So, it's very desirable to develop environmentally friendly strength additives from renewable, inexpensive and sustainable raw materials.

### 1.3 Development of new temporary wet strength and dry strength resins from wheat gluten

Wheat is one of the major cereals cultivated throughout the world [7]. Wheat flour contains about 10% protein that is called wheat gluten or just gluten [7]. Wheat gluten is commercially produced through a wet-milling process, in which the starch is washed away with water or a dilute salt solution. Commercial wheat gluten products normally contain 75 – 85% protein [7]. Most of the wheat gluten products go into high



protein bread items such as bagels, hearth breads, multi-grain breads, etc because they can add strength and elasticity to the dough [9, 10] In addition, wheat gluten is also used as an essential ingredient for producing restructured meaty chunks from meat by-products because it is able to bind with and restructure proteins of meat, poultry and fish muscle

Due to population growth and increased consumer preferences for healthy grain-based products, the consumption of wheat gluten in the US increased drastically in 1990s [10] Driven by the great demand for wheat gluten, the wheat gluten processing capacity in the US was rapidly increased by 62% during the 1990s [10] In the meantime, the import of wheat gluten from the European Union (EU), Australia, and other countries also greatly increased The intensive international competition largely drove down the domestic prices of wheat gluten and greatly damaged the domestic wheat gluten industry By 1997, only 44.5% of the wheat gluten processing capacity was utilized, as compared to 78.4% in 1993 [10] At present, the traditional food markets for wheat gluten have been saturated [11] The development of value-added products for new non-food applications from wheat gluten will greatly increase the competitiveness of the US wheat gluten industry

Wheat gluten has very unique chemical structures, which make it an ideal renewable raw material for wet-strength resins Furthermore, the backbone of wheat gluten is biodegradable, so paper treated with wheat

gluten-based wet strength resins are expected to be more recyclable. This research aims to investigate how to convert wheat gluten to temporary wet strength and dry strength resins with properties comparable to GPA copolymers. Both wheat gluten industry and the pulp and paper industry will greatly benefit from this research.

## Chapter 2 Literature Review

### 2.1 wet strength resins

#### 2.1.1 Introduction of wet strength resins

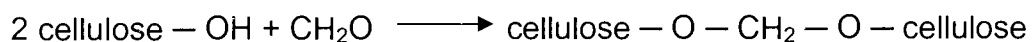
The ability of paper products to maintain a substantial proportion of their original strength after being completely saturated with an aqueous solution is known as wet strength ([http://www4.ncsu.edu/~hubbe/TShoot/G\\_WStren.htm](http://www4.ncsu.edu/~hubbe/TShoot/G_WStren.htm)) [12]. The wet tensile strength is defined in *The Dictionary of Paper* as “the tensile strength of paper after it has been wetted with water under specified conditions” [13]. The wet strength may be of a more or less temporary nature, as in paper towels and tissues, or of a more permanent nature, as in bag papers, cookery parchment, etc., where the paper is in contact with water for a long period of time [14]. Sometimes the criterion for defining a wet-strength grade of paper is that the relative wet strength, i.e., the ratio of wet to dry tensile or burst strength, is at least fifteen percent [15]. Therefore, the wet-strength papers are also defined as papers with wet-tensile strengths of more than 15% of the dry tensile strength [16].

Paper is a compact web of cellulosic fibers, which are bonded together through intermolecular hydrogen bonds. The hydrogen bonds among fibers are very sensitive to water and can be greatly disrupted by

water. The strength thus decreases steadily as the water content of the paper increases, up to the saturation point [17]. As a result, only about 1% to 5% of the original dry strength (at 50% relative humidity) can be retained in the wet paper [4]. However, wet strength is critical to the performance of many types of paper products such as filter paper, hygienic paper, paper bags, beverage containers, etc. Typically, wet-strength resins can increase the wet strength to 20 – 40% of the dry strength [15]. The annual consumption of wet-strength resins is about 50,000 tons in the US with the sales values of about US \$160 million [2].

### 2.1.2 Historic development of wet-strength resins

The earliest method to improve the wet strength of paper was to fuse the cellulosic fibers to one another [18]. The first additive used to improve the wet strength of paper was formaldehyde because formaldehyde can form methylene bridges between the hydroxyl groups of fibers (Figure 1) [4, 18].



Adopted from mechanisms of wet-strength development in paper [4]

Figure 1 Formation of methylene bridges between formaldehyde and the hydroxyl groups of fibers

However, formaldehyde was rarely used commercially because of its offensive odor and the brittleness of the resulting paper [15]. Dimethylolurea, a reaction product of formaldehyde and urea, was also used as a paper wet strength additive. But its efficiency of improving the paper wet strength was low because it was so readily soluble in water and not substantive to pulp fibers [15]. Then an insoluble resin was produced from a water-soluble, alkaline monomer, dimethylolurea, together with acid-forming catalysts and heat, and was used to increase the wet strength of viscose or cuprammonium cellulose threads [14]. The insolubility of this resin limited its application as a wet strength additive and was only used commercially as a tub-sizing additive [19]. In the 1930s, a water-soluble anionic urea-formaldehyde (UF) polymer was produced by modifying UF resin with either sodium bisulfate or glycine [20]. Because pulp itself is anionic, alum was used for bonding this resin onto pulp. The anionic UF resins were not very effective wet strength resins with pulps other than unbleached kraft pulp because of their slow absorption to pulps [18]. In 1946, cationic UF resins were successfully produced through reactions between UF resins and ethylenediamine, diethylenetriamine or other amino compounds [20]. The cationic UF resins had higher water solubility than typical UF resins and were better distributed onto fibers, thus resulting in a higher wet strength of paper. However, the UF resins cured slowly. About 10-14 days were required to fully cure cationic resins and 21-28 days to

cure anionic UF resins at 20 °C [18]. Another problem was that UF resins were readily to be hydrolyzed at pH 4-6. The next advance was the development of melamine-formaldehyde (MF) resins in 1942, and these resins were patented in 1944 [21]. Basically, the MF resins were developed by reacting melamine with formaldehyde. The ether linkage and the methylene linkage between two melamine molecules led to the homo-crosslinking of MF resins at a high temperature and a low pH [22]. This homo-crosslinking provided high wet strengths in paper. MF resins have relatively more reactive groups than UF resins, thereby providing higher paper wet strengths than UF resins. In addition, the wet strength development of MF resin-treated papers is less sensitive on the pH than that of UF resin-treated paper. The pH of the pulp slurry can be somewhat higher than 4.5 [23]. However, MF resins are more expensive than UF resins. Meanwhile, MF resins, like UF resins, are cured under acidic conditions, and the acidic conditions increase brittleness and deterioration of paper and reduce paper absorbency, which are especially undesirable for tissues and paper towels. Both UF and MF resins are readily hydrolyzed at low pH, leading to a gradual decrease in the wet strength during storage. Therefore, wet strength resins that can be used under neutral or alkaline conditions are preferable. Daniel and Landes developed a thermosetting wet strength resin from an alkylene polyamine and a polyfunctional halohydrin in 1952 [24]. This wet strength resin performed

very well at a pH range from 4 to 10. In 1960 Keim patented cationic thermosetting polyamide-epichlorohydrin (PAE) resins for preparing wet-strength paper [25, 26]. He treated a polyalkylene polyamine having 2 primary amine groups and at least 1 secondary amine with a dicarboxylic acid to form a water soluble long-chain polyamide. The secondary amino group in the polyamide reacted with epichlorohydrin to form an azetidinium group that carries a positive charge. These resins greatly enhanced the wet strength of paper at a pH as high as 9.0. Being highly cationic charged, PAE resins are readily absorbed onto negatively charged cellulosic fibers [27, 28]. The azetidinium group can react with the residual secondary amino group in PAE and carboxylic acid groups in pulp. Because the cured PAE cannot be readily hydrolyzed, the resulting wet strength can be retained for a long time. Therefore, PAE is called a permanent wet strength resin. However, permanent wet strength in the paper products is not always a necessary and desirable property. There are some applications such as towels and tissues where the wet strength is needed only on a temporary basis [29, 30]. In the late 1960s, a glyoxalated polyacrylamide (GPA) wet strength resin was introduced [15, 31]. GPA resins can only provide temporary wet strength because the hemiacetal and acetal linkages between GPA resins and cellulose hydroxyl groups can be gradually hydrolyzed [32]. Another temporary wet strength agent is dialdehyde starch (DAS) [33-39]. It is formed by selective

oxidation of vicinal hydroxyl groups of starch by periodic acid, and then it can be further modified in many possible ways to produce cationic or anionic wet strength resins. DAS forms acetal and hemiacetal linkages with hydroxyl groups of cellulose and hemicelluloses, thus improving the paper strengths. The application pH value for DAS is around 4.5 because the formation of the stronger and more stable acetal linkages other than hemiacetal linkages is favored at this pH [36, 37, 39].

There are several issues associated with PAE resins and GPA resins. Repulping of the recycled PAE- and GPA-treated paper products is difficult and these resins in the recycled paper products become stickies in the papermaking. In addition, these synthetic resins are produced from petrochemicals. Furthermore, the PAE resins are a source of chlorinated organic compounds. As a result, there are ongoing efforts in development of new re-pulpable and environmentally friendly wet strength resins from renewable materials. Kurosu and Pelton applied a series of lysine-containing polypeptides for laminating two-ply, wet, regenerated cellulose films [40, 41]. More carboxyl groups were introduced by oxidation of the cellulose films. The polylysine was found to give significant wet adhesion to cellulose if the cellulose films were dried and then rewetted. Chemically modified chitosan was investigated as a potential dry and wet strength resin [42, 43]. Laleg et al found that the modified chitosan was able to increase the strength of never-dried wet webs [43]. As a wet strength



resin, the chitosan-treated paper retained about 20% of its dry strength at a level of 1 wt% chitosan, which is not comparable with commercially used PAE resins and GPA resins [43]. Shannon et al demonstrated that aliphatic-moiety-modified polysaccharides (starches, gums, chitosans, celluloses, sugars, etc.) provided several potential benefits to paper products, such as wet strength improvement and the controlled absorbency of the additives [44]. Recently, Li et al investigated 20 types of proteins for the improvement of the wet peel strength of oxidized and non-oxidized cellulose membranes [45]. It was found that the  $\text{NH}_2$  group content in protein played an important role in development of the wet peel strength.

### 2.1.3 Mechanisms of wet-strength development

Mechanisms of wet-strength development have been extensively studied and reviewed [15, 18, 46-50]. Basically, there are two principal wet-strength development mechanisms: protection mechanism and reinforcement mechanism.

#### 2.1.3.1 *Protection mechanism*

The protection mechanism is also called homo-crosslinking mechanism. After wet-strength resins are absorbed onto the fibers, they react with themselves to form a highly crosslinked network during the

paper drying process. When the paper is re-wetted, the network restricts the re-hydration and swelling of the fibers, thus preventing fibers from separation and protecting the existing bonds among fibers [48].

### 2.1.3.2 Reinforcement mechanism

The reinforcement mechanism is also referred to as co-crosslinking mechanism. New covalent linkages are formed between fibers and wet-strength resins, which lead to supplement and reinforce the existing hydrogen bonding in the paper. The newly formed covalent linkages cannot be broken by water (permanent wet strength) or are hydrolyzed slowly (temporary wet strength) [48].

### 2.1.4 Common attributes that wet-strength resins should have for development of wet strengths in paper [15, 48, 49]

First of all, the wet-strength resins must be water-soluble or water-dispersible. Otherwise, they cannot be efficiently distributed onto fibers. Secondly, the wet-strength resins must have cationic charges. The concentration of an added additive is in the range of 10–100 ppm (parts per million) [4]. Cationic charges of wet strength resins facilitate the distribution of the resins onto the negatively-charged fibers by electrolytic attraction or sorption [51]. Thirdly, wet strength resins must be chemically

reactive thermosetting polymers, forming a network through homo-crosslinking or co-crosslinking during the paper drying process

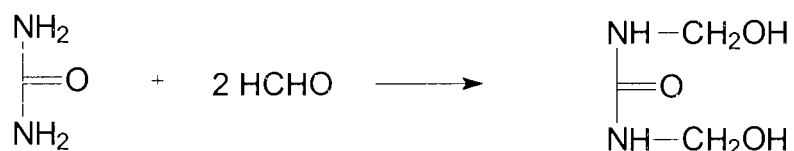
### 2 1 5 Commercial wet-strength resins

The principal commercial wet strength resins include urea-formaldehyde (UF) resins, melamine-formaldehyde (MF) resins, polyamide-epichlorohydrin (PAE) resins and glyoxal-polyacrylamide (GPA) resins

#### 2 1 5 1 Urea-formaldehyde resins

The chemistry involved in the formation and application of UF resins includes three stepwise stages [15, 22, 46, 50, 52, 53]

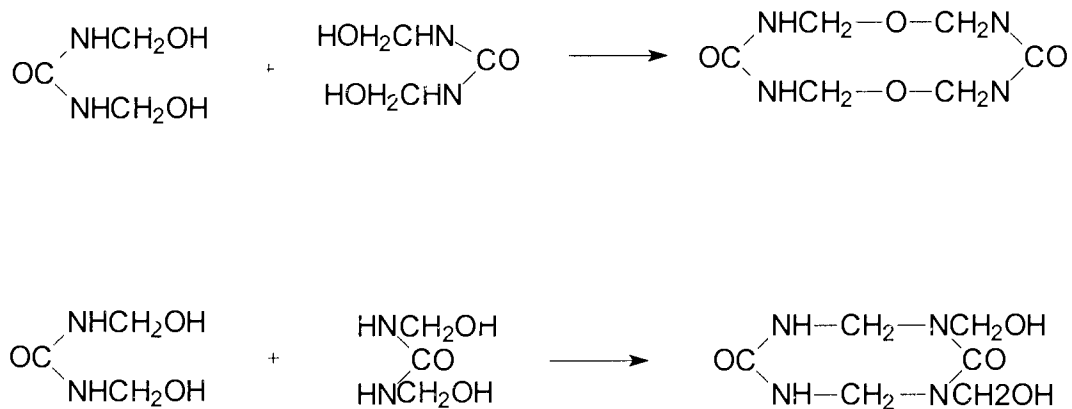
*Stage A or the monomeric stage* dimethylol urea (DMU) is formed under neutral or slightly alkaline conditions from urea and formaldehyde (Figure 2)



Adopted from Wet-strength chemistry [15]

Figure 2 The stage A in the synthesis of urea-formaldehyde resins

*Stage B* This stage is an intermediate stage in polycondensation UF resins are produced by further reaction of DMU to a controlled degree Both methylene (-CH<sub>2</sub>-) and methylene ether (-CH<sub>2</sub>-O-) linkages are formed (Figure 3) [53] In this stage, the UF resins are water-soluble and can be stored and transported as products to paper mills for application as wet strength additives



Modified from Factors in the composition of urea and melamine formaldehyde resins which affect their efficiencies when used to wet-strengthen paper [53]

Figure 3 The stage B in the synthesis of urea-formaldehyde resins

*Stage C* In this stage, UF resins after being adsorbed onto fibers are cured with an acidic catalyst at elevated temperature As a result, densely cross-linked insoluble polymers are formed during a paper drying process

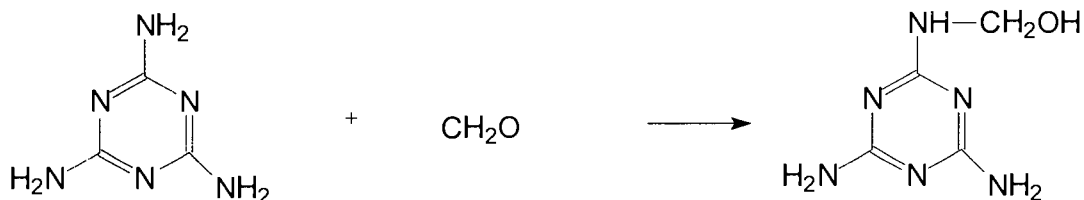
The insoluble, three-dimensional network formed in the stage C results in the wet strength development in UF-treated papers by protection of existing fiber-fiber bonds and restraint of fibers from swelling. In principle, the methylol groups in UF resins may react with other groups of the resins (homo-crosslinking), and with hydroxyl groups of the fibers (co-crosslinking). Some investigations revealed that UF resins did not form co-crosslinking with the fibers [54, 55]. The studies of curing kinetics of UF resins also suggested that the activation energy of wet strength development was independent of the nature of the paper [48].

#### 2.1.5.2 Melamine-formaldehyde resins [15, 22, 48, 50, 52]

The first step to produce MF resins is to react melamine with formaldehyde to give methylol melamine (Figure 4) [15]. A series of methylol derivatives of melamine can be formed from monomethylol melamine to hexamethylol melamine, depending on the molar ratio of formaldehyde to melamine. Among these derivatives, the trimethylol derivative (TMM) was found to give the best wet strength performance [15].

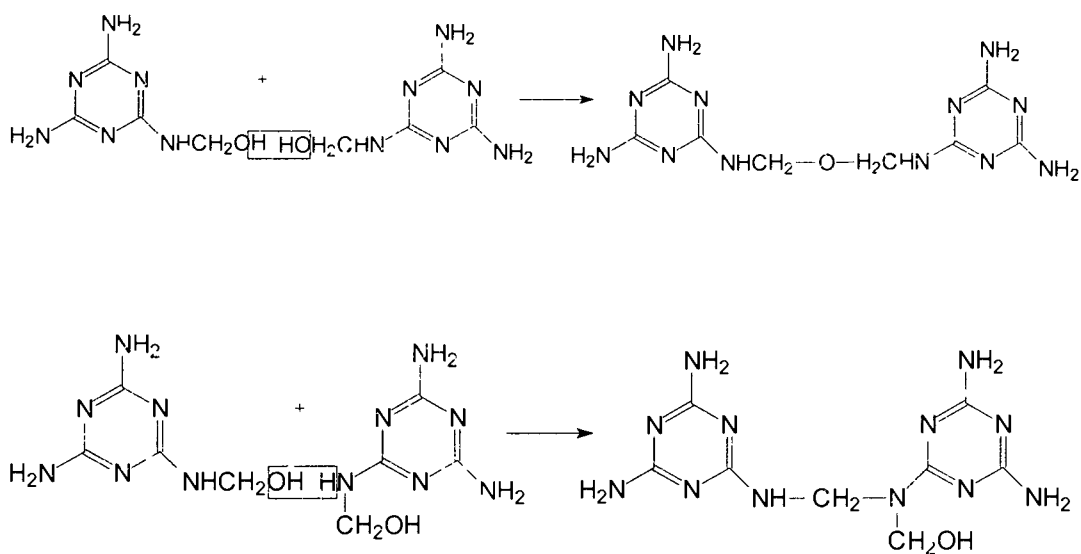
Similar to the synthesis of UF resins, the second step in the synthesis of MF resins involves the formation of methylene linkage and the ether linkage (Figure 5). High temperature and low pH value are required

in both reactions. The reactions have to be well controlled so that the formed MF resins are still water soluble.



Adopted from Wet-strength chemistry [15]

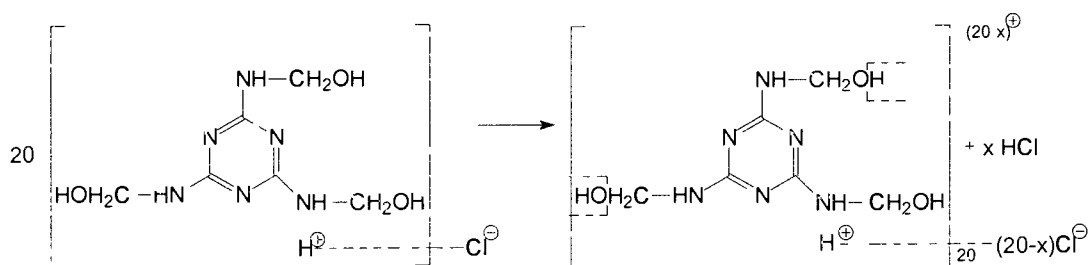
Figure 4 The first stage in the synthesis of melamine-formaldehyde resins



Adopted from Wet-strength chemistry [15]

Figure 5 Formation of ether and methylene linkages in the synthesis of melamine-formaldehyde resins

The aqueous solution of MF resins may be applied to cellulosic fibers by tub or spray, but the lack of attraction between fibers and the resins limits the improvement of wet strength of paper products and the use of the resins. Further development explored positively charged MF colloids through a self-limiting polymerization of methylol melamine in the presence of hydrochloric acid (Figure 6) [52]. These cationic MF resins are readily adsorbed onto cellulosic fibers. The subsequent polymerization to an insoluble three-dimensional network imparts the wet strength to paper products during the final curing process.



Modified from wet strength [of paper] [52]

Figure 6 Formation of melamine acid colloid

As described previously, the synthesis and the curing processes of MF resins are similar to those of UF resins. For MF resins, the predominant mechanism responsible for the development of wet strengths

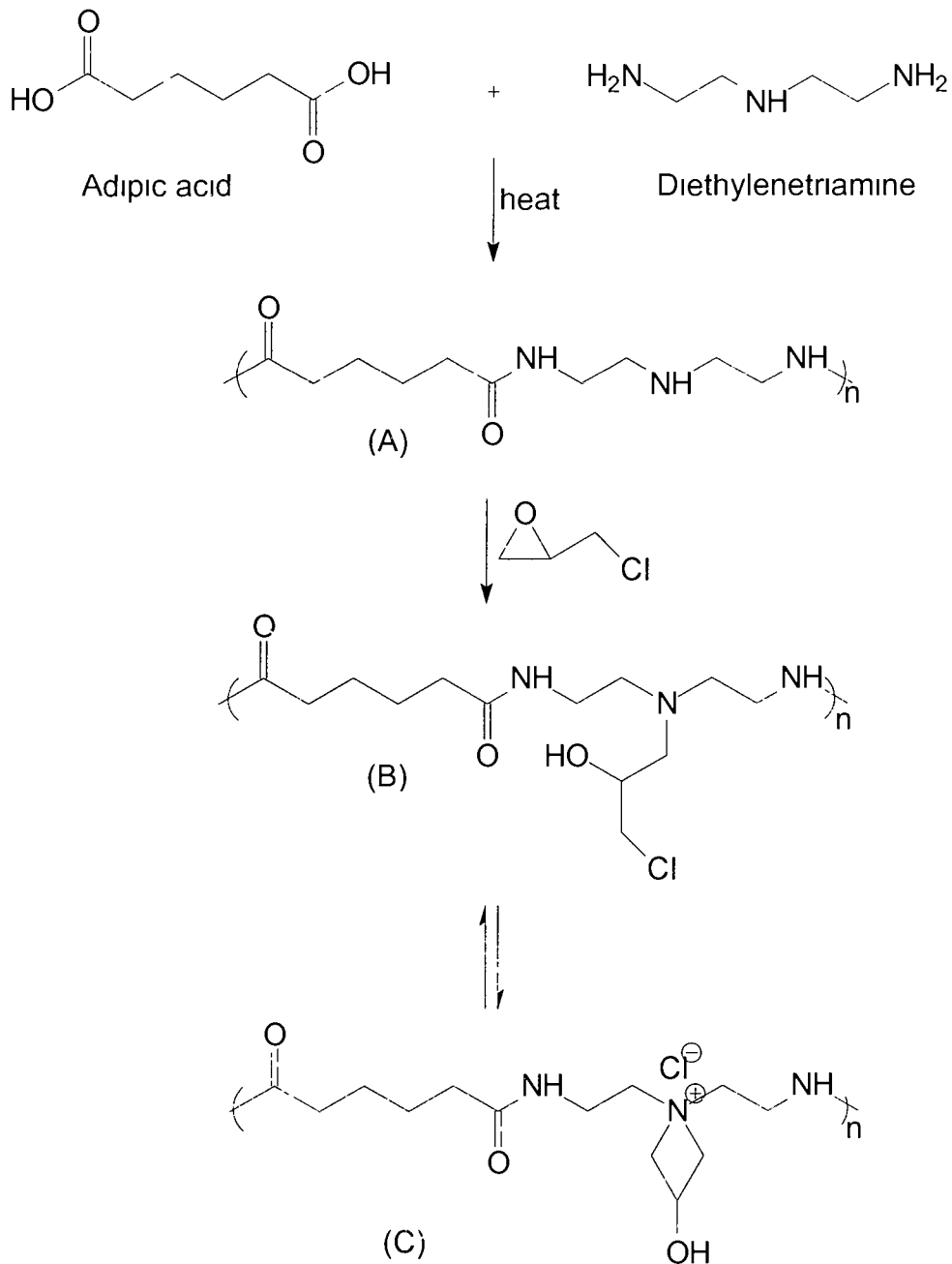
is the protection mechanism, i.e., the homo-crosslinking. However, an evidence has been found that the reinforcement mechanism also plays a role in the development of wet strengths [47]. The wet tensile failure was found to occur in the wet fiber wall rather than in the fiber-fiber interfaces [47]. This meant that the co-crosslinking between MF resins and fibers occurred during the curing process [47]. However, an extensive literature review reveals that most of the existing experimental data indicates that the protection mechanism rather than the reinforcement mechanism is mainly responsible for the development of wet strengths of MF-treated papers [48].

### 2.1.5.3 Polyamide-epichlorohydrin (PAE) resins

The production of polyamide-epichlorohydrin (PAE) resins has been described in many literatures [15, 26, 48, 50]. The process is shown in Figure 7.

Condensation of adipic acid with diethylenetriamine at high temperature produces a water-soluble polyamide polymer **A**. The secondary amino group of the polyamide **A** reacts with epichlorohydrin to give aminochlorohydrin **B** that forms a 3-hydroxyazetidinium group by self-alkylation. The hydroxyazetidinium group is the key functional group responsible for the reactivity and the cationic attribute of PAE resin **C**.

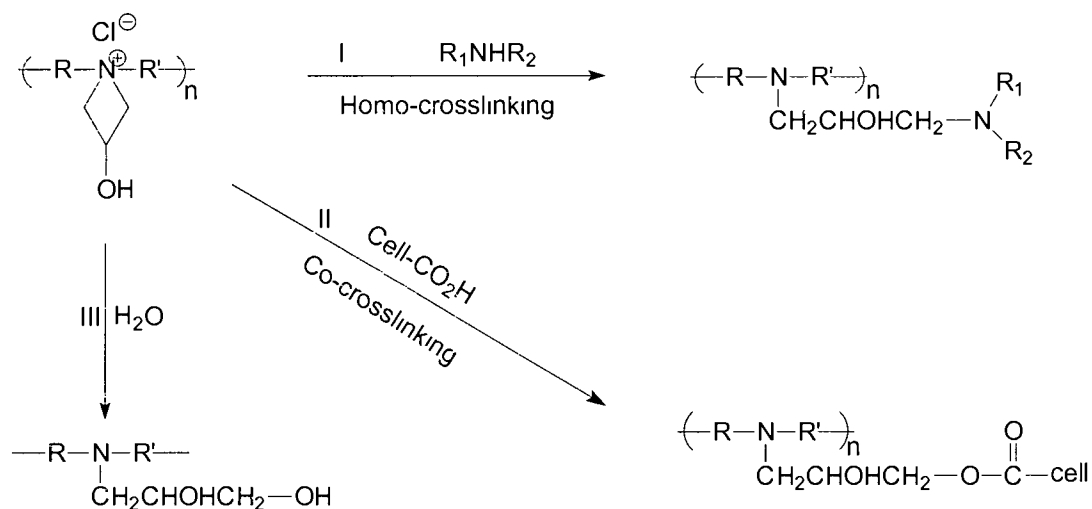




Adopted from Effects of a new compatibilizer system on the flexural properties of wood-polyethylene composites [56]

Figure 7 Production of PAE resins

Chemistry and wet-strength development mechanisms of PAE resins have been extensively studied [15, 23, 27, 28, 48, 49, 57]. There are two major reactions (I and II in Figure 8) that contribute to the development of wet strength in paper. The PAE resins can also slowly react with water (III in Figure 8) to form unreactive diol, thus decreasing the wet-strength enhancing ability of PAE resins.



Modified from Wet-strength chemistry [15]

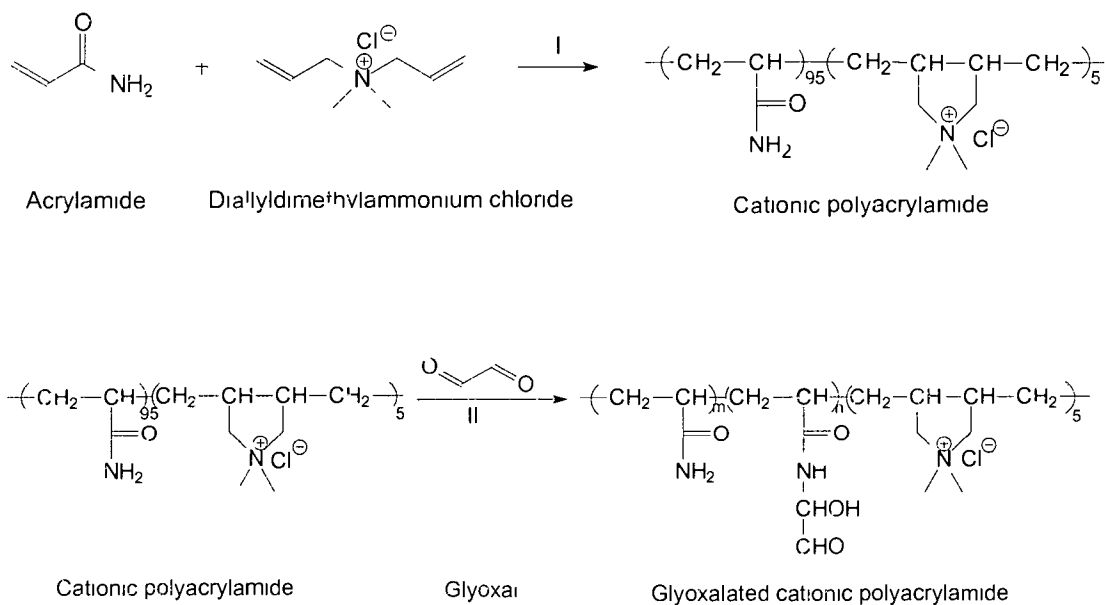
Figure 8 Reactions of the azetidinium group in PAE resins

In the reaction I, the azetidinium group in PAE resins reacts with remaining secondary amines of other resin molecules, resulting in homo-crosslinking (the protection mechanism). Bates found that there was no

chemical reaction between PAE resins and fibers [27] Espy and Rave confirmed that PAE resins did not react with hydroxyl groups of fibers, but suggested a mechanism that PAE resins first strengthened the fibers by forming ester linkages (the co-crosslinking and the reinforcement mechanism) with pulp carboxyl groups (reaction II in Figure 8) and then formed additional homo-crosslinking [28] At present, PAE resins are widely used in all types of wet strength paper products including household products, packaging materials, photographic papers, etc

#### 2.1.5.4 Glyoxal-polyacrylamide copolymer (GPA) resins

The preparation of glyoxal-polyacrylamide (GPA) wet strength resins are shown in Figure 9 [15-31] In the reaction I, a polyacrylamide copolymer is produced through the copolymerization of acrylamide and diallyldimethylammonium chloride that is a quaternary ammonium The molar ratio between acrylamide and diallyldimethylammonium chloride is about 95 to 5 [58] Further reaction (the reaction II in Figure 9) between the polyacrylamide copolymer and glyoxal gives GPA resins In this reaction, most, but not all, of the amide groups react with glyoxal [31]

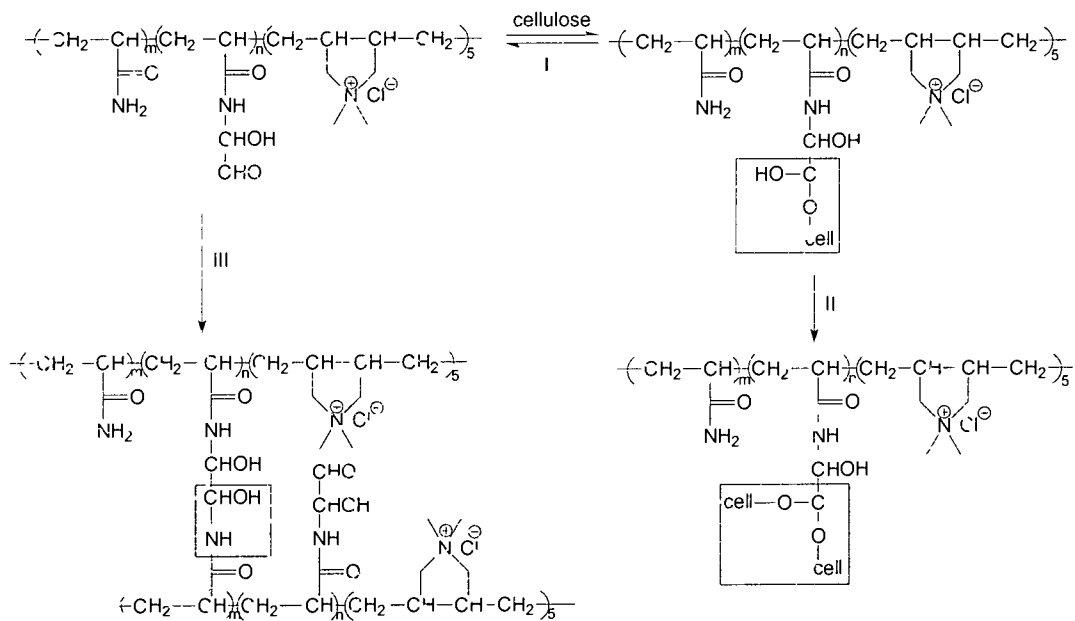


Adopted from Wet-strength chemistry [15]

Figure 9 Preparation of glyoxal-polyacrylamide resins

The wet strength development by GPA resins involves both the protection mechanism and the reinforcement mechanism. It has been suggested that the wet strengths imparted by GPA resins are primarily from the covalent fiber-resin-fiber hemiacetal or acetal bonds (co-crosslinking, reinforcement), which can be seen in the reactions I and II in Figure 10 [15, 31]. These bonds are formed by rapid reactions between aldehyde groups of GPA resins and hydroxyl groups of cellulosic fibers at neutral pH (5 - 8). The reactions are so fast that about 80–100% of the wet strength is developed on the paper machine. The protection mechanism is

also worthy of noting. The remaining amide groups of GPA resins homo-crosslink with aldehyde groups of other GPA resin molecules to form water-insoluble networks. The reaction is shown as the reaction III in Figure 10.



Modified from Wet-strength chemistry [15]

Figure 10 Wet strength chemistry of GPA

The reaction of GPA resins with hydroxyl groups of pulp fibers is reversible when water is present. Therefore, GPA-treated paper products, when wet will lose their wet strength gradually. As a result, GPA-treated paper has a high initial wet strength and the strength decays rapidly. This

is why GPA is called a temporary wet strength resin. The temporary wet strength of paper products is a desirable feature in some applications such as toilet paper. Toilet paper rapidly loses most of its strength in sanitary systems, which makes its disposal easy. Another advantage that a temporary wet strength resin has is that the treated paper is easier to repulp than PAE-treated paper.

## 2.2 Dry strength additives

### 2.2.1 Introduction

The dry strength is an inherent structural property of paper. It refers to the mechanical strength of a dry paper sheet. The dry strength of paper means different things to different people, depending upon the primary use for which the product is intended [59]. Thus, the dry strength may refer to the tensile strength, burst strength, fold endurance, etc.

There are several factors that contribute to the dry strengths of paper, including the strength of individual fibers, the strength of inter-fiber bonds, and the number of inter-fiber bonds [60]. It is well accepted that hydrogen bonding between hydroxyl groups on the surfaces of adjacent fibers in paper is the primary source for the dry strengths of paper [59]. In addition, the strengths of the fiber-to-fiber bonds are usually weaker than

those of individual fibers. Therefore, the most effective method to increase the dry strengths of paper is to increase sites for hydrogen bonding.

### 2.2.2 Refining versus dry strength additives

There are several ways to increase the sites for hydrogen bonding. The two most important ways are the refining of pulp and the addition of dry strength additives. Refining or beating perhaps is the most frequently used tool to increase the dry strengths of paper. During refining, pulp fibers are swollen, cut, macerated and fibrillated [61]. The refined pulp fibers have larger contact areas than unrefined pulp fibers. The refining process also creates tiny fibrils on the fiber surfaces and releases hemicelluloses [62]. The tiny fibrils and hemicelluloses are more flexible and compressible than cellulose fibers, thus providing more sites for hydrogen bonding. However, this method has some limitations. First, the refining slows down the water drainage on the wire, which may decrease the paper production rate. Second, the refining may significantly reduce the strength of individual fiber, thus lowering the tearing strength of the resulting paper to an unacceptable level. Thirdly, the refining increases the density of the paper and decreases the porosity and bulk of paper. The incorporation of certain chemical additives can maintain these important paper properties and increase the dry strength of paper products at the

same time. These chemical additives are called paper dry strength additives.

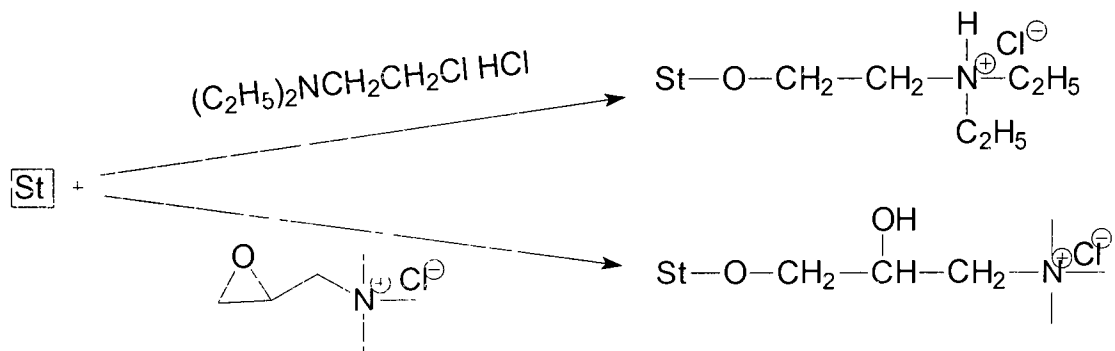
### 2.2.3 Commercial dry strength additives

The most commonly used commercial dry strength additives are cationic starch and polyacrylamide. All commercial dry strength additives are water soluble.

#### 2.2.3.1 *Cationic starch*

Starch is one of the oldest and the most commonly used additives to improve the dry strengths of paper products. In the past, unmodified or native starches were used in papermaking, but they were not used to any great extent because of the poor retention of native starches onto pulp fibers [63]. Since pulp fibers are normally negatively charged when suspended in water, the grafting of cationic charges onto the starches facilitates the sorption of the modified starches onto pulp fibers. The most commonly used reagents for grafting the cationic charges include N-(2-chloroethyl) diethylamine hydrochloride and glycidyltrimethylammonium chloride. The resulting modified starches are shown in Figure 11.





Modified from Starch in papermaking [63]

Figure 11 Grafting positive charges onto starches

It has been demonstrated that the enhancement of dry strength by cationic starches is due to the creation of new bonding sites on the fiber surfaces [60–64]. This means that the strength increase results from the additional hydrogen bonds among fibers. It is well known that hydrogen bonds are only effective in a very short distance (ca. 0.3 nm). There are a lot of voids and gaps in paper where hydrogen bonds cannot be formed among fibers. When cationic starches are used, they fill out the voids and gaps, thus strengthening the bonding among fibers through fiber-starch interactions.

### 2.2.3.2 Polyacrylamide resins

Polyacrylamide resins are the most commonly used synthetic dry strength resins because they have many advantages [62, 65]. First, they

have abundant primary amide groups that are capable of forming hydrogen bonds with pulp fibers. Second, polyacrylamide resins are completely water soluble, resulting in a good dispersion and sorption onto the pulp fibers. Finally, either anionic or cationic charges can be readily introduced onto Polyacrylamide.

The increase in the paper dry strength by polyacrylamide resins results from additional hydrogen bonds between the primary amide groups of polyacrylamide resins and the hydroxyl groups of pulp fibers [60, 62, 65]

### *2.2.3.3 Use of wet strength additives, glyoxal-Polyacrylamide (GPA) resins, as dry strength additives*

GPA resins not only work as good temporary wet strength additives, but also contribute significantly to the dry strength of GPA-treated papers. This is because the unreacted amide groups on the GPA resins can readily form hydrogen bonds with pulp fibers. The dry strength enhancement by GPA resins is largely independent of wet strength chemistry, and is typical of that obtained with the conventional polyacrylamide dry strength resins [31]. This provides GPA resins an advantage as a means of reducing cost and improving quality of those papers that require temporary wet strengths as well as sufficient dry strengths.

### 2.3 Issues associated with commercially used wet and dry strength resins

Initially, the standards for the cost, performance and easiness of handling for wet strength resins were based on the UF and MF resins. But these formaldehyde-based resins have many disadvantages. First of all, their applications require an acidic curing condition, which causes embrittlement and deterioration of paper, the corrosion of paper machines and the reduction of paper absorbency. The gradual shift of making paper under an acidic condition to under an alkaline condition has decreased the use of the formaldehyde-based wet strength resins. Another important threat to the continued use of UF and MF resins was the designation of formaldehyde as a possible carcinogen in 1978 [66]. In 1987, Occupational Safety and Health Administration (OSHA) revised standards for occupational exposure to formaldehyde [67]. As a consequence, the environmental concern of formaldehyde emission further reduced the application of formaldehyde-based resins in the pulp and paper industry. The world health organization recently concluded that formaldehyde is indeed a human carcinogen, which may result in banning the use of UF and MF resins. In addition, formaldehyde is derived from non-renewable natural gas. These formaldehyde-based resins, especially UF resins, are readily hydrolyzed at low pH leading to a gradual wet-strength reduction during storage. As a result in the last decade, the usage of formaldehyde-

based wet strength resins has declined significantly, and been almost completely replaced by PAE resins and GPA resins [2, 67]

PAE resins and GPA resins are formaldehyde-free and can be used as wet strength additives at neutral or alkaline conditions (pH 6-9). Consequently, the embrittlement and deterioration of paper and the corrosion of paper machines caused by the acid curing system are avoided. Being highly cationic charged, PAE and GPA resins are readily attracted onto the pulp fibers and can provide the same dry and wet strength at a lower dosage than UF and MF resins. However, these synthetic wet-strength resins contribute to stickies and contaminants in the recycling process, thus making the recycling of the treated papers difficult [5, 6]. The stickies can cause many problems, including the increased machine downtime, the reduced product quality, the increased replacement costs for wires and felts, the reduced efficiency of converting and printing operations, and the limited levels of fiber substitution [5]. Instead of recycling, most paper strengthened by synthesized resins is now burned. The paper recycling, as we know, is now a trend to reduce the cost of municipal solid waste treatment and to preserve forest resources. Efforts must be made to produce more recyclable paper. Meanwhile, the raw materials of PAE, GPA and polyacrylamide are from non-renewable petrochemicals. It is critical to develop new resins from renewable natural resources for the continued success and the sustainable growth of the

paper industry. There is an additional issue related to PAE resins, which is the introduction of new chlorinated organic compounds such as dichloropropanol and chloropropanediol [68-71]. These two compounds are the hydrolysis products of epichlorohydrin and are suspected carcinogens. Extensive efforts in modifying the production process of PAE resins in recent years have dramatically reduced the residual chlorinated organic compounds.

## 2.4 Wheat gluten

### 2.4.1 Basics of wheat gluten

Wheat is one of the major crops cultivated throughout the world [7]. Wheat plays a predominant role in the grain trade and is utilized as food (67%), feed (20%), seed (7%) and industrial products (6%) [72]. Wheat flour contains about 10% protein that is called wheat gluten [7]. Wheat gluten is commercially prepared by removing starch from wheat flour and carefully drying the remaining protein in such a manner that the native properties of the wheat gluten are retained [8]. Most of the wheat gluten utilized by US processors goes into high protein bread items such as bagels, hearth breads, multi-grain breads, etc. because wheat gluten can add strength and elasticity to the dough [9, 10]. Also, wheat gluten is used as an essential ingredient for producing restructured meaty chunks from

meat by-products because it is able to bind with and restructure proteins of meat, poultry and fish muscle

The consumption of wheat gluten in the US has risen drastically in 1990s due to two factors population growth and increased consumer preferences for healthy grain-based products The US International Trade Commission (USITC) reported that domestic wheat gluten utilization increased from roughly 255 million lb in 1993 to approximately 299 million lb in 1997 and imports of wheat gluten rose from 128 million lb in 1993 to 177 million lb in 1997 [10] Driven by the great demand, the wheat gluten processing capacity was rapidly increased by 62% during the 1990s However, in the meantime, wheat gluten import was also increased from European Union (EU), Australia, and other countries The rapidly grown import of foreign wheat gluten drove down the domestic prices of wheat gluten and greatly damaged the domestic wheat gluten industry Only 44.5% of the wheat gluten processing capacity was utilized in 1997, as compared with 78.4% in 1993 [10] Since the production of wheat gluten increases continuously and the traditional market for wheat gluten as food additives has been saturated, the development of value added products from wheat gluten for non-food applications is one of the key efforts to make the wheat gluten industry competitive[11]

## 2.4.2 The chemical and physical properties of wheat gluten

Typically, wheat gluten contains a large amount of amide groups and relative small amounts of amino groups in lysine and arginine moieties and the mercapto group in cysteine moiety (Table 1) [11]. In this research, the amino groups are expected to react with glycidyltrimethylammonium chloride (GTA) to graft positively charged ammonium group onto wheat gluten. The mercapto group is also a strong nucleophile. However, there is little free mercapto group in wheat gluten because it readily forms a disulfide bond [11]. Cleavage of the disulfide bond is needed before the mercapto group becomes available for a chemical modification.

Table 1. The chemical composition of wheat gluten

Functional group	Amount (mol %)
Amide	30
Carboxylic acid	5
Phenol	2.5
Amino groups	5
Sulfur	2

Adopted from modification of wheat gluten for nonfood applications [11]

Wheat gluten is primarily a mixture of gliadin and glutenin, which can be separated by their different solubilities in 70% ethanol. Gliadin is the fraction soluble in 70% ethanol and glutenin is the insoluble fraction. The gliadin and glutenin have a similar amino acid composition [73]. However, gliadin and glutenin have very different physical properties, which can be attributed to their different molecular sizes [74]. The gliadin has lower molecular weight than glutenin. Gliadin samples from different cultivars have very similar molecular weights (ca 40 kDa). On the other hand, glutenin samples from different cultivars have widely variable molecular weights, ranging from 2,000 kDa to 3,000 kDa [75]. Gliadin contains exclusively intra-molecular disulfide bonds, whereas glutenin has both intra molecular and inter-molecular disulfide bonds that link protein chains into high-molecular-weight polymers [74].

A number of methods have been investigated for the modification of wheat gluten for non-food applications [11, 76-79]. For example, the enzyme transglutaminase has been used to covalently cross-link wheat gluten [77]. A ultrasonic treatment was used to break down the large glutenin and to improve the solubility of wheat gluten [78]. Small alkyl groups were grafted onto gluten backbone by esterification or by using aldehyde to increase water resistance [76]. Crosslinking was formed by covalently linking protein chains to improve the strengths of products made out of wheat gluten [11, 76, 79]. Deamidation has been used to convert



the large number of amide groups on glutamine to carboxylic acid groups to improve the solubility of wheat gluten [76, 78] In this study, we aimed to introduce some positively charged groups onto the basic residues of wheat gluten to make it more water soluble

#### 2.4.3 Non-food applications of wheat gluten

Wheat gluten itself has many unique properties that can be utilized for non-food applications [11, 72] Wheat gluten is abundant, readily available, renewable and biodegradable In addition, wheat gluten has good adhesive, cohesive and film forming properties For example, films produced from wheat gluten have good mechanical and gas-barrier characteristics Many non-food applications such as adhesives, paper coatings thermoplastic products, and wheat-based cosmetics have been investigated [11, 76, 80]

#### 2.5 Development of temporary wet strength and dry strength resins from wheat gluten

This research is about the development of GPA-like dry/wet strength additives from wheat gluten As described previously, GPA is a reaction product of Polyacrylamide and glyoxal The primary amide group in Polyacrylamide is the functional group that reacts with glyoxal, serves as

crosslinking sites during the development of wet strength in paper, and forms hydrogen bonds with hydroxyl groups of pulp fibers during the development of dry strength. In wheat gluten, about one third of amino acids is glutamine whose side chain contains a primary amide group [11]. Both Polyacrylamide and wheat gluten are polymeric materials and contain high amounts of primary amide groups. In this thesis, we studied whether wheat gluten could be converted to a GPA-like paper additive.

Gliadin has a lower and more uniform molecular weight than glutenin, and can be more easily handled and modified than glutenin. Therefore gliadin was selected for this pioneer study. As described previously, gliadin and glutenin have similar amino acid compositions [73]. Results from this study should be useful for the modification of glutenin or whole gluten if the molecular weight of glutenin can be reduced. In this research, the modification of gliadin involves the grafting of a cationic group and the subsequent reaction with glyoxal.

## Chapter 3 Experiment

### 3.1 Materials

Bleached hardwood pulp, bleached softwood kraft pulp, and Hercobond<sup>®</sup> 1000 were provided by Hercules Inc (Wilmington, DE). Wheat gluten was provided by MGP Ingredients, Inc (Atchison, KS). Glycidyltrimethylammonium chloride (GTA), Polyacrylamide and glyoxal were purchased from Sigma-Aldrich Inc (Milwaukee, WI).

### 3.2 Separation of gliadin from gluten

Gliadin was isolated from gluten according to a literature procedure [81]. A mixture of wheat gluten (50 g) and 0.2% sodium chloride solution (500 mL) was stirred at room temperature for 60 min and then centrifuged (2000 g) for 20 min to remove the residual starch. The precipitate was mixed with 0.2% sodium chloride solution (500 mL) stirred at room temperature for 30 min, and centrifuged (2000 g) for 20 min. The resulting precipitate was dispersed in 70% (v/v) ethanol (1000 mL) under mechanic stirring. The mixture was adjusted to a pH value of 6.4 by adding 1 N NaOH solution and then placed in a refrigerator (1.5 °C) overnight. The mixture was centrifuged (2000 g) for 20 min. The resulting supernatant, the gliadin fraction, was concentrated with a rotavapor at 50 °C to remove ethanol. The concentrated solution was placed in a refrigerator overnight.

and the gliadin was precipitated out. The precipitate was collected through filtration and freeze-dried to provide gliadin (6.8 g).

### 3.3 Modification of gliadin with GTA

Gliadin (2.0 g) was dissolved in 70% (v/v) ethanol (20 mL) and the solution was adjusted to pH 9.5 by triethylamine. GTA (1.5 g, 75% based on the dry weight of gliadin) was added into the gliadin solution dropwise at 70 °C and the resulting reaction solution was stirred at 70 °C for 8 h. The reaction solution was then evaporated under a diminished pressure to remove ethanol. The resulting GTA-modified gliadin (GTA-gliadin) solution was mixed with deionized water (200 mL) and then concentrated to 5 mL with an Amicon® membrane concentrator with a 5 kDa molecular weight cutoff membrane. The concentrated gliadin solution was diluted with deionized water (195 mL) and concentrated again to 5 mL. Such dilution-concentration operation was repeated three times. The resulting GTA-gliadin was then freeze-dried to provide dry GTA-gliadin. This procedure was used to prepare other GTA-gliadin products through uses of different GTA/gliadin ratios (30%, 60% and 90% of GTA based on the dry weight of gliadin) or different reaction times (4 h, 6 h and 10 h).

### 3.4 Reaction between Polyacrylamide and GTA

An aqueous solution of Polyacrylamide (1.0 g) and water (20 mL) was mixed with GTA (0.75 g) and the reaction mixture was stirred for 10 h at 70 °C and pH 9.5. The reaction solution was poured into methanol (100 mL) under stirring and precipitation occurred. The precipitate (Polyacrylamide-GTA) was washed with excess methanol to remove unreacted GTA and other by-products, and dried in an oven at 65 °C for 1 h to evaporate methanol. The dry Polyacrylamide-GTA was characterized with nuclear magnetic resonance (NMR) spectrometry.

### 3.5 Characterization of GTA-gliadin samples

The freeze-dried GTA-gliadin samples and Polyacrylamide-GTA samples were characterized with NMR. <sup>1</sup>H-NMR spectra of the GTA-gliadin samples in DMSO/D<sub>2</sub>O (v/v, 60/40) and Polyacrylamide-GTA samples in D<sub>2</sub>O were obtained with 400 MHz NMR spectrometer in the Department of Chemistry at Oregon State University.

### 3.6 Preparation of GTA-gliadin-glyoxal resins

Glyoxal (0.055 g, 30% based on the dry weight of GTA-gliadin) was added into a solution of GTA-gliadin (0.185 g) and water (1.05 mL). The

pH value of the reaction solution was adjusted to 9 ~ 10 by adding 1 N NaOH solution under magnetic stirring. Due to the homo-crosslinking reaction, the viscosity of the reaction solution increased slowly at the beginning and became faster and faster later on. When a dramatic viscosity increase was observed, the reaction was quenched by adjusting pH to 3 ~ 4 with 10% sulfuric acid. The resulting GTA-gliadin-glyoxal solution was stored in a refrigerator and used for making handsheets. Other GTA-gliadin-glyoxal products were prepared with this procedure through use of different glyoxal dosages (10%, 20% and 40% based on the dry weight of GTA-gliadin).

### 3.7 Preparation of handsheets

Handsheets with a grammage of 60 g/m<sup>2</sup> were made from bleached kraft pulps. Pulp boards (12 g of softwood kraft pulp and 12 g of hardwood kraft pulp) were soaked in water (500 mL) overnight and then torn into pieces with the size of about 30 x 30 mm. The soaked pulps and wet strength resins were added into a disintegrator together. The mixture were diluted to 1.2% consistency with deionized water, and disintegrated at 3000 rpm for 10 min. The disintegrated stock was then used to make handsheets according to the Technical Association of the Pulp and Paper

Industry (TAPPI) standard T205 sp-95. The wet handsheets were fitted into drying rings and dried in an oven (103 °C) for 2 h.

### 3.8 Preparation of test specimens

Three strips with the width of 2.54 cm were cut from each handsheet (159 mm in diameter). These specimens were conditioned at 23 °C and 50% relative humidity overnight according to the TAPPI test standard T-402.

### 3.9 Evaluation of paper strengths

Dry tensile strength and wet tensile strength of paper sheets that were treated with a gliadin-GTA-glyoxal resin, and Hercobond<sup>®</sup> 1000, separately, were evaluated according to the TAPPI standard T 494 om-96 and T 456 om-87, respectively.

The tensile strength of paper sheets is defined as the maximum tensile force required for the rupture of a test specimen divided by the width of the test specimen under prescribed conditions. Considering the influence of grammage on the tensile strength, the tensile index was used instead of tensile strength. Tensile index is defined as the tensile strength divided by the grammage. The unit for tensile index is N m/g. For the evaluation of wet tensile strength, specimens were soaked in deionized

water for 1 min, 10 min and 2 h, respectively, and then evaluated for the tensile strength, using Sintech machine (Figure 12)

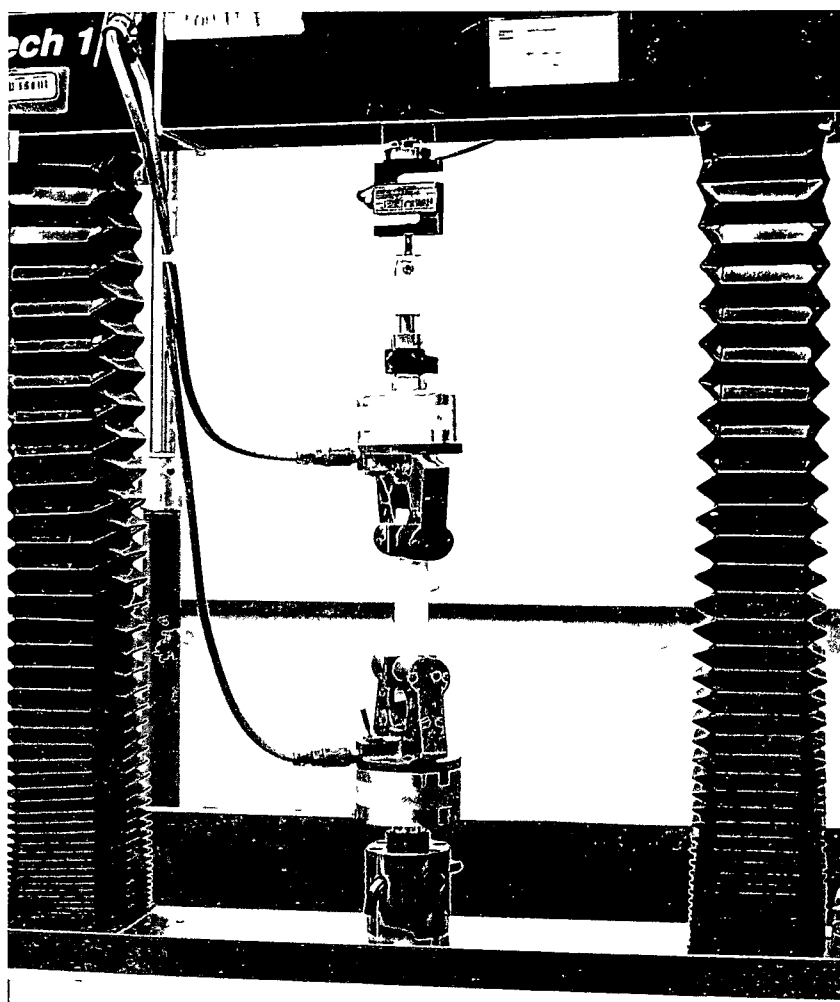


Figure 12 The Sintech machine used for the evaluation of tensile strengths

All data were analyzed with standard two-sample t-test using S-plus® statistic software (Edition version 6 1 2, Lucent Technologies Inc ) at



a 95% confidence level    The  $p$  values are included in the Results and Discussion chapters

## Chapter 4 Results

### 4.1 Preparation of GTA-gliadin-glyoxal resins

Gliadin is composed of 21 different amino acids [73]. The polar functional groups that can potentially react with GTA mainly include amino groups in the side chains of lysine and arginine. The proposed reactions are shown in Figure 13.

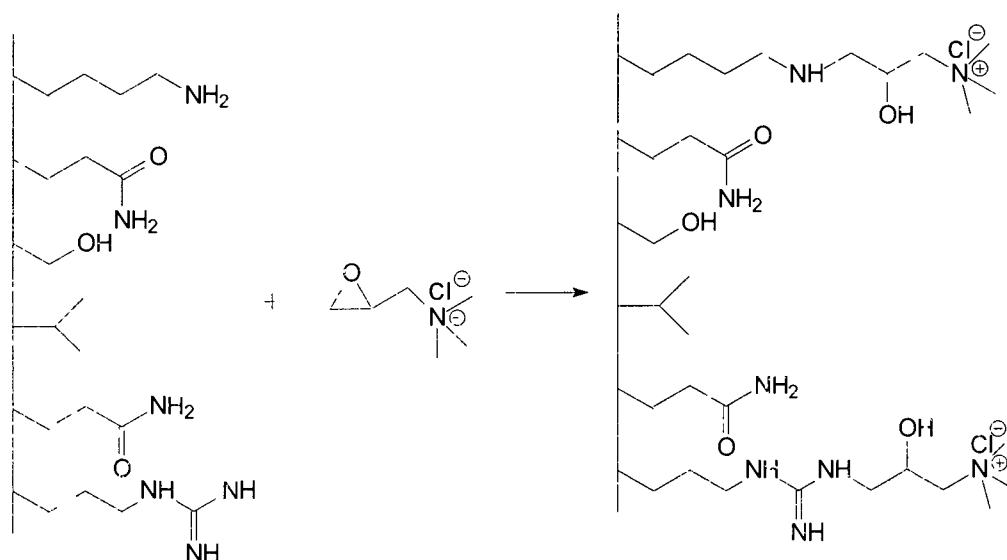


Figure 13 Proposed reactions between GTA and gliadin

The  $^1\text{H}$  NMR spectra of gliadin and GTA-gliadin show a strong extra peak at 3.1 ppm (the methyl groups in GTA) when compared with gliadin, which indicates that GTA was indeed covalently attached to gliadin (Figure 14).

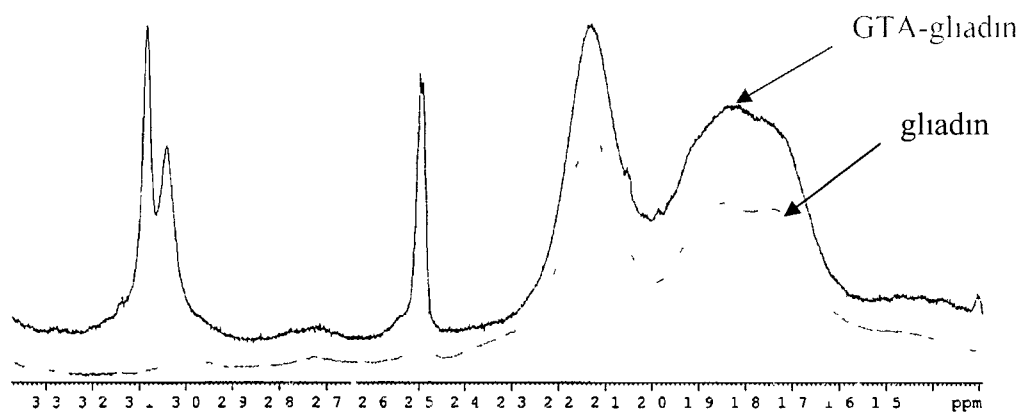


Figure 14  $^1\text{H}$  NMR spectra of gliadin and GTA-gliadin

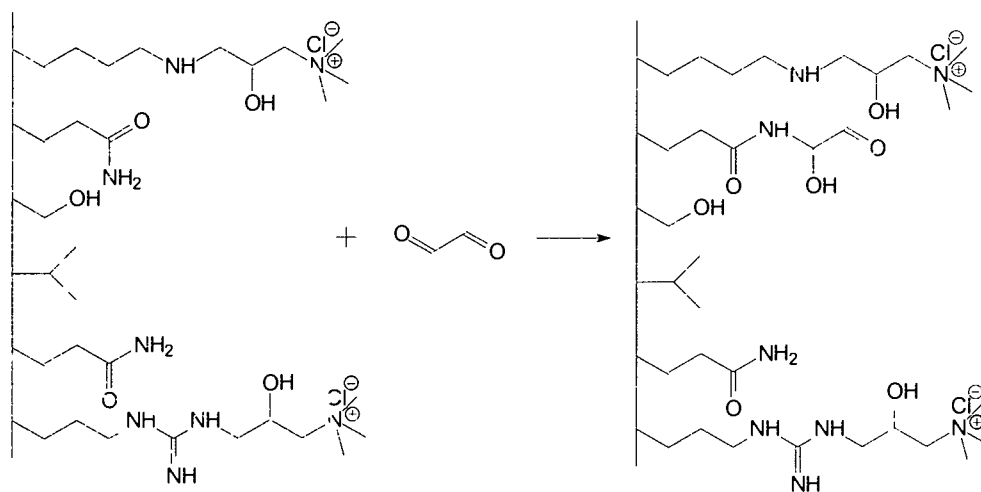


Figure 15 Representative reactions between glyoxal and GTA-gliadin

The representative reactions between GTA-gliadin and glyoxal are shown in Figure 15. An abrupt increase in the viscosity of the reaction solution was observed during the reaction between GTA-gliadin and glyoxal. The time ( $T_v$ ) required for the abrupt increase in the viscosity was dependent upon the GTA dosage in the reaction between GTA and gliadin (Table 2). The higher the GTA dosage the longer the  $T_v$  (Table 2). It is worthy of noting that the  $T_v$  for 90 wt% GTA was much longer than that for other GTA dosages.

Table 2 Influence of the GTA dosage on  $T_v$

<i>The GTA dosage based on gliadin</i>	$T_v$
<i>(wt%)</i>	<i>(min)</i>
30	1
60	2.5
75	6
90	20

#### 4.2 Effects of the GTA dosage in the GTA-gliadin reactions on the tensile strengths of the treated paper

Compared with the control, GTA-gliadin-glyoxal resins resulted in a higher dry tensile index ( $p = 0$ , Figure 16). The dry tensile index increased when the GTA dosage in the reaction of GTA and gliadin was increased from 30 wt% to 75 wt% ( $p = 0.0002$  for the increase from 30 wt% to 60 wt% and  $p = 0$  for the increase from 60 wt% to 75 wt%, Figure 16). When the GTA dosage was further increased from 75 wt% to 90 wt%, the dry tensile index decreased ( $p = 0$ , Figure 16).

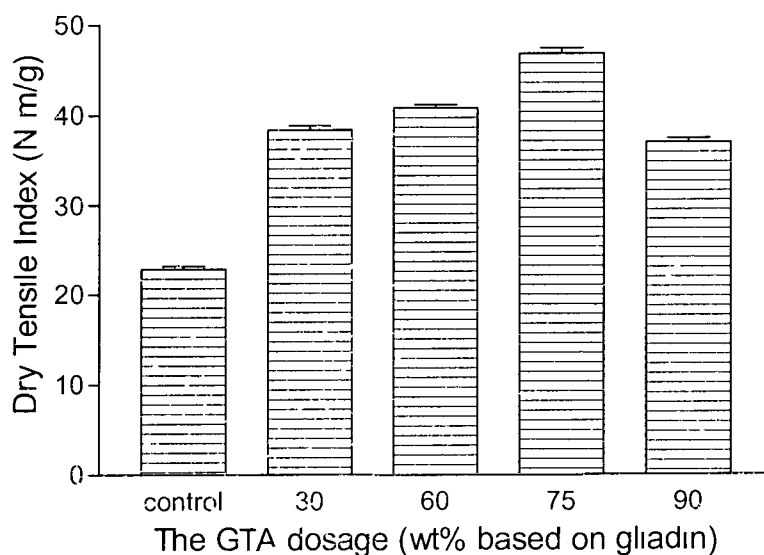


Figure 16 Effect of the GTA dosage on the dry tensile strength of the treated paper (Reaction conditions in the reaction between GTA and gliadin: 70°C, 8 h. Reaction conditions in the reaction between GTA-gliadin and glyoxal: 30 wt% glyoxal based on the dry weight of GTA-gliadin). The data are the mean of 10 replicates and the error bar represents one standard error of the mean.

The relative wet strength is described as the ratio of the wet tensile index to the dry tensile index of the same treated paper. For the three soaking times (1 min, 10 min, and 2 h), the effects of the GTA dosage on the relative wet strength had the same trend (Figure 17). More specifically, for each soaking time, the relative wet strength increased when the GTA dosage was increased from 30 wt% to 75 wt%. The relative wet strength decreased for each soaking time when the GTA dosage was further increased from 75 wt% to 90 wt%. It appeared that 75 wt% GTA was the optimum dosage for enhancing the dry and relative wet strengths. For each GTA dosage the relative wet strength at the soaking time of 10 min was the same or slightly lower than that at the soaking time of 1 min ( $p = 0.8888$  for 30 wt% GTA,  $p = 0.0172$  for 60 wt% GTA,  $p = 0.0182$  for 75 wt% GTA and  $p = 0.0955$  for 90 wt% GTA), which indicated that GTA-gliadin-glyoxal resins were effective wet strength additives. When the soaking time was increased from 10 min to 2 h the relative wet strength significantly decreased for each dosage ( $p = 0.0004$  for 30 wt% GTA and  $p = 0$  for other GTA dosages, Figure 17). This implied that GTA-gliadin-glyoxal resins were temporary wet strength additives.

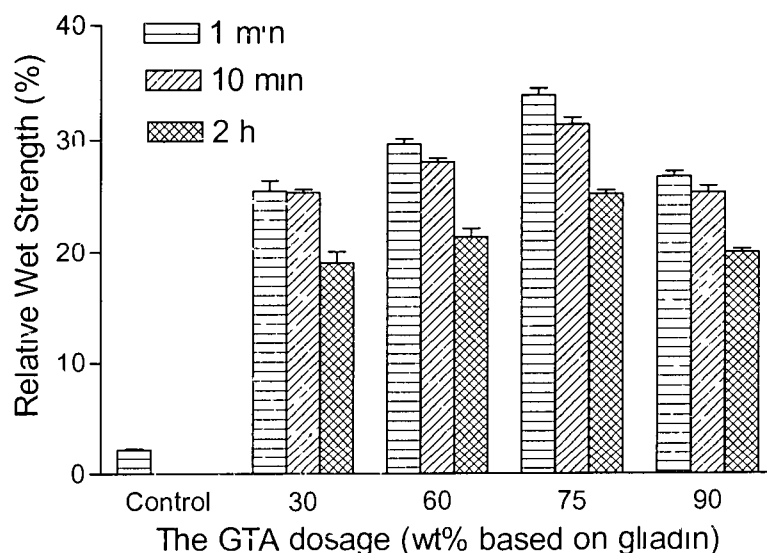


Figure 17 Effect of the GTA dosage on the relative wet tensile strength of the treated paper (Reaction conditions in the reaction between GTA and gliadin 70°C, 8 h Reaction conditions in the reaction between GTA-gliadin and glyoxal 30 wt% glyoxal based on the dry weight of GTA gliadin 1 0 min soaking time (□), 10 0 min soaking time (▨), 2 0 h soaking time (▩)) The data are the mean of 10 replicates and the error bar represents one standard error of the mean

#### 4 3 Effects of the reaction time between GTA and gliadin on the tensile strengths of the treated paper

The dry tensile strengths are statistically the same when the reaction was increased from 4 h to 6 h ( $p = 0.206$ , Figure 18) Further increase the reaction time to 8 h, the dry tensile index increased notably ( $p = 0.0135$ ) However the dry tensile index significantly decreased when the reaction time was further increased from 8 h to 10 h ( $p = 0$ , Figure 18)

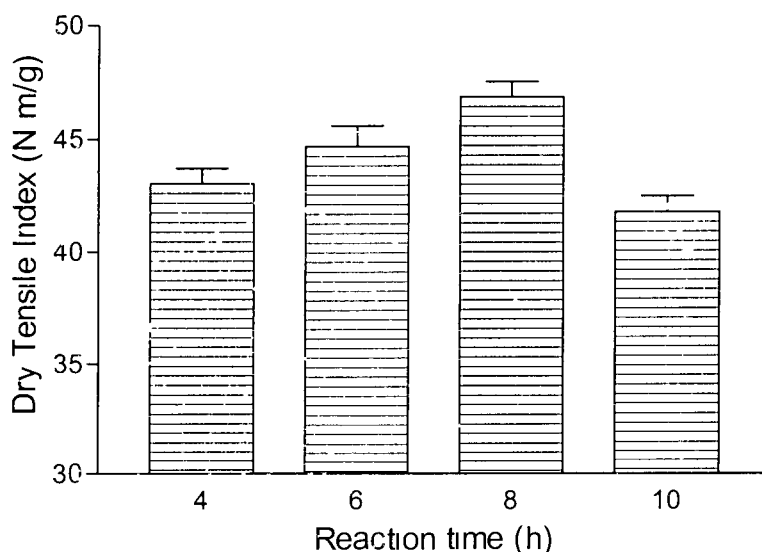


Figure 18 Effect of the reaction time of the reaction between GTA and gliadin on the dry tensile strength of the treated paper (Reaction conditions in the reaction between GTA and gliadin 75 wt% GTA based on the dry weight of gliadin, 70°C Reaction conditions in the reaction between GTA-gliadin and glyoxal 30 wt% glyoxal based on the dry weight of GTA-gliadin) The data are the mean of 10 replicates and the error bar represents one standard error of the mean

At the soaking time of 1 min, the relative wet strength gradually increased when the reaction time was increased from 4 h to 8 h and then decreased when the reaction time was further increased from 8 h to 10 h ( $p = 0.0026$ , Figure 19). At the soaking time of 10 min, the relative wet strength significantly increased when the reaction time was increased from 4 h to 6 h ( $p = 0.0001$ ). No significant change of the relative wet strength was observed when the reaction time was increased from 6 h to 8 h ( $p =$



0.2901, Figure 19) However, further increase in the reaction time from 8 h to 10 h resulted in a considerable decrease in the relative wet strength ( $p = 0.0002$ , Figure 19) At the soaking time of 2 h, the relative wet strength at the 8 h reaction time was noticeably higher than those at other reaction times (Figure 19) At the 2 h soaking time, the relative wet strengths were statistically the same at the reaction times of 4 h, 6 h and 10 h ( $p = 0.6311$  between 4 h and 6 h,  $p = 0.2181$  between 6 h and 10 h Figure 19)

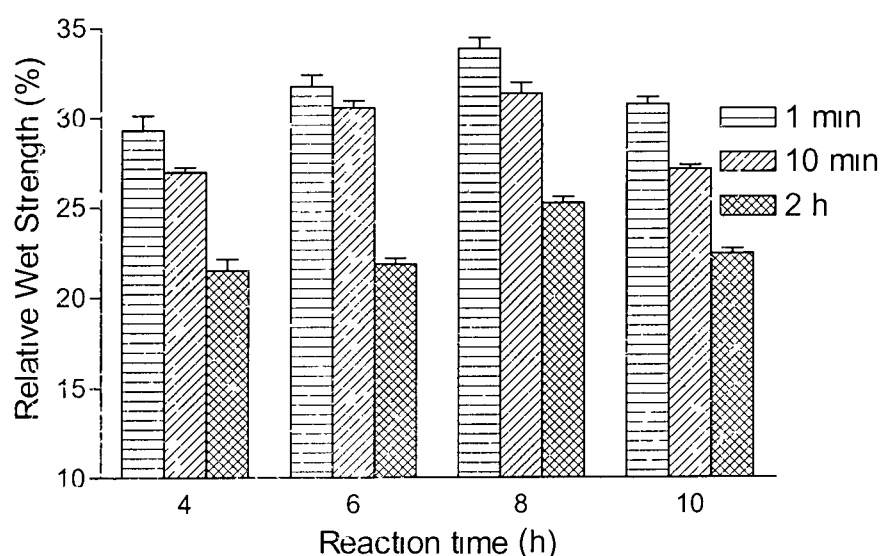


Figure 19 Effect of the reaction time of the reaction between GTA and gliadin on the relative wet tensile strength of the treated paper (Reaction conditions in the reaction between GTA and gliadin: 75 wt% GTA based on the dry weight of gliadin, 70°C. Reaction conditions in the reaction between GTA-gliadin and glyoxal: 30 wt% glyoxal based on the dry weight of GTA-gliadin. 1.0 min soaking time (▨), 10.0 min soaking time (▩), 2.0 h soaking time (▧)). The data are the mean of 10 replicates and the error bar represents one standard error of the mean.

It appeared that 8 h was the optimum reaction time for enhancing the dry and relative wet strengths

#### 4.4 Effects of the glyoxal dosage on the tensile strengths of the treated paper

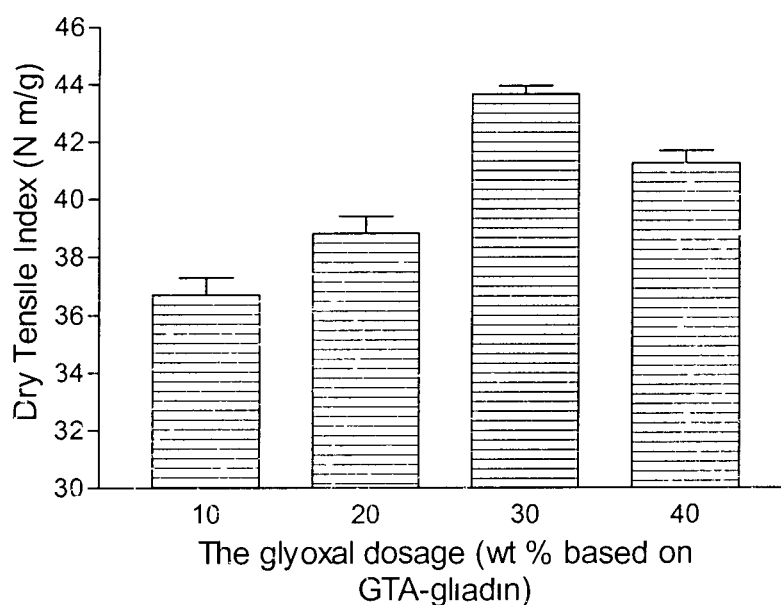


Figure 20 Effect of the glyoxal dosage on the dry tensile strength of the treated paper (Reaction conditions in the reaction between GTA and gliadin 75 wt% of GTA based on dry weight of gliadin, 70°C, and 8 h) The data are the mean of 10 replicates and the error bar represents one standard error of the mean

The dry tensile index increased when the glyoxal dosage in the reaction between glyoxal and GTA-gliadin was increased from 10 wt% to 30 wt% ( $p = 0.0249$  for increase from 10% to 20% and  $p = 0$  for increase from 20% to 30%, Figure 20). However, the dry tensile index decreased when the glyoxal dosage was further increased from 30 wt% to 40 wt% ( $p = 0.0004$ , Figure 20). At each soaking time, the relative wet strength increased when the glyoxal dosage was increased from 10 wt% to 30 wt% (Figure 21). When the glyoxal dosage was further increased from 30 wt% to 40 wt%, the relative wet strength decreased at the soaking times of 1 min and 10 min ( $p = 0.0061$  for the soaking time of 1 min and  $p = 0.0062$  for the soaking time of 10 min), and remained statistically the same at the soaking time of 2 h ( $p = 0.5954$ , Figure 21). At each glyoxal dosage, the relative wet strength decreased with increasing the soaking time (Figure 21). It appeared that the optimum glyoxal dosage was 30 wt% based on the dry weight of GTA-gliadin.

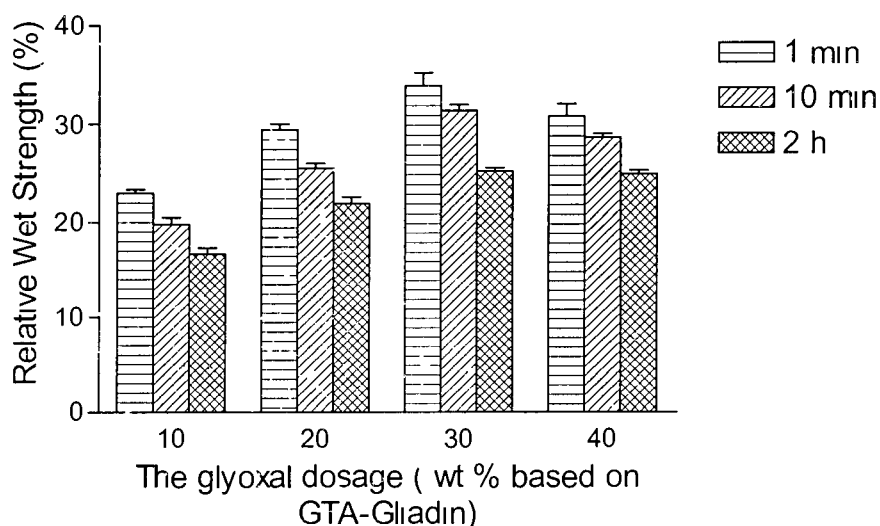


Figure 21 Effect of the glyoxal dosage on the relative wet tensile strength of the treated paper (Reaction conditions in the reaction between GTA and gliadin 75 wt% of GTA based on dry weight of gliadin, 70°C, and 8 h 1 0 min soaking time (□), 10 0 min soaking time (▨), 2 0 h soaking time (▩)) The data are the mean of 10 replicates and the error bar represents one standard error of the mean

#### 4.5 Effects of the dosages of wet strength additives on the tensile strengths of treated paper

The dry strength index of paper treated with the gliadin-GTA-glyoxal resin increased when the resin dosage was increased from 0.5 wt% to 1.0 wt% ( $p = 0$ , Figure 22). However, the dry strength index was statistically the same when the resin dosage was further increased from 1.0 wt% to 1.5 wt% ( $p = 0.1992$ ). For the paper treated with a commercial GPA resin, the dry tensile index kept increasing when the resin dosage was increased from 0.5 wt% to 1.5 wt% ( $p = 0.0009$  for the increase from

0.5 wt% to 1.0 wt% and  $p = 0$  for the increase from 1.0 wt% to 1.5 wt%, Figure 22) At the resin dosages of 0.5 wt% and 1.5 wt%, the GTA-gliadin-glyoxal resin resulted in a lower dry tensile index than the GPA resin ( $p = 0$  for both dosages) At the resin dosage of 1.0 wt% the GTA-gliadin-glyoxal resin was comparable with the GPA resin in terms of enhancing the dry tensile index ( $p = 0.2858$ , Figure 22)

At each soaking time, 0.5 wt% GPA resulted in much a higher relative wet strength than 0.5 wt% GTA-gliadin-glyoxal (Figure 23) At the 1.0 wt% dosage level, the relative wet strength of paper treated with the GTA-gliadin-glyoxal resin was slightly lower than that of paper treated with the GPA resin at the soaking time of 1 min or 10 min ( $p = 0.0062$  for the soaking time of 1 min and  $p = 0.0025$  for the soaking time of 10 min, Figure 23) However, the relative wet strength for the GPA-treated paper was significantly higher than that for the GTA-gliadin-glyoxal-treated paper at the soaking time of 2 h ( $p = 0$ , Figure 23) At the 1.5 wt% dosage level, the GPA resin resulted in a higher relative wet strength at each soaking time than the GTA-gliadin-glyoxal resin ( $p = 0$  for the soaking time of 1 min,  $p = 0.0002$  for the soaking time of 10 min and  $p = 0$  for the soaking time of 2 h, Figure 23)

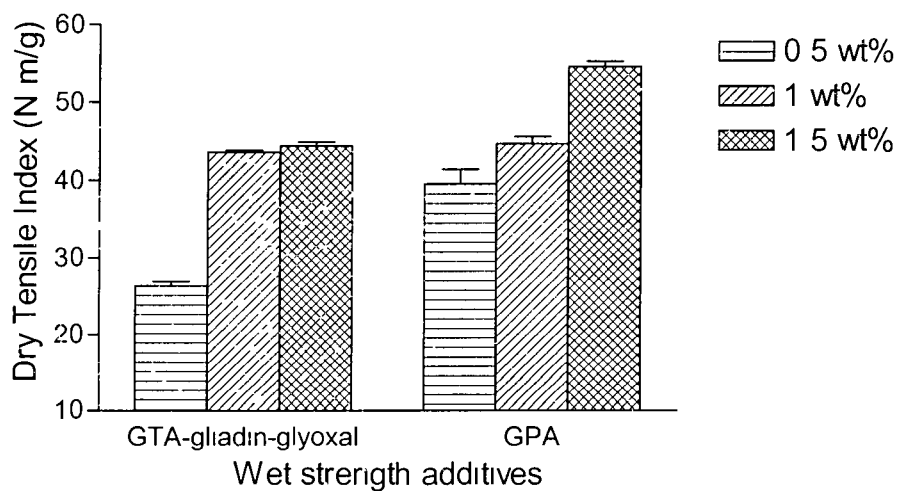
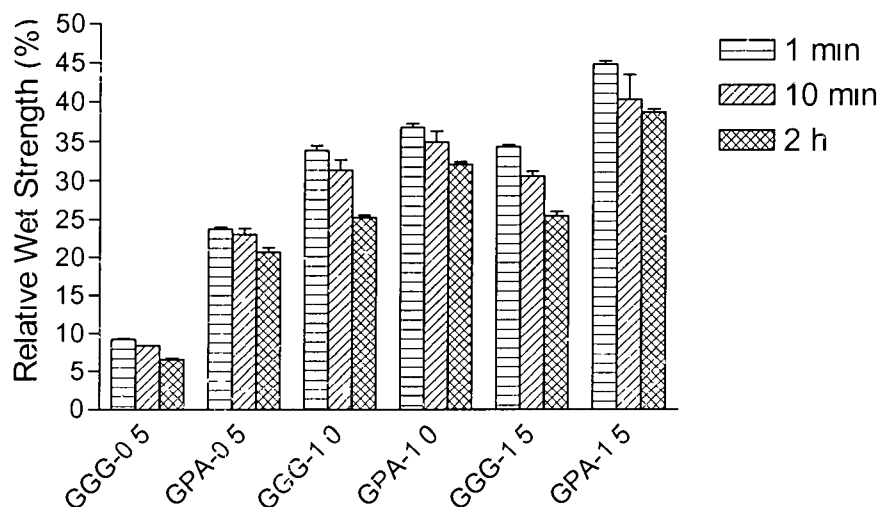


Figure 22 Comparison of the GTA-gliadin-glyoxal resin and the GPA resin for their effects on dry tensile strength of the treated paper (Preparation of the GTA-gliadin-glyoxal resin reaction conditions in the reaction between GTA and gliadin 75 wt% of GTA based on dry weight of gliadin, 70°C, and 8 h Reaction conditions in the reaction between GTA-gliadin and glyoxal 30 wt% glyoxal based on the dry weight of GTA-gliadin 0.5 wt% of a wet strength additive based on dry pulp (▨), 1.0 wt% of a wet strength additive based on dry pulp (▩), 1.5 wt% of a wet strength additive based on dry pulp (▧)) The data are the mean of 10 replicates and the error bar represents one standard error of the mean



Wet strength additives and their dosages

Figure 23 Comparison of the GTA-gliadin-glyoxal resin and the GPA resin for their effects on the relative wet tensile strength of the treated paper (Preparation of the GTA-gliadin-glyoxal resin reaction conditions in the reaction between GTA and gliadin 75 wt% of GTA based on dry weight of gliadin, 70°C, and 8 h Reaction conditions in the reaction between GTA-gliadin and glyoxal 30 wt% glyoxal based on the dry weight of GTA-gliadin GTA-gliadin-glyoxal resin (GGG), 10 min soaking time (□), 100 min soaking time (▨), 20 h soaking time (▩)) The data are the mean of 10 replicates and the error bar represents one standard error of the mean

## Chapter 5 Discussion

Pulp fibers are negatively charged under alkaline conditions. The goal of modifying gliadin with GTA was to graft the positively charged quaternary ammonium group onto gliadin. When the GTA/gliadin ratio and the reaction time increased, a higher amount of the positively charged ammonium group was grafted onto gliadin, making the modified gliadin more substantive to negatively charged pulp fibers. Gliadin is not very soluble in water. Grafting the positively charged ammonium group increased the water-solubility of the modified gliadin, thus facilitating the uniform dispersion of the modified gliadin onto pulp fibers. The increased amount of the positive charge and the increased water-solubility may account for the facts that the increase in the GTA dosage from 30 wt% to 75 wt% and the increase in the reaction time from 4 h to 8 h both enhanced the dry and wet strengths of the treated paper (Figures 16, 17, 18 and 19).

The reaction between the primary amide group of Polyacrylamide and GTA has been reported in a patent, although the primary amide group is a very weak nucleophile [82]. The  $^1\text{H}$  NMR spectrum of the Polyacrylamide-GTA that was prepared in our study under the reaction conditions similar to those for the gliadin/GTA reaction showed an extra peak at 3.25 ppm when compared with Polyacrylamide, which further demonstrated that the reaction between a primary amide and GTA did



occur. Therefore, the primary amide group of the glutamine moiety should be able to react with GTA although the reaction is much slower than the reactions between amino groups and GTA. When the excessive amount of GTA is present or a prolonged reaction time is used, the reaction between the primary amide group of glutamine moiety and GTA may significantly reduce the amount of the primary amide group in the GTA-gliadin-glyoxal resin. The reduced amount of the primary amide group in GTA-gliadin would negatively affect the efficiency of grafting glyoxal onto gliadin and homo-crosslinking reactions with free aldehyde groups in the GTA-gliadin-glyoxal resin during the wet strength development. The remaining primary amide group in the GTA-gliadin-glyoxal resin can form hydrogen bonds with hydroxyl groups of pulp fibers, thus increasing the dry strength of the treated paper. The abrupt increase in the viscosity of the GTA-gliadin/glyoxal reaction solution was due to the homo-crosslinking reactions between the aldehyde group of grafted glyoxal and the remaining primary amide group of the glutamine moiety. The results in the Table 2 that the  $T_v$  increased with increasing the GTA dosage appear to suggest that a high GTA dosage might significantly reduce the amount of the remaining primary amide group, thus reducing the homo-crosslinking efficiency during the wet-strength development and the efficiency of forming hydrogen bonding with pulp fibers. We speculate that the undesirably high consumption of the primary amide in gliadin occurred when the GTA

dosage was increased from 75 wt% to 90 wt% and the reaction time was increased from 8 h to 10 h, which resulted in the reduced dry and wet strengths of the treated paper

The reaction between GTA-gliadin and glyoxal aimed at imparting free aldehyde groups to the modified gliadin. The free aldehyde groups form covalent linkages with pulp fibers and the remaining primary amide group in the GTA-gliadin-glyoxal resin. Therefore, the amount of free aldehyde groups plays an important role in the enhancement of the dry and wet strengths of the treated paper. When the glyoxal dosage in the reaction between glyoxal and GTA-gliadin increased, the amount of free aldehyde groups in the resulting GTA-gliadin-glyoxal resin increased. Consequently, the dry and wet strengths of the treated paper would also increase, which is consistent with results shown in Figures 20 and 21. However, the amount of remaining primary amide group in the resulting GTA-gliadin-glyoxal resin would be too low to have efficient homo-crosslinking reactions, which would in turn reduce the dry and wet strengths of the treated paper. That 40 wt% glyoxal resulted in lower dry and wet strengths than 30 wt% glyoxal is proposed to be due to over reaction of the primary amide group, i.e., the insufficient amount of the remaining primary amide group in the GTA-gliadin-glyoxal resin.

At the 1 wt% dosage level, the GTA-gliadin-glyoxal resin was comparable with a commercial GPA resin in terms of enhancing the dry strengths and only slightly lower than a GPA resin in terms of enhancing the wet strengths of treated paper. However, at other dosage levels, the GTA-gliadin-glyoxal resin resulted in lower dry and wet strengths than the GPA resins. The reasons for these results are not well understood. The following factors may contribute to the relative lower dry and wet strengths of the GTA-gliadin-glyoxal treated paper. First, gliadin has a lower content of a primary amide group than the synthetic GPA resin. As discussed previously, the amount of the remaining primary group is supposed to play an important role in the enhancement of the dry and wet strengths. The GTA-gliadin-glyoxal resin had lower water-solubility than the GPA resin which may prevent the uniform distribution of the GTA gliadin-glyoxal resin onto pulp fibers. The GPA resin is a commercial product. The structures of the GPA resin, such as the amount of positive charges, the ratio of free aldehyde groups to the free primary amide group, and the molecular weight have been optimized for enhancing the dry and wet strengths. This study demonstrated that it is feasible to develop an effective temporary wet strength additive from renewable gliadin. Further investigation of this gliadin-based wet strength resin, such as the improvement of the water-solubility of the modified gliadin and the optimization of the molecular weight of gliadin, may further improve the strength-enhancing effects of this

resin. Gliadin is renewable, readily available, and easily biodegradable. Results from this study may prompt more research efforts in the development of effective and bio-degradable wet strength additives from renewable natural resources.

## Chapter 6 Conclusions

GTA was successfully grafted onto gliadin, thus imparting the modified gliadin with positive charges. Further modification of GTA-gliadin with glyoxal provided an effective temporary paper wet strength additive. Effects of the GTA dosage and the reaction time in the reaction between GTA and gliadin on the dry and wet strengths were investigated. The 75 wt% GTA based on the dry weight of gliadin and the 8 h reaction time were optimum in terms of enhancing the dry and wet strengths of the treated paper. The optimization of the glyoxal dosage revealed that 30 wt% glyoxal based on the dry weight of GTA-gliadin resulted in the highest dry and wet strengths of the treated paper. The GTA-gliadin-glyoxal had comparable dry strength-enhancing effects to the GPA resin and only slightly lower wet strength-enhancing effects than the GPA resin at the 1 wt% dosage level. At other two dosage levels (0.5 wt% and 1.5 wt%), the GTA-gliadin-glyoxal was less effective than the GPA resin in terms of enhancing the dry and wet strengths of the treated paper.

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