ABSTRACT

THOMASON, SPENCER TREXLER. Optimization of Ionic Crosslinking. (Under the direction of Dr. Peter Hauser and Dr. Brent Smith.)

Durable press treatment with formaldehyde-based finishes produce excellent durable press performance, however they also significantly reduce the strength of the fabric and release formaldehyde, a suspected human carcinogen. Ionic crosslinking has been explored as a potential alternative for durable press treatment. Previous work has shown significant improvements in wrinkle recovery angle with carboxymethylation and ionic crosslinking of cotton fabric with cationic glycerin. Optimal conditions from previous work are further optimized and evaluated. This research models the effect of this treatment on a number of physical and chemical properties of the fabric. With selected ionic treatments, wet wrinkle recovery angles (WRA) can be increased by 83% and dry WRA can be increased by 19%. The durable press (DP) performance only increased slightly with these treatments on this fabric. There is a weak correlation between WRA and DP performance. Under certain conditions, this treatment improved WRA and DP performance, but not nearly as much as DMDHEU treatment. The treatment can produce tensile strength increases of up to 25%, breaking strain increases of up to 340%, and tear strength increases of up to 80%. This is in sharp contrast to decreases in each of these properties with DMDHEU treatment. Whiteness index (WI) of carboxymethylated and ionically crosslinked fabrics were only slightly lower than untreated fabric, while DMDHEU causes a considerable reduction in WI. Fabrics could be produced with this treatment with stiffness similar to untreated fabric, whereas DMDHEU treatment always results in considerable stiffness increase. Ionic treatment can produce a slight increase in DP performance with none of the adverse affects which are observed with traditional finishes.

OPTIMIZATION OF IONIC CROSSLINKING

by

Spencer Thomason

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Approved by:

Dr. Peter Hauser
Committee Chair

Dr. Brent Smith
Committee Co-Chair

Dr. Behnam Pourdeyhimi
Committee Minor Representative

DEDICATION

This work is dedicated to my parents who have provided loving support for all of my endeavors.

BIOGRAPHY

I was born in Salisbury, NC and grew up in Concord, NC. After completing high school, I attended North Carolina State University. I completed B.S. degrees in Chemical Engineering and Textile Chemistry with a concentration in Polymer Science.

During college I had two internships. My first internship was with Collins and Aikman. I filled in for an advanced development chemist who was on maternity leave. I was in charge of development of their Universal Backing System for four months. This technology involved backcoating and laminating automotive fabrics with hot melt adhesives.

My second internship was with Milliken Chemical as a process engineer intern. At Milliken Chemical I was involved with a project designed to optimize and improve control of alkoxylation reactions. We used FTIR Attenuated Total Reflectance to monitor alkoxylation reactions real time for molecular weight control.

I graduated from college in 2001 and accepted a position with Corning in their Optical Fiber Division. I was hired as a manufacturing engineer. I was involved in a large scale capital expansion of an optical fiber manufacturing facility located outside of Charlotte, NC. My primary focus was in a portion of the process which involved high precision gas delivery systems and chemical vapor deposition to form the core of the optical fiber. As the telecommunications sector experienced considerable economic weakness, the facility expansion was halted and I was relocated to a new position as a process engineer in Wilmington, NC. In this position I was still focused on the same portion of the optical fiber manufacturing process, but my responsibilities were in next generation equipment design and in process optimization through cost reduction and capacity improvements.

As the economy continued to slow, I realized that I needed to transition into a new industry. In 2002 I accepted a position with Mississippi Polymer Technologies initially as a project engineer. I transitioned to a process engineer and then to a production engineer. This was a small company so my responsibilities were quite broad. We developed and produced a new high performance thermoplastic based on a polyphenylene copolymer. My initial responsibility was to develop a process for production of this material. As the process was developed, I became responsible for design and installation of a facility in which to run this process. Of course, as the facility was completed it was necessary to actually run the plant. I was responsible for training and supervising operators, implementing manufacturing systems, procuring materials, and continuous improvement of the process and facility. It offered me a tremendous amount of responsibility and a broad range of experiences. I was able to design, build, and operate a 500,000 lb/yr advanced engineered plastics production facility from a laboratory scale process.

While in south Mississippi, I was also involved in the startup of a microbrewery. Lazy Magnolia Brewing Company was started in late 2004 and will be distributing throughout the state of Mississippi in 2006. I was responsible for design and construction of the facility and manufacturing systems.

As my role in developing the production process and building and starting up the facility was completed, the company was sold to Solvay Advanced Polymers. I determined that it was a good time to complete the M.S. Textile Chemistry degree which I had begun part time. I moved back to Raleigh, NC and continued studies toward this degree in 2005. This research project was begun at this time.

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1 Introduction

Durable press (DP) finishes are an important treatment for cotton fabrics which provide wrinkle resistant and permanent press performance for apparel. This treatment became important in the 1930's and has continued to play an important role in the apparel industry.

Cotton fabric is particularly prone to wrinkling. Hydrogen bonding holds cellulose fibers together. Under stress these bonds can shift and hold fabrics in a new orientation, particularly when cotton is wet. Water molecules lubricate the cellulose chains and disrupt hydrogen bonding thus allowing them to shift more easily under stress. When the fabric is dried, the cellulose retains its new shape as the hydrogen bonds reform in a new configuration.

This problem has been overcome by covalently bonding the cellulose chains together, forming covalent bonds that are not disrupted by water. Formaldehyde-based crosslinking agents are the dominant products used to accomplish this in industry. These products provide excellent wrinkle resistance and durable press performance. They also produce several adverse effects. They reduce the strength of the fabric. They increase the stiffness of the fabric and cause yellowing. These properties considerably reduce the wear and abrasive properties of treated fabrics. They also release formaldehyde over time, which is undesirable since formaldehyde is a suspected human carcinogen.

There has been considerable effort to develop a product that could provide wrinkle resistant and durable press performance without these adverse effects. Low formaldehyde release products and products that are not based on formaldehyde have been developed. Polycarboxylic acid crosslinking is one approach that has been investigated. These products overcome some of these disadvantages, but have failed to capture a significant portion of the durable press market due to high costs and other factors.

Ionic crosslinking has been explored as a potential durable press treatment. Previous work has shown significant increases in both wet and dry wrinkle recovery angle by producing ionic cellulose and crosslinking it with an ionic crosslinking agent of the opposite charge. Significant strength and elongation gains have also been demonstrated with ionic crosslinking techniques. This research further explores ionic crosslinking as a durable press finish. (*1*,*2*,*3*)

2 Background

2.1 The Nature of Cotton

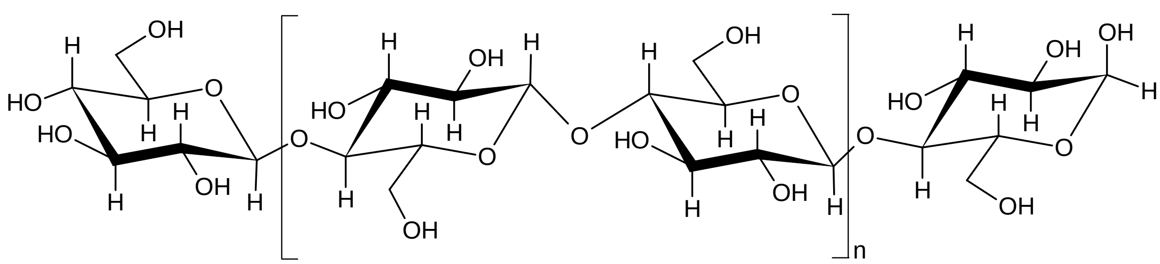
Cotton fibers are each a single plant cell. American Upland cotton used for traditional textiles range in length from ⅞ to 1¼ inches. The fiber diameter is 16 to 20 micrometers. The width is fairly uniform along the length of the fiber. Mature fibers are flat, twisted ribbons. The cross-section is commonly described as kidney bean shaped. The fibers taper to a conical point at the tip. (*4*)

Cotton fibers are composed of five regions. The outer layer is the cuticle. It is a very thin waxy layer that can be removed by scouring and bleaching. The primary cell wall is next. It is composed of fibrils spiraling around the fiber axis at an angle of 20 to 30 degrees. This layer is thick in mature cotton. The secondary cell wall is below the primary cell wall. The secondary cell wall makes up the majority of the fiber volume. It is composed of concentric layers of spiraling fibrils. The structure of the outermost layer is slightly different and referred to as the winding layer. The lumen is the hollow center of the fiber. Collapsing of the lumen after the cell dies and dries produces the twisted, kidney bean shaped appearance of the fiber. (*4*)

2.1.1 Cellulose Chemistry

The fibrils are composed of linear cellulose polymer chains. After scouring and bleaching, cotton is over 99% cellulose. (*5*) The cellulose polymer is shown in Figure 2.1. Cellulose molecules are composed of cellobiose units joined together by 1,4-β glycosidic bonds. The degree of polymerization ranges from 6,000 to 14,000 and the molecular weight is greater than 570,000g/mol. (6,7) Approximately 65 to 70% of the cellulose is crystalline and 30 to 35% is amorphous. (*4*)

Intermolecular forces are dominated by hydrogen bonding. (8) Hydrogen bonding occurs between the oxygen atom between rings and the primary hydroxyl group attached to C_6. The hydroxyl groups impart a high affinity to water and can be reacted to modify the cellulose chemical structure.



Cellulose

Figure 2.1: Chemical structure of cellulose

2.1.2 Wrinkling of Cellulose Fabrics

Cotton fabric is particularly prone to wrinkling. Wrinkling occurs when fibers are stressed. The hydrogen bonds which hold them in their original orientation are broken and new bonds are formed in the new orientation. When the stress is removed, there are no forces to cause the fibers to return to their original orientation. They are left in the new orientation until some force is applied which will reorient the fibers. (*9*)

This phenomenon is clear when viewed on a molecular level. When a fiber is bent, the cellulose chains on the outside of the bend are stretched while the cellulose chains on the inside of the bend are compressed. Neighboring molecules are attracted to each other through hydrogen bonding. The forces cause hydrogen bonds to be broken, and new hydrogen bonding occurs in the stressed arrangement. When the stress which caused the bend is removed, there is no restoring force to return the bonding to the original arrangement.

Wrinkling occurs most easily when cotton fabric dries from 25% moisture content to 5% moisture content. When fabric is wet, water molecules are attracted to the chains and disrupt hydrogen bonding. This lubricates the cellulose chain. The polymer chains slide past each other more easily when forces are applied. When the fabric dries, the lubrication is removed and wrinkles are ‘set’ as the hydrogen bonds reform. This explains why washing and drying cotton fabrics results in wrinkling of the fabric.

The construction of the yarn and fabric affects wrinkling. (*9*) Thicker fibers experience more wrinkling because the stress on the inside and outside of the fiber is greater when it is bent. Tight constructions wrinkle more than loose constructions and high twist yarns wrinkle more than low twist yarns for the same reason.

2.2 Durable Press Treatment

To reduce wrinkling, the bond permanence between cellulose chains must be increased. The hydrogen bonds can be replaced with covalent bonds. These bonds are not disrupted by water because they are much stronger and provide a restoring force to return the chains to their original orientation after the stress is removed. (*10*) There are a number of approaches to producing a stronger bond through reaction with the hydroxyl groups on the cellulose chain.

2.2.1 Traditional Durable Press Finishes

Cellulose can be crosslinked using aminoplasts which react to form bonds with themselves and with cellulose or using reactants which will only form bonds with cellulose to form crosslinks. Urea / formaldehyde and melamine / formaldehyde are two aminoplasts which are used for durable press treatments. Aminoplasts are known as self crosslinking and film forming materials. Cyclic urea methylol compounds are used as crosslinking agents. They will react with cellulose, but will not self crosslink.

The simplest crosslinker is formaldehyde. This crosslinking reaction is shown in Figure 2.2. It can react with cellulose at high temperature in the presence of $MgCl_2$ to form methylene bridges. This is a very strong crosslink and does not release formaldehyde.

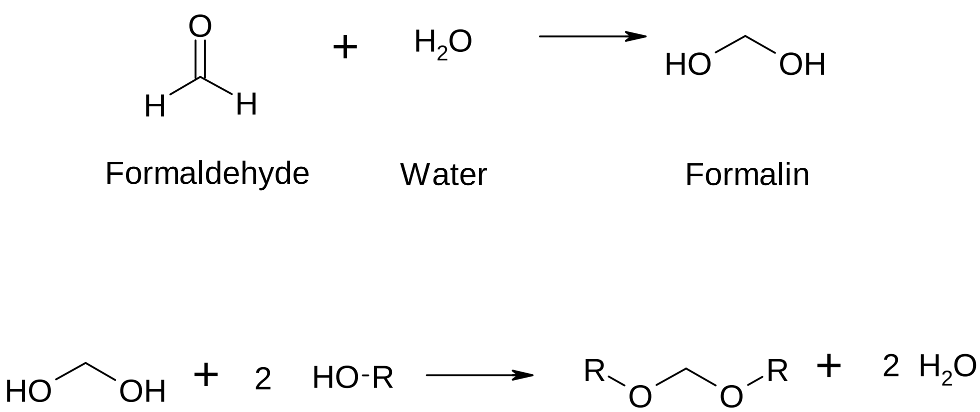


Figure 2.2 Formaldehyde crosslinking reactions

2.2.1.1 Urea / Formaldehyde

Crosslinking with urea and formaldehyde was developed in the late 1920’s. (*11*) Urea and formaldehyde will react to form a cellulose crosslinking precursor. One mole of urea and two moles of formaldehyde react to form dimethylol urea (DMU). This reaction is shown in Figure 2.3. DMU can react to form a crosslink between the methylol group on DMU and the hydroxyl groups of cellulose chains. The reaction with cellulose requires an acid catalyst. The crosslinking reaction is shown in Figure 2.4.

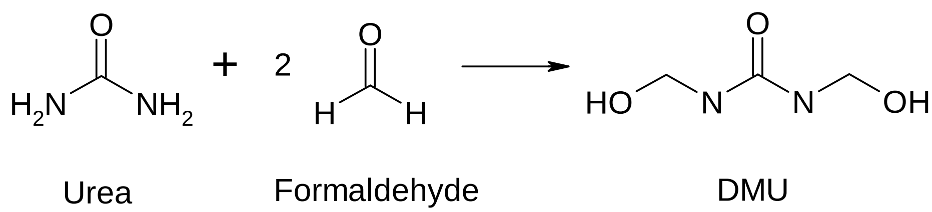


Figure 2.3 Urea / formaldehyde reaction to form dimethylol urea (DMU)

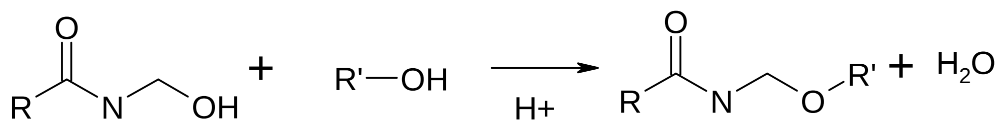


Figure 2.4 N-methylol crosslinking reaction

DMU treatments produce excellent crease recovery and are easy to cure. The chemicals are inexpensive and very efficient. However, they have several undesirable properties. The reactants are not stable for long periods of time and must be used shortly after mixing. They also produce a stiff hand. They have poor chlorine resistance. They can form a chloramide in the presence of bleach which can later produce hydrochloric acid (HCl) in the presence of a weak acid. Chlorine retention occurs at the secondary amine. The HCl causes yellowing and tendering of the fabric. (*9,12,13,14*)

Alkylated urea / formaldehyde can be used as well. These chemicals are more stable and therefore are more stable solutions for production and produce a softer hand since there is less reaction between the crosslinking agent itself. (*9*)

2.2.1.2 Melamine / Formaldehyde

Melamine and formaldehyde will form a crosslinking agent. Reaction of one mole of melamine (2,4,6-triamino-1,3,5-triazine) with three moles of formaldehyde produces trismethyloxymethylol melamine. Reaction of one mole of melamine with six moles of formaldehyde produces hexamethoxymethylol melamine. Reaction with methyl alcohol is required because the intermediate is not stable. This reaction is shown in Figure 2.5. Both of these chemicals will react with the hydroxyl groups on cellulose in the presence of an acid catalyst to form crosslinks.

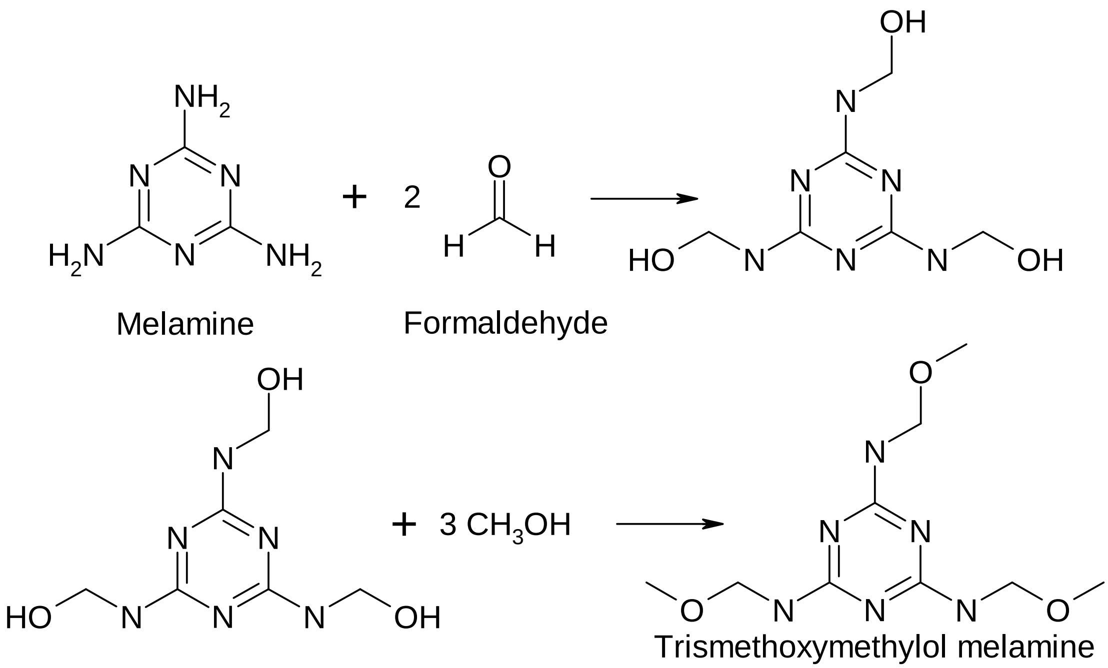


Figure 2.5 Melamine / formaldehyde reaction to form trismethoxymethylol melamine

Melamine / formaldehyde resins have greater durability and stability than urea / formaldehyde and are also more expensive. Trismethyloxymethylol melamine produces a stiff hand. It has excellent laundry durability and poor chlorine resistance. The chlorine produces yellowing, but less degradation than with urea / formaldehyde. Hexamethoxymethylol melamine produces a softer hand and has less chlorine retention. (*9,15,16*)

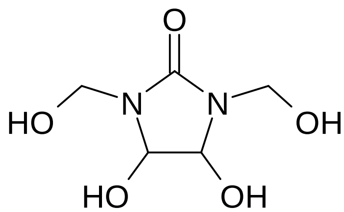
Both urea / formaldehyde and melamine / formaldehyde have serious drawbacks as finishes for cotton. They produce good durable press performance, but they also produce a stiff hand and they are not chemically stable. They release considerable formaldehyde, resulting in around 3,000 mg/kg formaldehyde release. (*9*) Since they are film formers, they can form a coating around fibers if they are not applied under appropriate conditions.

2.2.1.3 Cyclic Urea Methylol Durable Press Finishes

Cyclic ureas can be reacted with formaldehyde to form crosslinking agents. These compounds will react with cellulose but are not film formers. They cannot produce a thermoset plastic material, so they generally do not cause as much stiffness in the fabric. One mole of ethylene urea will react with two moles of formaldehyde to form dimethylol ethylene urea (DMEU). DMEU will react to form crosslinks between the hydroxyl groups on cellulose when an acid catalyst is present and will not self-crosslink. It is stable and has a long shelf and pad bath life. It produces good durable press performance and a softer hand than seen with aminoplasts. It has less than desirable durability and poor chlorine resistance. It also has a formaldehyde release above 1,000 mg formaldehyde / kg fabric. DMEU is inexpensive and was widely used up until around 1960. (*9,17*)

One mole of propylene urea will react with two moles of formaldehyde to produce dimethylol propylene urea. Dimethylol propylene urea will react with the hydroxyl groups on cellulose in the presence of an acid catalyst to produce crosslinks. It is more stable than DMEU, has better chlorine resistance, and is more durable to laundering. It does not yellow like most formaldehyde based finishes. (*18*) It is also more expensive than DMEU. (*9*)

4,5-Dihydroxy ethylene urea will also react with formaldehyde to form a crosslinking agent. One mole of 4,5-dihydroxy ethylene urea reacts with two moles of formaldehyde to form dimethylol dihydroxy ethylene urea (DMDHEU). The structure of DMDHEU is shown in Figure 2.6. DMDHEU currently accounts for over 85% of all durable press treatments. (*9,19,20*) DMDHEU has a lower reactivity which allows for a delayed cure step. The chemicals also have a longer shelf and pad bath life. DMDHEU has better durability to laundering than DMEU and less effect on dyes. It will yellow and is not typically used for white fabrics. It has a lower formaldehyde release, but the formaldehyde release is still about 1,000 mg/kg. (*9*)



Dimethylol dihydroxy
ethylene urea
(DMDHEU)

Figure 2.6 Dimethylol dihydroxy ethylene urea (DMDHEU)

While there are a large variety of chemistries available for producing DP finishes, DMDHEU and alkylated DMDHEU (discussed in section 2.2.3) are almost universally used for textile applications. Prior treatments such as urea / formaldehyde and melamine / formaldehyde are obsolete due to properties such as harsh hand, chlorine retention, and formaldehyde release. Newer treatments have not been able to provide sufficient improvements over DMDHEU because of generally poorer DP performance and higher cost. DMDHEU is the industry standard for DP finishing of textiles.

2.2.2 Other Formaldehyde Based Durable Press Finishes

Carbamates can be used to produce precursors to crosslink cotton. These chemicals show no chlorine retention and no yellowing. They also have excellent laundry durability. However, they cause high strength loss in the fabric and high formaldehyde release. (*9*)

Vapor phase formaldehyde treatment can also be used to treat fabrics. This can be used for garment processing. The garment is placed in a sealed chamber and then formaldehyde, steam and sulfur dioxide are added. This process produces excellent durable press performance, excellent durability, and very low formaldehyde release, but this process is also very expensive. (*9*) There was considerable interest in this chemistry in the 1960's and 1970's, but it has never become commercially important.

2.2.3 Low Formaldehyde Release Durable Press Finishes

Untreated cotton fabric has the potential to release between 0 and 20 mg formaldehyde / kg fabric. Traditional durable press finishes dramatically increase the formaldehyde release of finished fabrics. Formaldehyde is an irritant. It is classified as a probable human carcinogen by the U.S. Environmental Protection Agency (*21*) and as a known human carcinogen by the International Agency for Research of Cancer. (*22*) The U.S. Occupational Safety and Health Administration indicates that formaldehyde is a potential cancer hazard. (*23*) As a result, low formaldehyde release durable press finishes have been developed and non-formaldehyde finishes are widely sought after.

Alkylated DMDHEU releases less formaldehyde than DMDHEU. The structure of alkylated DMDHEU is shown in Figure 2.7. If DMDHEU is partially methylated, it has the potential to release around 500 mg formaldehyde / kg fabric. If it is fully methylated, it has the potential to release approximately 300 mg formaldehyde / kg fabric. (*9*)

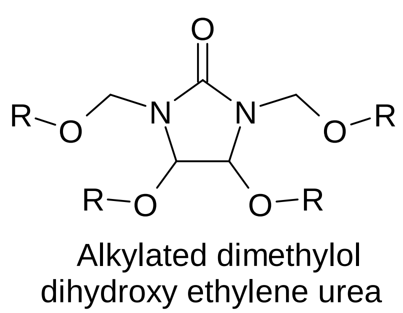


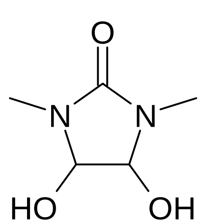
Figure 2.7 Alkylated dimethylol dihydroxy ethylene urea (alkylated DMDHEU)

Ultra low formaldehyde release (ULF) can be achieved by crosslinking with a mixture of one mole DMDHEU to two moles diethylene glycol. It has a formaldehyde release of less than 50 mg/kg. (*9*)

2.2.4 Non-Formaldehyde Durable Press Finishes

All formaldehyde based crosslinking agents produce two undesirable properties if applied by pad-dry-cure mehods. They cause considerable strength reductions in the fabrics. (*24,25*) Strength reduction is a result of both rigid crosslinks and molecular weight reduction. The largest factor is that the rigid crosslinks prevent the polymer chains from sliding to allow stresses to be absorbed by many chains. Many acid catalysts produce a decrease in molecular weight during treatment which further decreases strength. These finishes also contain formaldehyde. Low formaldehyde release finishes deal with the health issues with formaldehyde, however there are still marketing concerns which drive a desire for non-formaldehyde finishes.

Dimethyl-4,5-dihydroxy ethylene urea (DMeDHEU) can be used to crosslink cellulose. The structure of DMeDHEU is shown in Figure 2.8. It is difficult to cure and has relatively poor durable press performance. It is two to three times more expensive than ULF finish. (*9*)



Dimethyl dihydroxy
ethylene urea
(DMeDHEU)

Figure 2.8 Dimethyl dihydroxy ethylene urea (DMeDHEU)

A number of polycarboxylic acid anhydrides have been used as durable press finishes. The carboxylic acid groups on these molecules react with the hydroxyl groups on cellulose to form ester bonds. These treatments are formaldehyde free and generally produce a softer hand than formaldehyde based finishes.

1,2,3,4-Butane tetra carboxylic acid (BTCA) was developed for use as crosslinking agent by the USDA. It reacts to form an anhydride which in turn forms ester bonds with the hydroxyl groups on cellulose in the presence of sodium hypophosphite catalyst. It is the most effective polycarboxylic acid for durable press applications. The durable press properties are similar to those of DMDHEU, however it has less durability then N-methylol compounds because the ester bond is much easier to hydrolyze than the ether bond. The reaction requires a large amount of catalyst. Approximately 30% catalyst is required. It is also expensive at approximately four times the cost of DMDHEU.

BTCA has been replaced with less expensive chemicals such as polymaleic acid and polyacrylic acid. Citric acid, maleic acid, and tartaric acid are the most economical alternatives which have been explored. (*26,27*) Citric acid and maleic acid / itaconic acid mixtures have also been used with phosphorous containing catalysts. (*28*) Durable press performance is somewhat lower than with BTCA, but strength loss is lower. (*29*) These chemistries are less efficient than BTCA and less durable. (*30*) A combination of citric acid and a terpolymer of maleic acid, acrylic acid, and vinyl alcohol has shown improved performance and durability over most other polycarboxylic acid options. (*30*) A combination of polycarboxylic acid and citric acid has also produced improved properties. (*27*) These processes still require high concentrations of catalyst and all cause yellowing of the fabric. (*26*)

1,3-Dihydroxy-4,5-dimethyl-2-imidazolidinone (DHDMI) is a commercially available non-formaldehyde durable press finish. (*30*) It is much less efficient than DMDHEU and requires high levels of resin add-on. It is less expensive than BTCA, but far more expensive than DMDHEU.

Short chain polycarboxylic acids produce strength loss like formaldehyde based finishes. However, the strength loss is not generally as large. Long-chain polycarboxylic acids can be used to produce finishes with little to no strength loss. (*31,32*)

Polycarboxylic acids require large amounts of an acid catalyst. The typical catalysts are phosphorous containing compounds. Sodium hypophosphite is the most effective catalyst. (*28*) This can produce problems through cellulose degradation causing strength loss, high cost because of the large concentration requirements, and environmental concerns with the waste stream. Sodium hypophosphite is known to produce shade change with certain dyes. (*28*)

Other catalysts have been tested with positive results. N-heterocyclic compounds have been studied. Imidazole and its alkyl derivatives have been shown to produce similar durable press properties to sodium hypophosphite and better mechanical properties. (*28,33*) Mono- and disodium salts of fumaric acid, maleic acid, and itaconic acid have been used as catalysts with BTCA to produce high durable press ratings and wrinkle recovery angles. (*28,34*)

Boric acid is often added to suppress the reactions which cause yellowing during the curing process. (*28*) Trials with boric acid actually produce an increase in strength properties of the treated fabrics. (*35*)

Treatment with a combination of citric acid and chitosan has also been investigated. (*36*) In this case, the esterification occurs both between citric acid and cellulose and between citric acid and chitosan. This produces slight improvements in wrinkle recovery angle and durable press performance and in tensile and tear strength. The treatment has a higher durability than most other polycarboxylic acid treatments.

2.3 Ionic Crosslinking as a Durable Press Finish

2.3.1 Variety of Chemistries Available for Ionic Crosslinking

Ionic crosslinking has been investigated as a mechanism for producing durable press performance. (*1*,*2*) There is currently a patent pending for a process which produces an ionically crosslinked fibrous material. The process involves applying a polyelectrolyte to an ionic fibrous material to form an ionically crosslinked material, such that the polyelectrolyte has a charge opposite that of the ionic fibrous material. Ionically crosslinked fabrics have demonstrated improvements in WRA without strength loss. (*1*,*3*)

Cotton fabric has been ionically crosslinked using a variety of techniques. Cationizing agents have been used to produce cationic cellulose. Then the cationic cellulose has been crosslinked with an anionic crosslinking agent. Anionizing agents have also been used to produce anionic cellulose. The anionic cellulose has been crosslinked with a cationic crosslinking agent.

Fabric has been treated with chloroacetic acid (CAA) to produce anionic sites on the polymer chains and crosslinked with cationized chitosan and other polycations. Cotton fabric has also been treated with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) to produce cationic polymer chains and crosslinked with polyanions.

Most research has focused on utilizing chitosan as the crosslinking agent. (*1,2,3*) It can be reacted with CHTAC to form cationic chitosan or with chloroacetate to form anionic chitosan. Since the nature and number of ionic sites on both cellulose and chitosan can be controlled, chitosan provides considerable flexibility as a crosslinking agent. Cationic chitosan can be produced through substitution at the ring NH2 site (*37*) or through substitution at the C_6 and ring hydroxyl sites. (*1*)

Numerous treatment methods have been evaluated. Trials have been performed using pad-batch processes, exhaust fixation processes, pad-steam processes, and pad-dry-cure processes. (*1*)

Anionization of cellulose with chloroacetate and crosslinking with cationic chitosan produces an average increase in WRA of 130° and a strength increase between 10 and 60%. Durability to home laundering has also been evaluated. Cationic chitosan as a crosslinking agent appears to be extremely durable, with almost no decrease in crosslinking agent after three wash cycles. (*1*)

2.3.2 Preceding Ionic Crosslinking Research

The most recent work has shown promising results using wrinkle recovery angle as a gauge of performance. (*2*) Plain weave, 100% cotton fabrics were evaluated using a number of ionic crosslinking procedures.

Cellulose was reacted with CAA and crosslinked with cationic chitosan, cationic glycerin, calcium chloride, magnesium chloride, cationized ethylene glycol, cationized dextrose, cationized D-celobiose, and cationized β-cyclodextrin. All of these crosslinking agents demonstrated improvements in wrinkle resistance, but the cationic chitosan and cationic glycerin produced the best results. They were evaluated using pad-dry-cure, pad-batch, and exhaustion application methods. (*1*,*2*)

Cellulose was also reacted with CHTAC and crosslinked with PCA, BTCA, EDTA, NTA, HEDTA, oxalic acid, citric acid, and maleic acid. Each polyanion showed positive results, but the best were observed with PCA and BTCA. The same application procedures were evaluated. (*1*,*2*)

Ionic crosslinking with a variety of chemistries has shown significant increase in wet and dry wrinkle recovery angle. (*1*,*2*) It has also shown increases in fabric strength. Anionic cotton crosslinked with cationic glycerin produced using pad-batch carboxymethylation and exhaustion application of the crosslinking agent yielded the best results. Compared to untreated fabric, increases of 140° were observed in wet WRA and increases of 100° were observed in dry WRA. A 58% increase in tensile strength was produced. (*2*)

2.3.3 Optimal Chemistry for Ionic Crosslinking

Optimal ionic crosslinking treatments involve three principal chemical processes. (*2*) Anionic cellulose is produced through carboxymethylation with the sodium salt of chloroacetic acid in the presence of sodium hydroxide. Cationic glycerin is obtained from reaction of glycerin and CHTAC. Then the anionic cellulose is crosslinked with the cationic glycerin.

2.3.3.1 Chemistry of Carboxymethylation of Cellulose

Carboxymethylation of cellulose produces carboxymethylcellulose (CMC). This molecule is shown in Figure 2.9. It is formed by reacting chloroacetic acid with cellulose under alkaline conditions. Different preparation methods and conditions will result in different degrees of substitution. (*20*) Substitution occurs first on the primary alcohols and then on the secondary alcohols. Substitution is most likely to be 6-O-linked, followed by 2-O-, then 2,6-di-O-, 3-O-, 3,6-di-O-, 2,3-di-O-, and finally 2,3,6-tri-O- linking.

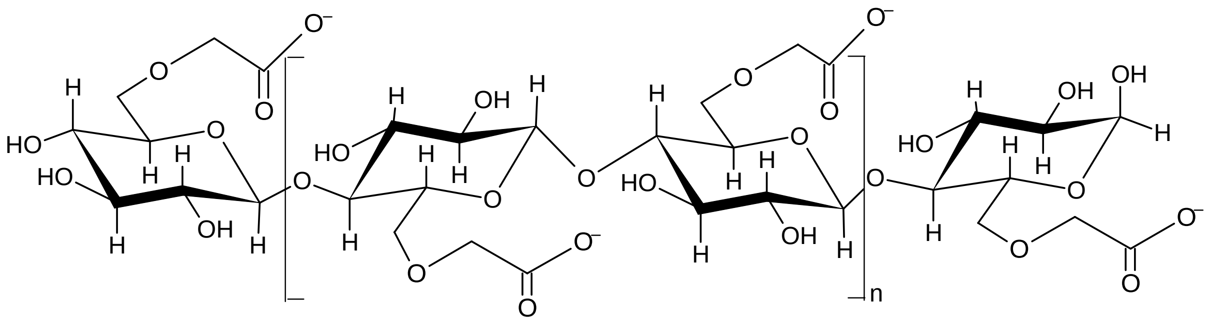


Figure 2.9 Carboxymethylated cellulose

The degree of carboxymethylation is one factor that influences the properties of fibers. Substitution may or may not be evenly distributed along the chain. Substitution is dependent on the accessibility of the functional groups. The accessibility of the modified functional groups is also important for determining the properties of the modified cellulose. The accessibility of the groups is related to the degree of carboxymethylation, but there is not a direct correlation. The reaction conditions affect the accessibility of the groups. (*38*)

Carboxymethylation begins with the most accessible hydroxyl groups on the cellulose molecule. For example, substitution will occur more rapidly and be more homogeneous in regions where the crystallinity is lower, because the reactants can travel through lower crystallinity regions more easily than higher crystallinity regions. As the reaction proceeds, the reactants penetrate into the more highly ordered regions of the cellulose structure. At early stages of the reaction, the distribution of the carboxymethyl groups is very inhomogeneous. As the reaction time is lengthened, the distribution of the carboxymethyl groups becomes more homogeneous. (*38*)

Desirable carboxymethylation treatments for ionic crosslinking have been evaluated. (*1,2,3*) The cotton fibers are treated with sodium hydroxide. This removes the hydrogen atom from the hydroxyl groups leaving a negatively charged oxygen atom. This reactive form of cellulose is known as soda cellulose. Chloroacetate reacts with cellulose at these sites. This treatment can be performed by soaking, padding, and drying the fabric prior to treatment with the chloroacetate, or the NaOH and chloroacetate may be combined in solution for a single step treatment to carboxymethylate the fabric. 20 to 40% NaOH solutions are used which are prepared by dissolving solid NaOH pellets in deionized water.

The fabric is carboxymethylated using the sodium salt of chloroacetic acid. The solution is prepared from chloroacetic acid and sodium carbonate. Solutions were prepared approximately one hour prior to fabric treatment but are stable for several days. A solution of chloroacetate is prepared by dissolving solid chloroacetic acid flakes in deionized water. Solutions in the range from 0.0 to 2.0M were prepared. Once the solid is fully dissolved, sodium bicarbonate powder is added to the chloroacetic acid solution. One mole of sodium carbonate is added for every two moles of acetic acid. Carbon dioxide is generated and the chloroacetate is formed in solution.

Cotton fabric is treated with chloroacetate by soaking or padding. Then the reaction is allowed to proceed at a number of different conditions. The chloroacetate reacts with the hydroxyl groups on the cellulose chain forming an ether linkage and generating hydrochloric acid. This reaction is summarized in Figure 2.10.

The fabric is rinsed in deionized water and soaked in dilute acetic acid. 2 g/L acetic acid solutions are used. The acetic acid neutralizes any residual alkali in the fabric. This is necessary because alkali is very difficult to wash out of cotton.

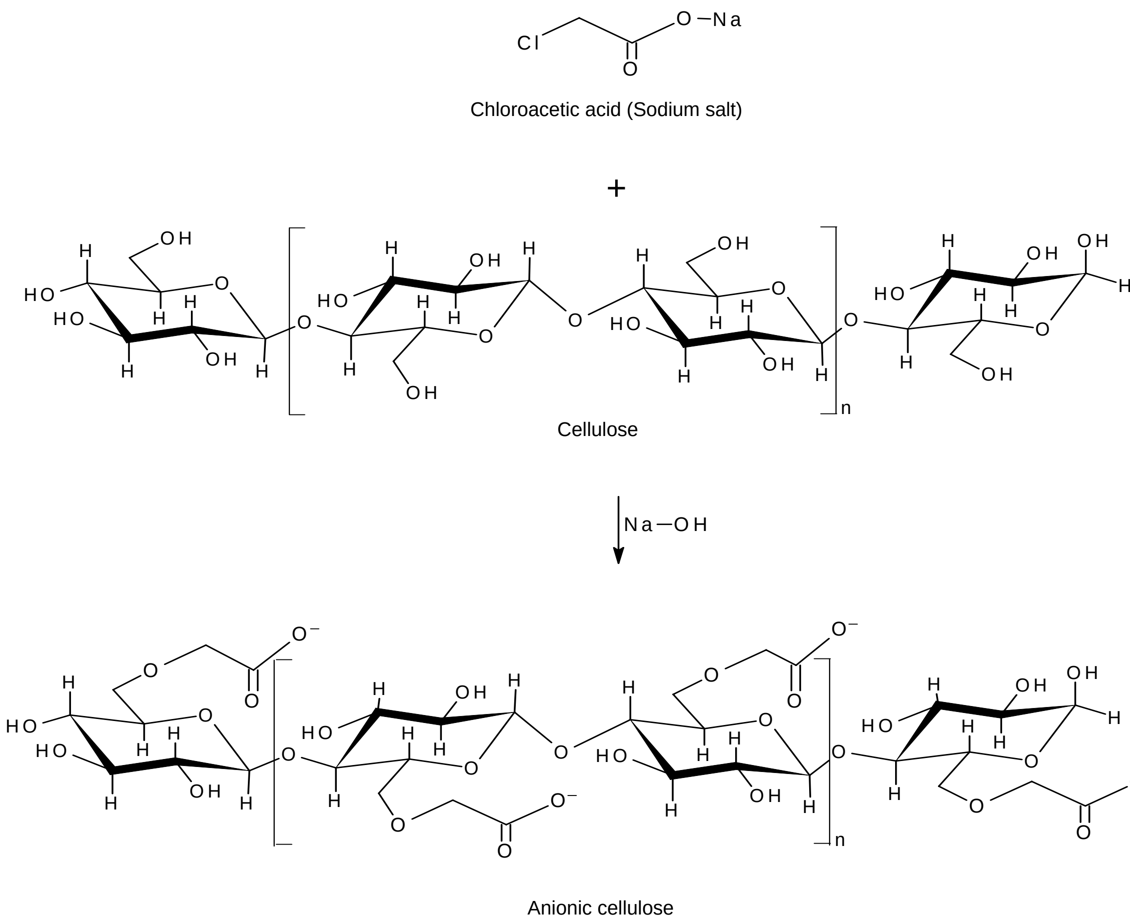


Figure 2.10 Carboxymethylation of cellulose with chloroacetic acid

2.3.3.2 Chemistry of Cationic Glycerin

Cationic glycerin is produced from glycerin and CHTAC. (*1,2*) The reaction for production of cationic glycerin is summarized in Figure 2.11. A solution of 69% 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) is mixed with 50% by weight aqueous NaOH at room temperature. This is performed slowly by adding the NaOH solution dropwise into the CHTAC solution. Addition proceeds until the solution has reached a pH of between 10 and 11. This reaction produces epoxypropyl trimethyl ammonium chloride

(EPTAC) and sodium chloride. Since there is a large quantity of NaCl formed which precipitates from solution, the solution is filtered to remove the majority of the salt.

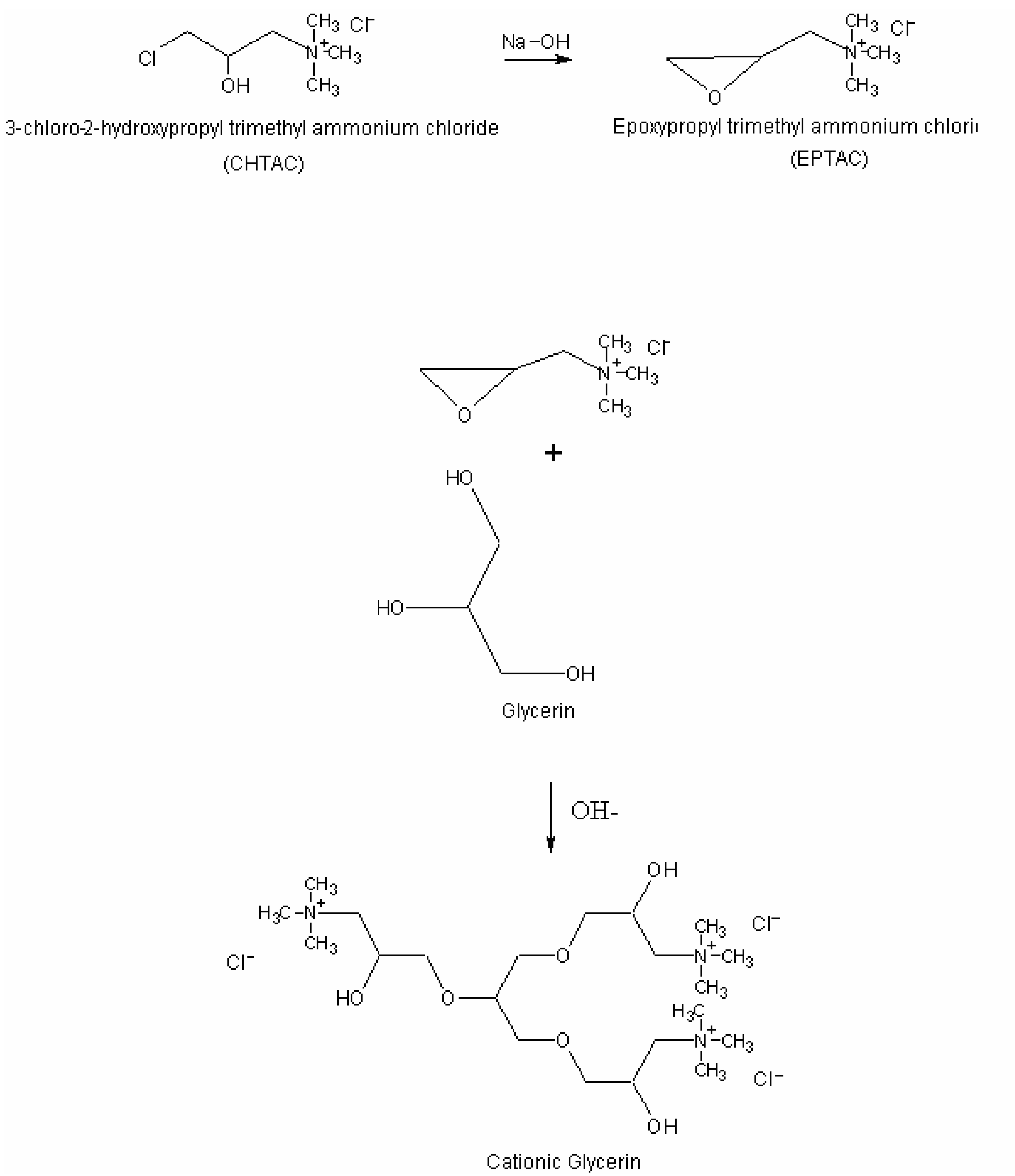


Figure 2.11 Cationization of glycerin

Glycerin is then added to the solution at a mole ratio of one mole of glycerin to 8 moles of CHTAC. The mixture is stirred for ten minutes at room temperature. It is then moved to a preheated water bath and held at 60°C for 20 hours with agitation. The solution gradually becomes viscous and the color changes from clear to yellowish. The product is cooled to room temperature and filtered. The pH is then adjusted to 7.0 using acetic acid.

2.3.3.3 Chemistry of Crosslinking

The anionic cellulose molecules are crosslinked using the cationic glycerin molecules. The fabric is soaked in a solution of between 3 and 9% by weight cationic glycerin. The cationic glycerin exhausts onto the fabric. Over a period of time, positive charges on the cationic glycerin form ionic bonds with negative charges on anionic cellulose. Figure 2.12 shows this crosslink.

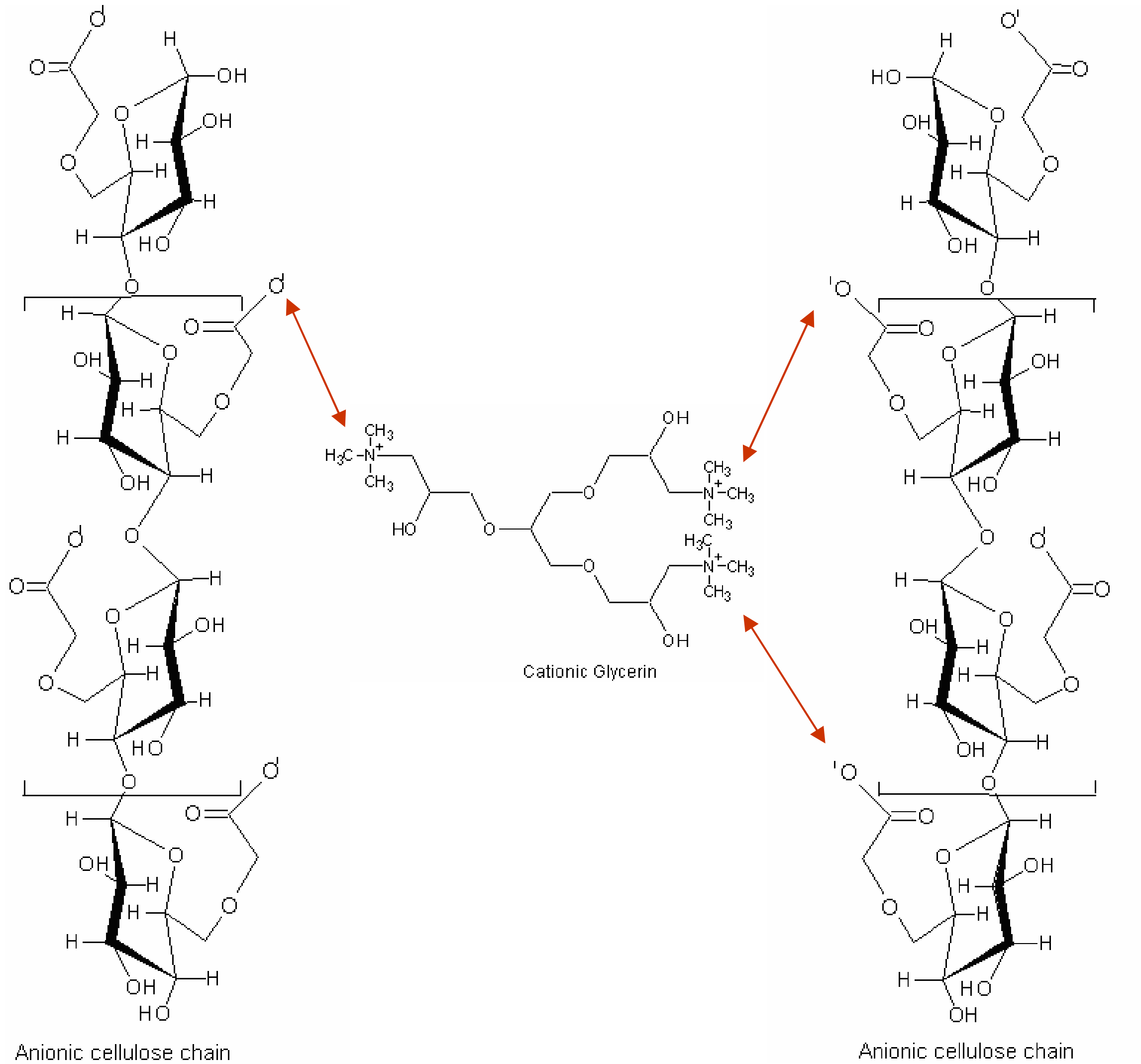


Figure 2.12 Anionic cellulose crosslinked with cationic glycerin

2.4 Proposed Research

The objective of this research was to further optimize the ionic crosslinking of cellulose, to improve understanding of the process and chemistry, to scale up the laboratory process to an economically viable pilot plant process, and to use additional evaluation techniques to measure the effects on final product properties particularly DP rating.

First, a variety of parameters were evaluated to develop an understanding of some of the key portions of the treatment process and how they impact fabric properties. After some initial trials, statistically designed experiments were performed to develop quantitative models for how to optimize the process for desired properties. This led to small scale trials using pilot plant scale equipment to validate these models and analyze scale-up of the treatment.

The larger runs were evaluated to determine the effects of this treatment on an array of fabric characteristics. DP rating was particularly important because it is the industry standard for DP treatment evaluation. Previous evaluation of ionic crosslinking has relied on WRA. WRA was assumed to correlate with DP rating but had to be validated.

3 Experimental Procedures

3.1 Raw Materials

The fabric and chemicals used for this research are all industrially available. In developing the ionic cross-linking process, cost was a primary concern. As a result, low cost, readily available raw materials were selected.

3.1.1 Fabric

Cotton Incorporated provided white shirting fabric for this research. This is a 100% cotton fabric which has been scoured, desized, bleached, and heat set. It is a plain weave construction. No sizing was present on the fabric and no additional finishing had been performed. The original fabric width is 120 cm. The fabric basis weight is 112 g/m^2. The picks and ends are 44x27 yarns/cm. The yarns are ring spun. Prior to any treatment, the CIE whiteness index is 77.64.

Three fabrics with a 3x1 twill construction were also provided by Cotton Incorporated. The first twill fabric is white with a CIE whiteness index of 82.39. It has a basis weight of 260 g/m^2, a yarn count of 48x20 yarns/cm, and an original width of 150 cm.

The second twill fabric is grey with L*=63.30, a*=1.62, and b*=9.67. It has a basis weight of 250 g/m^2, a yarn count of 48x20 yarns/cm, and an original width of 162 cm. The third twill fabric is reddish tan with L*=58.38, a*=8.38, and b*=18.64. It has a basis weight of 225 g/m^2, a yarn count of 48x20 yarns/cm, and an original width of 149 cm.

The fabrics were tested for the presence of starch and polyvinyl alcohol sizing and found to be free of these sizings. The fabrics had a pH of 7.0 as determined by AATCC Test Method 81-2001 pH of Water-Extract from Bleached Cotton. (*39*) They were also tested for absorbency. They were more absorbent than the range of AATCC Test Method 79-2000 Absorbency of Bleached Textiles (*40*) and AATCC Test Method 35-2000 Water Resistance: Rain Test. (*41*)

3.1.2 Chemicals

The primary chemicals used for this project were the following:

- Sodium hydroxide (pellets)
- 3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (69% aqueous solution)
- Glycerin (99+%)
- Chloroacetic acid (flakes)
- Sodium carbonate (powder)

3.2 Equipment

Fabric treatment was completed in the North Carolina State University College of Textiles pilot plant. The fabric was padded using a Werner Mathis AG padding machine. It was capable of padding fabric up to 18 inches in width in either continuous or batch processes. The trough was approximately one liter in volume. Both the fabric speed and the pressure between the padding rolls could be controlled. Batch drying was performed in a

Werner Mathis AG forced air curing oven. This dryer allowed fabric to be mounted on 7”x12” metal pin frames or placed in a loose container. The time and temperature was both controlled in this oven. Continuous drying was performed in a Werner Mathis AG dryer. Fabric could travel directly from the padder to the dryer or directly to the dryer. Maximum width for this dryer is approximately 18 inches. This dryer allowed for tension control in the warp direction but not in the weft direction. The tension, speed, temperature, and air speed could all be controlled in this dryer.

3.3 Procedures

The process used in this research evolved from the previous work. (*1,2,3*) The optimal procedure determined from previous work was used as the starting point for this research. The procedure was first duplicated. Then several series of single (or small number) variable trials were run with small samples. The next several series of trials were run as a Design of Experiment (DOE) and subsequent additions to that DOE. After optimal conditions were determined from small scale trials, larger continuous or semi-continuous trials were run.

3.3.1 Baseline Procedures

The initial procedure for this research was the procedure optimized by Bilgen. (*2*) This procedure involves three major steps. First, the fabric is treated with NaOH. Second, the fabric is treated with the chloroacetate, washed, treated with acetic acid, and washed again. Finally, the partially carboxymethylated fabric is treated with cationic glycerin.

Fabric is treated with NaOH using a pad-dry method with prior soaking in the solution. The fabric is placed in a solution of 20% by weight aqueous NaOH. The fabric is soaked for 10 minutes in this solution at room temperature. It is then padded to approximately 100% WPU. The samples are dried in a forced air curing oven under tension for 10 minutes.

The fabric is treated with chloroacetate using a similar soak then pad-dry procedure. It is placed in a 2.0 M aqueous solution of chloroacetate. The fabric is left in the solution for 5 minutes at room temperature. It is padded to approximately 100% WPU. The fabric is placed in a polyethylene bag and the air is removed from the bag. It is held in the sealed bag at 70°C for one hour. After one hour, the fabric is rinsed in hot tap water three times and cold tap water once. It is treated with a 2 g/L acetic acid solution. Finally, it is rinsed with cold deionized water three times. The fabric is centrifuged and dried at room temperature for 24 hours without tension.

The partially carboxymethylated fabric is then cross-linked with cationic glycerin using an exhaust-pad-dry-cure method. It is soaked in 3% by weight cationic glycerin in water for one hour. Then the fabric is padded to approximately 100% WPU. It is dried in a forced air curing oven at 85°C for 5 minutes under tension. It is then cured in the same oven at 140°C for 90 seconds. The fabric is washed using 2 g/L of a nonionic wetting agent at 100°C for 10 minutes. It is rinsed in cold tap water, centrifuged, and dried at room temperature for 24 hours without tension.

The first series of experiments (Series 1) was run to duplicate the optimal conditions as determined by previous work and to evaluate new fabrics which would be used for this research. Prior to the first trials, considerable time was spent observing and running trials with Bilgen. Series 1 was run exactly as described above. Sample 1.A was the fabric used in previous work. Sample 1.B was a 100% cotton fabric with a plain weave very similar to the fabric used in previous work. Samples 1.C, 1.D, and 1.E were a variety of different cotton fabrics with a twill construction.

3.3.2 Single (or Small Number) Variable Trials

Series 1 was followed by several series of experiments designed to determine the effects of specific variables. A basic understanding of the effects of some of these variables was developed in previous work, however further evaluation was necessary. Other variables had not been evaluated at all in previous work.

Series 2 was run to evaluate a double treatment of the carboxymethylation steps of the procedure. Variations in series 2 treatments are summarized in Table 3.1. Sample 2.A was run using the baseline procedure with the plain weave fabric used in previous work. Sample 2.B was run using the baseline procedure with the plain weave fabric selected for this work. Samples 2.C and 2.D were run by a procedure in which the carboxymethylation procedure were performed twice, then the sample was crosslinked. Samples were treated with NaOH, treated with chloroacetate, treated with NaOH, treated with chloroacetate, and cross-linked. Sample 2.C was the fabric used in previous work, and sample 2.D was the fabric selected for this work.

Table 3.1 Variations in series 2 treatments

Sample	Fabric	Carboxymethylation Treatment
2.A	Old	Once
2.B	New	Once
2.C	Old	Twice
2.D	New	Twice

Samples were then prepared using the same procedures without tension. These samples were labeled 2.A.NT, 2.B.NT, 2.C.NT, and 2.D.NT.

Series 3 evaluated treatment of the plain weave fabric and was performed to evaluate the effect of chloroacetate concentration in the range from 0.0 to 2.0M. 200 mL were prepared at 0.00, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00M concentrations of chloroacetate.

Samples were soaked in 20% aqueous NaOH solution for 10 minutes at room temperature. They were padded to approximately 100% WPU. The samples were dried at 60°C for 10 minutes. They were dried with 2 kp tension in the warp direction and no tension in the fill direction. After drying was complete the tension had reduced to between 0.5 and 1 kp in the warp direction. The alkali treated samples were then soaked in aqueous solutions of the chloroacetate. The sample identifications and associated chloroacetate concentrations are summarized in Table 3.2. Each sample was soaked for 5 minutes at room temperature and then padded to approximately 100% WPU. They were placed in polyethylene bags and held at 70°C for one hour. They were rinsed three times in cold tap water, one time in 2 g/L aqueous acetic acid, and one final time in cold tap water. They were centrifuged and dried at room temperature for 24 hours.

Table 3.2 Variations in series 3 treatments

Sample	**Na salt of CAA concentration (M)**
3.A	0.00
3.B	0.25
3.C	0.50
3.D	0.75
3.E	1.00
3.F	1.25
3.G	1.50
3.H	1.75
3.I	2.00

Series 3 samples were crosslinked with 6% cationic glycerin. They were soaked for 15 minutes and then padded to approximately 100% WPU. They were dried at 85°C for five minutes with 2 kp tension in the warp direction and no tension in the fill direction. They were cured at 140°C for 90 seconds under the same tension.

Solutions which were used for Series 3 were reused to evaluate whether they could be reused which might effect the transition to a continuous process. Series 4 repeated a portion of Series 3 to evaluate repeatability. Series 4 also included trials in which NaOH and CAA steps were combined and in which the pad-batch CAA step was replaced with a pad-dry procedure. Variations in series 4 treatments are summarized in Table 3.3.

Table 3.3 Variations in series 4 treatments

Sample	**Carboxymethylation Method**	**Number of Steps for Carboxymethylation**	**Chloroacetate Concentration (M)**	**NaOH Concentration (%)**
4.A	Pad-batch	2	0.00	20
4.B	Pad-batch	2	0.25	20
4.C	Pad-batch	2	0.50	20
4.D	Pad-batch	2	0.75	20
4.E	Pad-batch	1	1.00	20
4.F	Pad-dry	1	1.25	20
4.G	Pad-batch	1	1.50	20
4.H	Pad-dry	1	1.75	20
4.I	Pad-batch	1	2.00	40

Samples 4.B, 4.C, and 4.D were prepared with exactly the same procedure as used for 3.B, 3.C, and 3.D. These were also the plain weave fabric. The only difference is that the chloroacetate solutions were reused. Series 4 was run one day after series 3, so the solutions also aged for approximately 24 hours. Samples 4.E and 4.G were prepared using one step to the carboxymethylate the fabric. The 1.00M and 1.50M solutions were each mixed with equal parts by weight of 20% aqueous NaOH. The mixtures were stirred for one minute. Then the fabrics were soaked in the solutions for 30 seconds and padded to approximately 100% WPU. They were then placed in polyethylene bags at 70°C for one hour. Samples 4.F and 4.H were also produced by mixing the 1.25M and 1.75M chloroacetate solutions with 20% NaOH. The same soak and padding was performed. Rather than placing 4.F and 4.H in

bags, they were just dried at 70°C for 10 minutes. Sample 4.I required mixing the 2.00M chloroacetate with 40% aqueous NaOH, soaking for 30 seconds, padding to approximately 100% WPU, and placing the sample in a polyethylene bag at 70°C for 1 hour. All samples were rinsed in cold tap water three times, 2 g/L aqueous acetic acid one time, and a final rinse in cold tap water. They were centrifuged and dried at room temperature for 24 hours. Portions of the samples were left unwashed and portions were washed with tap water for comparison.

Series 5 involved both the plain weave fabric and the three twill fabrics. Sample 5.A was the plain weave fabric, and samples 5.B, 5.C, and 5.D were twill fabrics. They were all treated with the baseline procedure. A section of each sample was left unwashed, and a section was washed with tap water for comparison.

Series 6 trials were prepared following the baseline procedures with an increase in the soaking temperature. The solutions were heated to determine if soak temperature affects the results. Samples were soaked at room temperature, 40°C, and 60°C. Sample 6.A was the plain weave fabric, and samples 6.B, 6.C, and 6.D were twill fabrics. A section of each sample was left unwashed, and a section was washed with tap water for comparison.

3.3.3 Design of Experiment (DOE) Trials

A number of process parameters were identified which were either likely to affect the final properties of the fabric or whose effects were unknown. Statistical software (SAS JMP) was used to verify that a designed set of experiments would allow for analysis of each variable. Number of steps, CAA concentration, NaOH concentration, carboxymethylation temperature and method, crosslink concentration and method, and soak time were all analyzed. Series 7 onward evaluated the plain weave fabric only.

Series 7 was the first of three series run to generate statistical data for design of the 10 yard trials. The variations in series 7 trials are summarized in Table 3.4. Sample 7.A was soaked for 30 seconds in 20% NaOH solution, padded to approximately 100% WPU, and dried at 60°C for 10 minutes under tension. It was soaked in 2.0M chloroacetate solution for 30 seconds, padded to approximately 100% WPU, and dried at 70°C for 10 minutes under tension. Sample 7.B was soaked in 20% NaOH solution for 10 minutes, padded to approximately 100% WPU, and dried 60°C for ten minutes under tension. It was soaked in 2.0M chloroacetate solution for five minutes, padded to approximately 100% WPU, and dried at 70°C for ten minutes under tension. Sample 7.C was soaked for ten minutes in a 50%/50% by weight mixture of 2.0M chloroacetate and 20% NaOH. It was padded to approximately 100% WPU, and dried at 70°C for ten minutes under tension. Sample 7.D was soaked for 30 seconds in a 50%/50% by weight mixture of 2.0M chloroacetate and 20% NaOH. It was padded to approximately 100% WPU, and dried at 70°C for ten minutes under tension. Sample 7.E was soaked for 30 seconds in 20% NaOH solution, padded to approximately 100% WPU, and dried at 60°C for ten minutes under tension. It was soaked for 30 seconds in 2.0M chloroacetate, padded to approximately 100% WPU, and placed in a polyethylene bag at 70°C for one hour. Sample 7.F was soaked for five minutes in 20% NaOH solution, padded to approximately 100% WPU, and dried at 60°C for ten minutes under tension. It was soaked for five minutes in 2.0M chloroacetate, padded to approximately 100% WPU, and placed in a polyethylene bag at 70°C for one hour. All samples were rinsed thoroughly in deionized water, soaked in 2 g/L acetic acid solution for five minutes, and rinsed again in deionized water. They were dried under tension at 60°C.

Table 3.4 Variations in series 7 treatments

Sample	Carboxymethylation Method	NaOH Concentration (%)	Chloroacetate Concentration (M)	Soak Times	Number of Steps in Process
7.A	Pad-dry	20	2.00	Short	3
7.B	Pad-dry	20	2.00	Long	3
7.C	Pad-dry	20	2.00	Long	2
7.D	Pad-dry	20	2.00	Short	2
7.E	Pad-batch	20	2.00	Short	3
7.F	Pad-batch	20	2.00	Long	3

Series 7 was crosslinked using cationic glycerin. The samples were soaked in 9% cationic glycerin for one hour. They were padded to approximately 100% WPU , dried at 85°C for five minutes under tension, and cured at 140°C for 90 seconds under tension. A section of each sample was isolated so that it was dried and cured without tension. The samples crosslinked without tension were labeled 7.A.NT, 7.B.NT, 7.C.NT, 7.D.NT, 7.E.NT, and 7.F.NT.

Series 8 continued the runs started in series 7. Variations in series 8 treatments are summarized in Table 3.5. Sample 8.A was soaked in 20% NaOH for 10 minutes, padded to approximately 100% WPU, and dried at 60°C for 10 minutes under tension. It was soaked in 1.0M chloroacetate for five minutes, padded to approximately 100% WPU, dried at 60°C for five minutes under tension, and cured at 110°C for 90 seconds under tension. Sample 8.B was soaked in 20% NaOH for 10 minutes, padded to approximately 100% WPU, and dried at 60°C for 10 minutes under tension. It was soaked in 1.0M chloroacetate for five minutes, padded to approximately 100% WPU, and placed in a polyethylene bag at 70°C for one hour. Sample 8.C was soaked for one minute in a 50%/50% by weight mixture of 2.0M chloroacetate and 40% NaOH. It was padded to approximately 100% WPU, dried at 60°C for five minutes under tension, and cured at 110°C for 90 seconds under tension. Sample 8.D was soaked for one minute in a 50%/50% by weight mixture of 2.0M chloroacetate and 40%

NaOH, padded to approximately 100% WPU, and placed in a polyethylene bag at 70°C for one hour. Sample 8.E was soaked for one minute in a 50%/50% by weight mixture of 2.0M chloroacetate and 20% NaOH. It was padded to approximately 100% WPU, dried at 60°C for five minutes under tension, and cured at 110°C for 90 seconds under tension. Sample 8.F was soaked for one minute in a 50%/50% by weight mixture of 2.0M chloroacetate and 20% NaOH, padded to approximately 100% WPU, and placed in a polyethylene bag at 70°C for one hour. Sample 8.G was soaked for one minute in a 50%/50% by weight mixture of 1.0M chloroacetate and 20% NaOH. It was padded to approximately 100% WPU, dried at 60°C for five minutes under tension, and cured at 110°C for 90 seconds under tension. Sample 8.H was soaked for one minute in a 50%/50% by weight mixture of 1.0M chloroacetate and 20% NaOH, padded to approximately 100% WPU, and placed in a polyethylene bag at 70°C for one hour. They were all rinsed in deionized water, soaked in 2 g/L acetic acid solution for five minutes, and rinsed a final time in deionized water. They were dried under tension at 60°C.

Table 3.5 Variations in series 8 treatments

Sample	Carboxymethylation Method	NaOH Concentration (%)	Chloroacetate Concentration (M)	Soak Times	Number of Steps in Process
8.A	Pad-dry-cure	20	1.00	Long	3
8.B	Pad-batch	20	1.00	Long	3
8.C	Pad-dry-cure	40	2.00	Short	2
8.D	Pad-batch	40	2.00	Short	2
8.E	Pad-dry-cure	20	2.00	Short	2
8.F	Pad-batch	20	2.00	Short	2
8.G	Pad-dry-cure	20	1.00	Short	2
8.H	Pad-batch	20	1.00	Short	2

Series 8 was crosslinked using the same procedure as series 7. The samples were soaked in 9% cationic glycerin for one hour. They were padded to approximately 100% WPU , dried at 85°C for five minutes under tension, and cured at 140°C for 90 seconds under tension. A section of each sample was isolated so that it was dried and cured without tension. The samples crosslinked without tension were labeled 8.A.NT, 8.B.NT, 8.C.NT, 8.D.NT, 8.E.NT, 8.F.NT, 8.G.NT and 8.H.NT.

Series 9 was performed to evaluate the one-step process. Samples 9.A and 9.B were produced using the same procedure. Sample 9.A was produced first, and then 9.B was produced reusing the same solution. The solution was prepared by mixing equal parts by weight of 20% NaOH solution, 2.0M chloroacetate solution, and 9% cationic glycerin solution. The samples were soaked for three hours. They were dried at 70°C and cured at 110°C. Then the samples were washed with deionized water. They were dried at 60°C and cured at 140°C to simulate the heat cycles that the other treatments underwent. All drying and curing was performed under tension.

3.3.4 Ten Yard Trials

After completing the small scale runs with 7”x12” samples, 10 yard trials were run. The fabric was cut to a width of 18 inches since this is the padder and dryer width. They were run in a semicontinuous fashion. For example, the equipment allowed for one pass through a padder and dryer. The fabric then had to be rolled, before it could be passed through the dryer for another pass or before it could be padded and dried with a second treatment.

Series 10 was the first set of 10 yard trials. Variations in series 10 treatments are summarized in Table 3.6. All four samples in series 10 were padded with approximately 100% WPU of 20% NaOH and dried at 80°C with approximately 3 minutes residence time in the oven. Sample 10.A was padded with approximately 100% WPU of 2.0M chloroacetate and dried at 70°C. Sample 10.B was padded with approximately 100% WPU of 2.0M chloroacetate, dried at 60°C, and cured at 110°C. Sample 10.C was padded with approximately 100% WPU of 1.0M chloroacetate, sealed in plastic, and placed in at oven at 70°C for one hour. Sample 10.D was padded with approximately 100% WPU of 2.0M chloroacetate, sealed in plastic, and placed in at oven at 70°C for one hour. The samples were rinsed with deionized water, soaked in 2 g/L acetic acid solution, and rinsed again with deionized water. They were dried at 60°C. Series 10 was crosslinked by padding approximately 100% WPU of 6% cationic glycerin solution, drying at 85°C with approximately 3 minutes residence time, and curing at 140°C with approximately 90 seconds residence time.

Series 11 was the second set of 10 yard trials. Variations in series 11 treatments are summarized in Table 3.6. Samples 11.A, 11.B, 11.C, and 11.D were carboxymethylated with the same procedure used for samples 10.A, 10.B, 10.C, and 10.D. Only the crosslinking procedure was different. They were soaked for one hour in a 3% solution of cationic glycerin at room temperature. They were then padded to approximately 100% WPU, dried at 85°C with approximately 3 minutes residence time in the oven, and cured at 140°C with approximately 90 seconds residence time in the oven. Sample 11.E was padded with 100% WPU of 20% NaOH solution and dried at 80°C. It was padded with 100% WPU of 2.0M chloroacetate and dried at 80°C. It was rinsed and soaked in acetic acid as usual. It was crosslinked by padding to 100% WPU of 9% cationic glycerin, holding at 70°C in plastic for 1 hour, drying at 85°C, and curing at 140°C.

Table 3.6 Variations in series 10 and 11 treatments

Sample	Carboxymethylation Method	Chloroacetate Concentration (M)	Cationic Glycerin Concentration (%)	Crosslink Method
10.A	Pad-dry	2.00	6	Pad-dry-cure
10.B	Pad-dry-cure	2.00	6	Pad-dry-cure
10.C	Pad-batch	1.00	6	Pad-dry-cure
10.D	Pad-batch	2.00	6	Pad-dry-cure
11.A	Pad-dry	2.00	3	Exhaustion-pad-dry-cure
11.B	Pad-dry-cure	2.00	3	Exhaustion-pad-dry-cure
11.C	Pad-batch	1.00	3	Exhaustion-pad-dry-cure
11.D	Pad-batch	2.00	3	Exhaustion-pad-dry-cure
11.E	Pad-dry	2.00	9	pad-batch-dry-cure

3.3.5 Traditional DMDHEU Treatment

Control fabrics were prepared with traditional DMDHEU treatment. Samples were prepared at both 7”x12” inch scales and at 10 yard trial scales, using a solution of 250 g/L Freerez® 900 Reactant (44% solids), 62.5 g/L Freecat® 9 Accelerator (30% solids), and 1 g/L Renex® 36 (60% solids). The fabric was submerged in the solution and then padded to 80 to 90 % WPU. The samples were dried in an oven at 105°C for five minutes, then cured at 177°C for two minutes.

3.4 Analysis

Fabrics were analyzed for a variety of chemical and physical attributes using a number of procedures. The extent of carboxymethylation was determined using a titration technique. (*1*) Dyeing and subsequent analysis of fabric reflectance was utilized to provide a more rapid determination of carboxymethylation. (*1*) Nitrogen content elemental analysis was used to determine the ionic crosslinker content of the fabric.

Final product attributes were analyzed with standard test methods. Wrinkle Recovery Angle and Durable Press rating were the primary measures of desired performance. Other properties evaluated included whiteness index, flexural rigidity, tensile strength, elongation, tear strength, and shrinkage. All samples were preconditioned for 24 hours and tested at 70°F and 65% relative humidity.

3.4.1 Carboxymethylation

After carboxymethylation, fabrics were evaluated to determine carboxylic acid content of the partially carboxymethylated cellulose. For the purposes of this document, extent of carboxymethylation is defined as the millimoles of carboxylic acid groups per 100 grams of fabric. Four in^2 specimens were soaked in 0.5% aqueous HCl solution for 16 hours. Multiple samples were soaked in the same beaker. Approximately 100 mL of solution was added to the beaker for each sample. The samples were then rinsed with deionized water until the HCl was completely removed from the sample and the rinse water had a ph of 7.0. A silver nitrate drop test was performed to insure that there is no chloride left in the rinse water. After they were rinsed, the samples were dried at 105°C for approximately 3 hours.

Approximately 0.2 gram specimens were prepared in duplicate and placed in 25.0 mL of 0.05N aqueous NaOH solution for four hours at room temperature. The solutions were sealed to ensure that the NaOH did not react with CO_2 in the atmosphere. A blank solution of 25 mL aqueous NaOH was included as a control. After four hours, solutions were titrated with 0.05N aqueous HCl solution. Both phenolphthalein indicator and a conductivity meter were used to determine the pH of the end point. The titrant used for each sample was recorded. The carboxyl content was then calculated using the following equation:

$$\text{Carboxyl Content (mmol/100g fabric)} = 100*(V_B-V_S)*N_{HCl}/M_S$$

where V_B is the volume in milliliters of titrant used for the blank solution, V_S is the volume in milliliters of titrant used for the specimen, N_{HCl} is the normality of the HCl, and M_S is the mass of the specimen in grams. All samples were run in duplicate.

A method to more rapidly determine the degree of carboxymethylation was also developed by dyeing the treated fabric with a cationic dye. Since a higher level of carboxymethylation produces more negatively charged functional groups, there are more sites with affinity for the positive charge of a cationic dye.

A dyeing procedure was performed at 100°C, using a solution containing 1.28 g methylene blue, 29.8 mL 1.0N NaOH, and 6.8 g potassium phosphate. Methylene blue is a cationic dye and is attracted to the anionic sites on the carboxymethylated fabric. Fabric samples were added to the solution for one minute, then removed and rinsed under a stream of tap water until all unfixed dye was removed as indicated by the color of the wash water. Washing was performed for approximately 10 minutes.

The reflectance of dyed samples was obtained using a Datacolor Spectraflash SF600X spectrophotometer with SheLyn SLI-Form Formulation software. Aamples were folded four thicknesses and a sample opening of 60 mm diameter was used. A standard D65 light source was used with specular light was excluded. Each sample was measured four times with 90° rotation between each test. The average of the four results was taken for each sample. K/S values for each sample correlated with the dye fixed on the fabric, which is directly related to the number of carboxyl sites on the cellulose molecule.

3.4.2 Nitrogen Content

Nitrogen content was used to determine the content of crosslinking agent on the treated fabric. It was analyzed using a Leuco CHN analyzer. EDTA was used as a standard.

3.4.3 Count

Count was measured using a pick glass. The yarns per centimeter were counted in the warp and fill directions.

3.4.4 Shrinkage

Shrinkage was determined using AATCC Test Method 135-2001 Dimensional Changes in Automatic Home Laundering of Woven and Knit Fabrics. (*42*) Laundering was performed in a Kenmore washer, using machine cycle (1) Normal/Cotton Sturdy and washing temperature (II) 27°C. They were tumble dried at 140°C (A, ii). Measurements were performed and percent shrinkage calculated after each wash / dry cycle.

3.4.5 Basis Weight

Basis weight was determined from ASTM D 1388-96 Standard Test Method for Stiffness of Fabrics. (*43*) The test method requires that basis weight be determined in order to determine bending rigidity. Samples which are 1 inch by 6 inches are weighed and the basis weight of the fabric is calculated. In this work, a minimum of 12 samples were averaged to determine each basis weight.

3.4.6 Bending Rigidity

Bending rigidity was determined using ASTM D 1388-96 Standard Test Method for Stiffness of Fabrics Cantilever Option. (*43*) A Fabric Development Tests Drape-Flex Stiffness Tester was used. This test method involves sliding a 1 inch by 6 inch specimen off the edge of a planar surface. The distance is recorded at which the fabric bends under its own weight to touch a surface extending at a 41.5° from the edge. From this distance and the basis weight of the fabric, the bending rigidity is calculated. At least six samples were tested in four orientations for both the warp and fill directions to determine the average bending rigidity.

3.4.7 Tear Strength

Tear strength was evaluated using ASTM D 5587-03 Standard Test Method for Tearing Strength of Fabrics by Trapezoid Procedure. (*44*) Testing was performed using a MTS QTet/5 Elite Controller constant-rate-of-extension tensile testing machine and Testworks 4 software. The specimen is prepared with the tear initiated and the sample loaded so that the tear will propagate across the sample. The specimen is loaded with 1 inch between clamps. The clamps are separated at 12 inches per minute. The force to continue the tear is measured. The peak force was recorded. Four specimens were measured in both the warp and the fill direction.

3.4.8 Tensile Strength

Peak tensile strength, strain at peak load, and energy to peak load were determined using ASTM D 5035-95 Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method). (*45*) Testing was performed using a MTS QTet/5 Elite Controller constant-rate-of-extension tensile testing machine and Testworks 4 software. One inch by six inch specimen were prepared in the warp and fill direction. They were loaded into the machine with a three inch gauge length and pulled at a constant rate of extension of 12 inches per minute. The force was measured and tensile strength, strain at break, and energy to break were calculated. Six specimens were prepared for each sample in both the warp and fill directions.

3.4.9 Dry Wrinkle Recovery Angle (WRA)

Wrinkle recovery angle (WRA) was determined using AATCC Test Method 66-1998 Wrinkle Recovery of Woven Fabrics: Recovery Angle. (*46*) Six 40 mm by 15 mm specimen were cut in each the warp and fill direction. They were folded and pressed under a 500 g weight for five minutes. They were then placed in a wrinkle recovery tester which allows the fabric to unfold without the influence of gravity. The angle at which the specimen has unfolded is recorded after five minutes. The sum of the average for the warp and fill directions is the WRA.

3.4.10 Wet WRA

Wet WRA was determined using the AATCC Test Method 66-1998 Wrinkle Recovery of Woven Fabrics: Recovery Angle. (*46*) Immediately prior to testing the samples were dipped into deionized water. They were then blotted with Kimwipes. The rest of the procedure was identical to dry WRA testing.

3.4.11 Durable Press Rating

Durable Press rating was determined using AATCC Test Method 124-2001 Appearance of Fabrics after Repeated Home Laundering. (*47*) Three 15 inch by 15 inch specimen were prepared for each sample. They were washed and dried five times. Washing was performed in a Kenmore washer with machine cycle (1) Normal/Cotton Sturdy and wash temperature (II) 27°C. They were tumble dried at 140°C (A, ii). 100% cotton ballast was used. The samples were graded from 1.0 to 5.0 compared to standards by three observers. The average rating was determined.

3.4.12 Whiteness Index

The CIE whiteness index was determined with a Datacolor Spectraflash SF600X spectrophotometer with SheLyn SLI-Form Formulation software. The instrument was calibrated with a white tile and black trap immediately prior to testing. The samples were folded four times and a sample opening for 60 mm was used. A standard D65 light source was used and specular light was excluded. Each sample was measured four times with 90° rotation between each test. The average of the four results was taken for each sample.

4 Results and Discussion

4.1 Carboxymethylation

4.1.1 Analysis of Carboxymethylation

Series 2, 3, 4, 7, 8, 10, and 11 were all analyzed to determine extent of carboxymethylation. Results from analysis of the twill fabrics were disregarded. The twill fabrics had undergone unknown processing steps including dyeing. The presence of other chemicals may have affected the analysis. Due to uncertainty about how to interpret the analysis, twill fabric has not been included.

Series 2 carboxymethylation data are summarized in Table 4.1 and in Figure 4.1. Series 2 was analyzed using paired student t-tests. The first analysis, which is summarized in Figure 8.1, compared the fabric used in previous work with fabric selected for this work. The analysis shows that the two fabrics do not yield significantly different carboxymethylation results of the baseline procedure, or the same procedure repeated a second time on the same samples.

Table 4.1 Degree of carboxymethylation for series 2 trials

Sample	Carboxymethylation – Average (mmol/100g)	Carboxymethylation - Std. Dev.
2.A	35	1
2.B	37	5
2.C	68	1
2.D	58	1

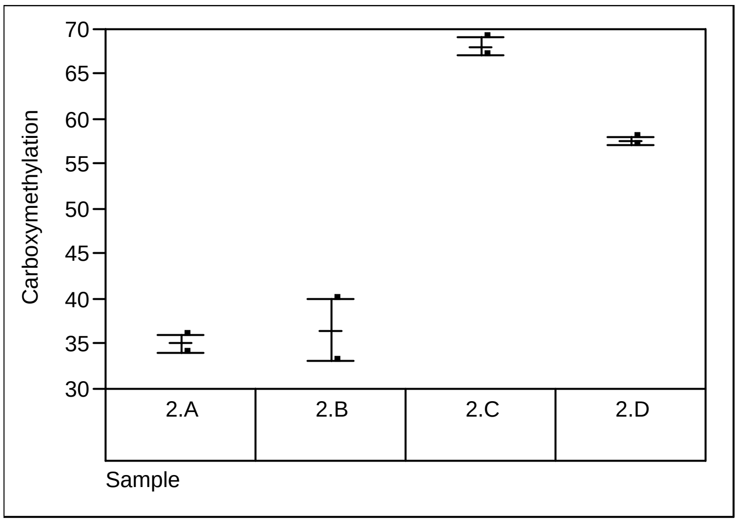


Figure 4.1 Degree of carboxymethylation for series 2 trials

The second analysis comparing a single pad-batch carboxymethylation treatment to a double pad-batch carboxymethylation treatment, is summarized in Figure 8.2. It shows that there is a significant difference between single and double treatments. The average carboxymethylation for one treatment using the pad-batch procedure is 36 mmol/100g and, for two treatments, is 62 mmol/100g. The second treatment increases the carboxymethylation by 72%.

Series 3 and 4 carboxymethylation data are summarized in Table 4.2 and Figure 4.2. Series 3 was run to determine the effect of chloroacetate concentration. Series 4 was performed to evaluate chloroacetate shelf life and investigate combining the NaOH and chloroacetate treatments. It also provided an initial evaluation of changing NaOH concentration, and compared a pad-dry-cure method of carboxymethylation to the pad-batch method.

Table 4.2 Degree of carboxymethylation for series 3 and 4 trials

Sample	Carboxymethylation – Average (mmol/100g)	Carboxymethylation - Std. Dev.
3.A	22	1
3.B	24	1
3.C	29	5
3.D	29	1
3.E	32	2
3.F	37	1
3.G	34	3
3.H	46	1
3.I	45	1
4.B	23	7
4.C	25	4
4.D	31	2
4.E	34	1
4.F	61	1
4.G	34	1
4.H	58	1
4.I	47	2
BLANK	19	1

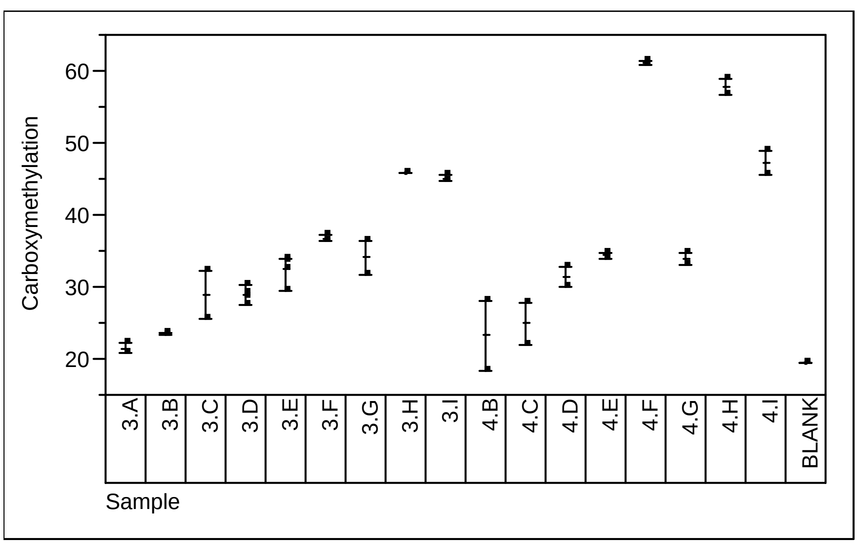


Figure 4.2 Degree of carboxymethylation for series 3 and 4 trials

Untreated fabric has a carboxymethylation of 19 mmol carboxymethyl content per 100 g fabric. The treated fabrics ranged from 22 to 61 mmol carboxymethyl content per 100 g fabric. All levels of treatment increased the carboxymethylation of the fabric.

This data were fit to a model. The initial analysis is shown in Figure 8.3. Analysis of variance was performed and parameter estimates were determined. The day on which the sample was prepared indicates the age of the chloroacetate solution. Day 1 solutions were fresh and day 2 solutions were reused from the previous preparation. The age and reuse of the solution does not have an effect on the carboxymethylation of the sample. NaOH concentration ranged from 20 to 40% and did not have an effect on carboxymethylation. Whether the sample was prepared in one step or two did not have an effect on the carboxymethylation.

Once the insignificant factors were determined, the data were fit to a model with only the significant parameters. This analysis is summarized in Figure 8.4. Only chloroacetate concentration and carboxymethylation method are significant. Using only these two factors and a linear function, the model was generated. A line fit to a graph of the actual values versus the predicted values has a R^2 value of 0.92. In the range from 0.0 to 2.0M the carboxymethylation increases 12 mmol/100g fabric for every 1.0 M increase in chloroacetate concentration with a standard error of 1 mmol/100g fabric. The batch process (indicated by the letter B in the analysis in Figure 8.4) produces 10 mmol/100g fabric lower carboxymethylation than the pad-dry-cure method. Therefore the highest level of carboxymethylation is achieved with 2.0 M chloroacetate and with the pad-dry-cure procedure.

Series 7, 8, 10, and 11 carboxymethylation data are summarized in Table 4.3 and Figure 4.3. These series included variation of chloroacetate concentration, carboxymethylation using pad-batch, pad-dry-cure, and pad-cure procedures. Soak time was also varied in series 7 and 8 to anticipate changes as the process was scaled up to a semi-continuous process. Series 7 and 8 was run as batch processes, while series 10 and 11 were scaled up processes and run as continuous or semi-continuous processes. The results of series 7, 8, and 9 were used to design the experiments for series 10 and 11. Then the results from all of these trials were combined and analyzed.

Table 4.3 Degree of carboxymethylation for series 7, 8, 10, and 11 trials

Sample	Carboxymethylation - Average	Carboxymethylation - Std. Dev.
BLANK	11	4
7.A	90	1
7.B	89	4
7.C	77	1
7.D	71	4
7.E	36	2
7.F	37	2
8.A	66	2
8.B	21	4
8.C	49	1
8.D	41	2
8.E	68	4
8.F	27	2
8.G	56	2
8.H	19	1
10.A	91	4
10.B	95	4
10.C	21	2
10.D	38	2
11.A	93	2
11.B	93	5
11.C	22	3
11.D	35	1
11.E	94	8

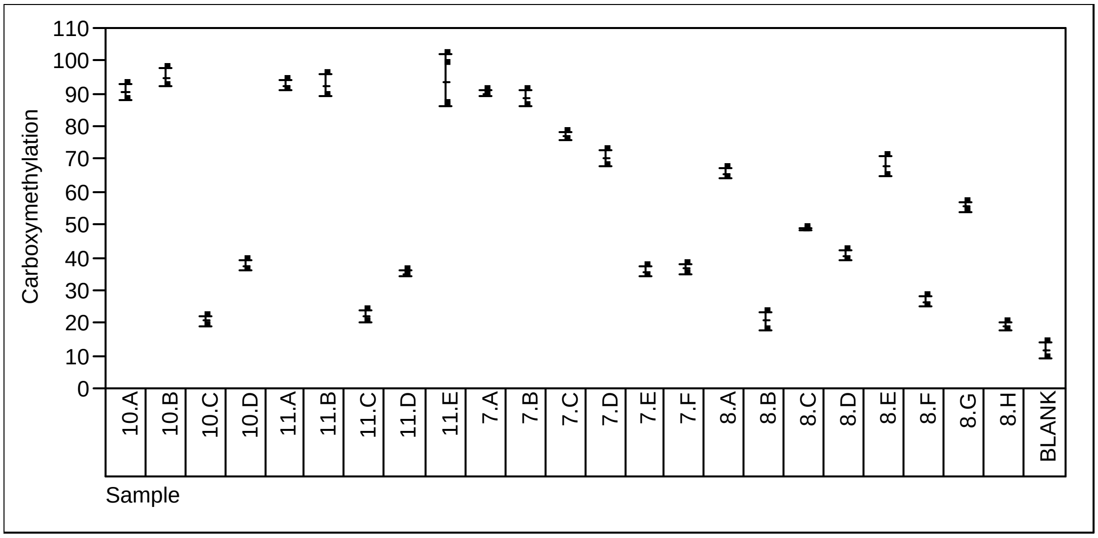


Figure 4.3 Degree of carboxymethylation for series 7, 8, 10, and 11 trials

Untreated fabric has a carboxymethylation of 11 mmol carboxymethyl content per 100 g fabric. Treated fabrics ranged from 19 to 95 mmol carboxymethyl content per 100 g fabric. All levels of treatment increased the carboxymethylation of the fabric.

The data were analyzed to determine which factors did not affect the carboxymethylation. The analysis is summarized in Figure 8.5. Similar results were seen with series 7, 8, 10, and 11 as were observed with series 3 and 4. Only the chloroacetate concentration and the carboxymethylation method significantly affected carboxymethylation. The NaOH concentration and the number of steps did not affect carboxymethylation. Neither did the soak time or whether the process was batch or semi-continuous/continuous.

The analysis was repeated with only the significant parameters. The analysis is summarized in Figure 8.6. A linear model was generated. A regression line of the actual values versus the predicted values has a R^2 value of 0.94. In the range from 1.0 to 2.0M the carboxymethylation increases 15 mmol/100g fabric for every 1.0 M increase in chloroacetate concentration with a standard error of 3 mmol/100g fabric. The pad-batch process (indicated by the letter B in the analysis in Figure 8.6) produces 31 mmol/100g fabric lower carboxymethylation than the pad-dry-cure method with a standard error of 2 mmol/100g fabric. The pad-cure process (indicated by the letter C in the analysis in Figure 8.6) produces 20 mmol/100g fabric higher carboxymethylation than the pad-dry-cure method with a standard error of 2 mmol/100g fabric. Therefore the highest level of carboxymethylation is achieved with 2.0 M chloroacetate and with the pad-cure procedure. A Pareto graph is included in Figure 8.6 to show the relative magnitude of the parameters which effect carboxymethylation.

4.1.2 Summary of Carboxymethylation

The degree of carboxymethylation is increased with this procedure. Carboxymethylation is affected by chloroacetate concentration and carboxymethylation method. Higher concentrations of chloroacetate produce higher carboxymethylation of the fabric in the range from 0.0 to 2.0M. Carboxymethylation is higher for pad-dry-cure and pad-cure procedures than for pad-batch procedures. In the range from 20 to 40%, NaOH concentration does not affect carboxymethylation. The time that the fabric is allowed to soak in solution and the number of steps in the carboxymethylation process do not affect the degree of carboxymethylation.

References (*20,38*) indicate that carboxymethylation is influenced by the method used, the NaOH concentration, and the chloroacetate concentration. These procedures use excess NaOH. In the range of concentrations used, there is no effect of NaOH because in all cases it is in excess. Higher concentrations of chloroacetate produce higher carboxymethylation because chloroacetate is one of the reactants. This is in agreement with basic thermodynamics. The equilibrium constant for the reaction dictates that if the concentration of the reactant is increased, the concentration of the product will increase.

Pad-dry-cure and pad-cure carboxymethylation methods produce higher levels of carboxymethylation than pad-batch methods because they affect the local concentration of chloroacetate. As the fabric is dried, water evaporates from the surface. Water within the fibers and yarns migrates to the surface to replace the water which has evaporated. This causes the chloroacetate which is dissolved in the water to become more concentrated on the surface. The higher concentration increases the carboxymethylation reaction. As a result, carboxymethylation is higher with pad-dry-cure and pad-cure methods and it is localized predominantly on the surface compared to the more homogeneous carboxymethylation in the pad-batch method.

4.2 Nitrogen Composition

4.2.1 Analysis of Nitrogen Content

Percent nitrogen was determined for series 10 and 11. It was also measured for series 11 after each of a number of washes to determine durability of the crosslinking agent to home laundering. Only the cationized glycerin and impurities that may be present contain nitrogen. Therefore, the nitrogen percentage is an indication of the amount of crosslinkeing agent on the fabric.

Series 10 and 11 data are summarized in Table 4.4 and Figure 4.4. Series 10 and 11 includes variation in chloroacetate concentration, carboxymethylation method using pad-batch, pad-dry-cure, and pad-cure procedures, and variation in crosslinking concentrations and methods.

Table 4.4 Nitrogen composition prior to washing for series 10 and 11 trials

Sample	Percent Nitrogen (%)
10.A	0.532
10.B	0.616
10.C	0.566
10.D	0.603
11.A	0.720
11.B	0.775
11.C	0.618
11.D	0.710
11.E	0.760
BLANK	0.246

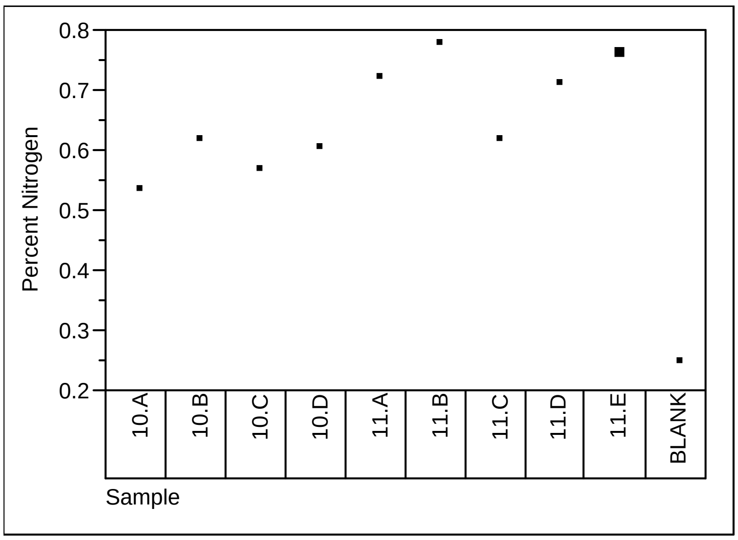


Figure 4.4 Nitrogen content prior to washing for series 10, and 11 trials

The untreated fabric has 0.246% nitrogen. The carboxymethylated and crosslinked samples range from 0.532 to 0.775% nitrogen. This treatment produces an increase in the nitrogen present on the fabric.

The data for series 10 and 11 were modeled using chloroacetate concentration, carboxymethylation method using pad-batch, pad-dry-cure, and pad-cure procedures, and variation in crosslinking concentrations and methods. No dependence on these parameters was observed. Between 30 and 40 mmol cationic glycerin / 100g fabric is present regardless of the procedure used. This is a result of the 100% WPU and concentration of cationic glycerin in solution and no other process parameters. Much of this crosslinking agent is unbound. The analysis is summarized in Figure 8.7.

Series 11 was analyzed after one wash. The data are summarized in Table 4.5 and Figure 4.5. Analysis of series 11 after one washing is summarized in Figure 8.8. Series 11 follows the same trend before washing and after washing. The nitrogen content increases with higher chloroacetate concentration. It is higher with pad-dry-cure and pad-cure methods than with pad-batch methods. It is higher with exhaustion crosslinking procedures than with pad-dry-cure procedures. There is not enough data to determine the statistical significance of these results.

Table 4.5 Nitrogen composition after washing for series 11 trials

Sample	Percent Nitrogen
11.A	0.322
11.B	0.439
11.C	0.193
11.D	0.318
11.E	0.285
BLANK	0.187

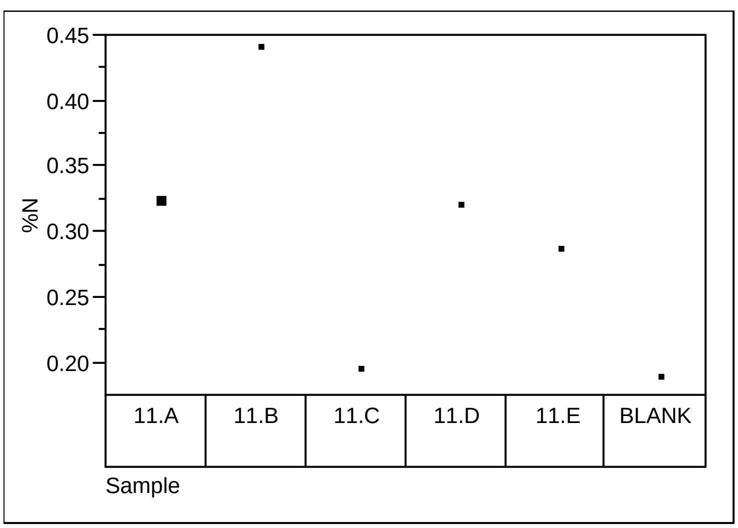


Figure 4.5 Nitrogen content after washing for series 11 trials

Additional washes were performed to evaluate durability. Laundering was performed using the procedure described in AATCC TM 124. Series 11 was washed for seven cycles. The nitrogen data are summarized in Table 4.6.

Table 4.6 Nitrogen composition for durability to laundering evaluation for series 11 trials

Sample	No Wash	Wash 1	Wash 2	Wash 3	Wash 4	Wash 5	Wash 6	Wash 7
11.A	0.720	0.322	0.294	0.283	0.242	0.245	0.220	0.241
11.B	0.775	0.439	0.348	0.359	0.317	0.292	0.273	0.250
11.C	0.618	0.193	0.205	0.218	0.220	0.191	0.211	0.202
11.D	0.710	0.318	0.277	0.263	0.259	0.207	0.212	0.213
11.E	0.760	0.285	0.275	0.263	0.256	0.261	0.223	0.233
BLANK	0.246	0.207	0.207	0.195	0.198	0.204	0.201	0.199

This analysis is summarized in Figure 8.9 and shows that nitrogen content increases with higher chloroacetate concentration. It is higher with pad-dry-cure and pad-cure methods than with pad-batch methods. It is higher with exhaustion crosslinking procedures than with pad-dry-cure procedures. The R^2 value from a regression of actual values versus predicted values from the model is 0.81. Nitrogen content steadily decreases with each wash cycle. It decreases by an average of 0.01% per wash, however this decrease is not actually linear. The concentration is gradually approaching the concentration of the untreated fabric.

4.2.2 Summary of Nitrogen Content

Nitrogen content is an indication of the amount of crosslinking agent on the fabric. It is highest with 2.0M chloroacetate concentration, pad-dry-cure or pad-cure methods, and exhaustion crosslinking procedures. Nitrogen content tends to increase with carboxymethylation, however the correlation is not strong as shown in Figure 4.6.

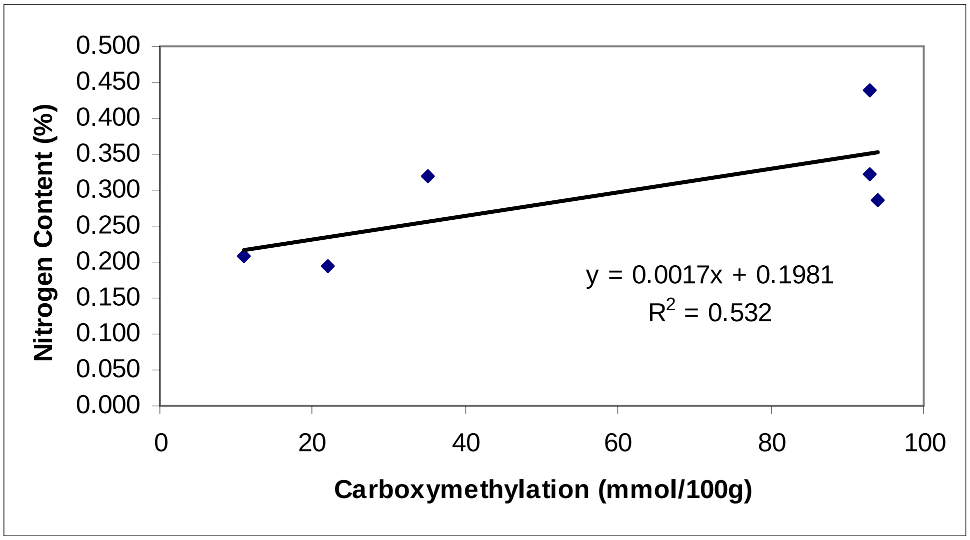


Figure 4.6 Correlation between nitrogen content and carboxymethylation

Durability of the crosslinking agent is moderate to low as indicated by nitrogen content. This is summarized in Figure 4.7. Blank fabric has a nitrogen content of approximately 0.25% prior to washing and 0.20% after washing seven times. After treatment the samples have between 0.62 and 0.78% nitrogen. One washing removes between 45 and 70% of that nitrogen. A large portion of the loss in the first wash is due to excess crosslinking agent on the fabric. After the first wash the nitrogen content continues to steadily decrease. After seven washes the fabric has between 0.20 and 0.27% nitrogen. This is gradually approaching the concentration on the blank fabric. Nitrogen retention is highest with fabrics with higher carboxymethylation, however the crosslinking agent is being washed from all fabric samples.

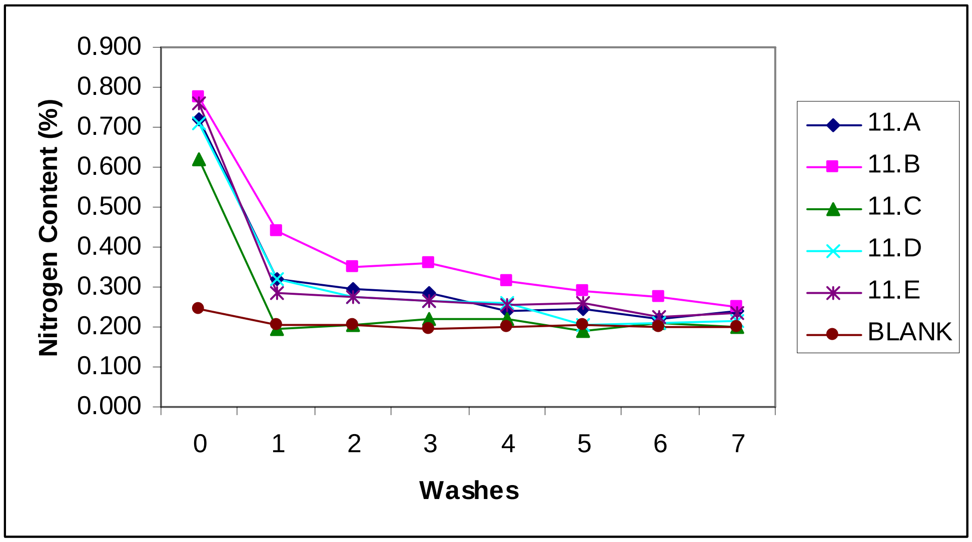


Figure 4.7 Durability to laundering as indicated by nitrogen content

Nitrogen content indicates the amount of crosslinking agent on the sample. The cationic glycerin concentration is highest when carboxymethylation is highest and therefore the fabric has the most anionic character. The crosslinking agent is retained best during laundering of the fabrics where carboxymethylation is highest. The first laundering step removes a large percentage of the cationic glycerin which is not bound to anionic sites. Then it gradually washes away the bound cationic glycerin during subsequent washes. Samples with the lowest carboxymethylation have almost no cationic glycerin after one wash.

The nitrogen content indicates that treated fabric that has not been washed containd 30 to 40 mmol cationic glycerin / 100 g fabric. After one wash they have 0 to 17 mmol cationic glycerin / 100 g fabric. This assumes that the amount of nitrogen in the untreated and washed sample is due to other impurities and occurs uniformly at the same concentration in the treated samples as well. The carboxymethylation of these samples varies from 22 to 94 mmol / 100 g fabric. Prior to washing the crosslinking agent concentration is consistent between treatments and does not correlate to carboxymethylation. Combining this with the fact that the majority of the crosslinking agent is washed away after one wash, indicates that most of the cationic glycerin is not bound to the anionic sites on the fabric. The cationic glycerin left after one wash is related to the carboxymethylation of the fabric. The amount left indicates that between 0 and 45 % of the anionic sites contain crosslinks. The samples with low carboxymethylation have a smaller percentage of crosslinking sites, because the smaller number of sites result in a lower probability that the sites will be spaced at the right distance for crosslinking.

4.3 Picks and Ends

Picks and ends were analyzed for series 11, DMDHEU, and untreated fabric. It is summarized in Table 4.7. This data shows that carboxymethylation and crosslinking cause the fabric to shrink. The yarn count for the treated samples increases between 8 and 30%. Shrinkage during processing appears to be slightly higher with pad-dry cure methods than with pad-batch methods. DMDHEU treatment causes no shrinkage of the fabric.

Table 4.7 Picks and Ends for series 11 trials

	Picks and Ends (yarns/inch)	
Sample	**Warp**	**Fill**
Blank	68	115
11.A	88	125
11.B	88	125
11.C	80	125
11.D	80	125
11.E	80	135
DMDHEU	68	115

Cotton fabric shrinks when the tension, which was produced in manufacturing the yarn structure, is released. This release of tension is facilitated through wetting the fibers, heat, and mechanical forces. They allow the tension of the yarns to be released which reduces their length and causes the overall structure to shrink.

DMDHEU does not shrink during treatment because the treatment provides dimensional stability. Carboxymethylation and ionic crosslinking does not appear to provide the necessary dimensional stability to lock the fabric into shape. The yarns can relax and cause the fabric to shrink. Pad-dry-cure methods provide more heat than pad-batch methods which promotes shrinkage. NaOH treatment also increases the fabric shrinkage. NaOH treatment swells the structure of cellulose, which increases the tension in the yarns. Therefore, there is even more tension that can be released during processing which further promotes shrinkage.

4.4 Shrinkage Due to Home Laundering

Shrinkage after laundering was measured after five cycles. Samples from series 11, DMDHEU, and untreated fabrics were compared. Shrinkage in the warp direction is summarized in Table 4.8 and shrinkage in the fill direction is summarized in Table 4.9.

Table 4.8 Percent shrinkage in the warp direction for series 11 trials

Sample	Original	Wash 1	Wash 2	Wash 3	Wash 4	Wash 5
Blank	0.00	2.60	3.65	3.65	3.65	3.65
11.A	0.00	15.63	16.15	16.15	16.15	16.15
11.B	0.00	15.63	16.67	17.19	17.19	17.19
11.C	0.00	7.29	7.29	8.85	8.85	8.85
11.D	0.00	10.94	10.94	10.94	10.94	10.94
11.E	0.00	17.71	19.27	19.27	19.27	19.79
DMDHEU	0.00	1.04	1.04	1.56	1.56	1.56

Table 4.9 Percent shrinkage in the fill direction for series 11 trials

Sample	Original	Wash 1	Wash 2	Wash 3	Wash 4	Wash 5
Blank	0.00	0.52	0.52	0.52	0.52	0.52
11.A	0.00	0.00	0.00	0.00	0.00	0.00
11.B	0.00	0.00	0.00	0.00	0.00	0.00
11.C	0.00	0.00	0.00	0.00	0.00	0.00
11.D	0.00	0.00	0.00	0.00	0.00	0.00
11.E	0.00	0.00	0.00	0.00	0.00	0.00
DMDHEU	0.00	1.04	1.04	1.04	1.04	1.04

There is virtually no shrinkage in the fill direction. Shrinkage in the warp direction is graphed in Figure 4.8. DMDHEU demonstrates less than 2% shrinkage. The untreated fabric demonstrates less than 4% shrinkage. Carboxymethylated and crosslinked fabrics shrink from 9 to 20%. Almost all of the shrinkage occurs after the first wash cycle for all samples tested.

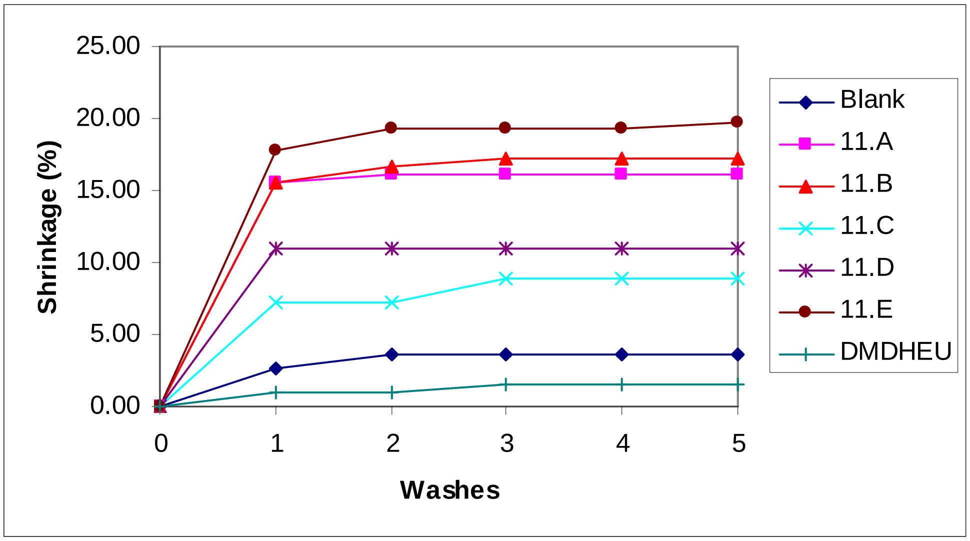


Figure 4.8 Shrinkage in the warp direction due to laundering

Shrinkage after laundering is related to carboxymethylation. Shrinkage increases with carboxymethylation as shown in Figure 4.9. Shrinkage appears to be related to extent of carboxymethylation and geometry of carboxymethylation in the same manner as observed with nitrogen content.

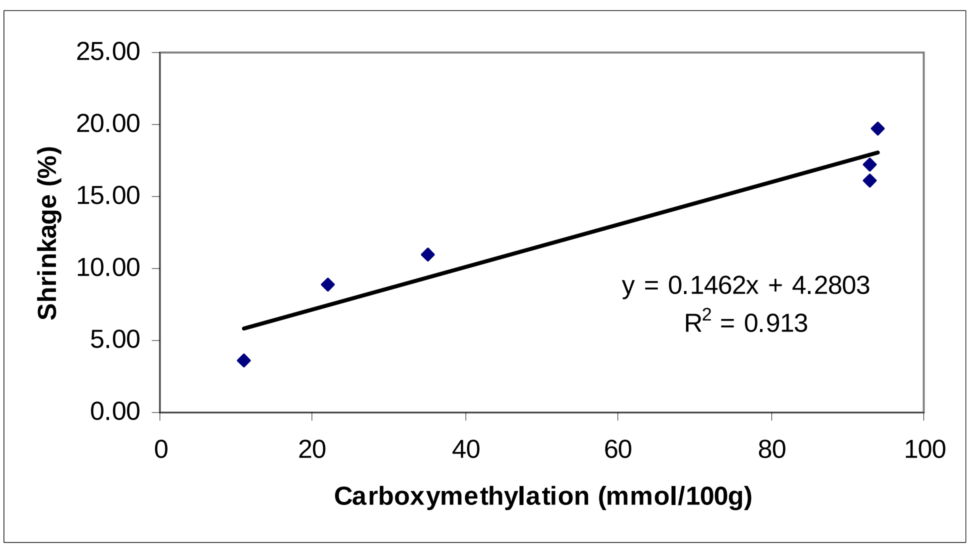


Figure 4.9 Correlation between shrinkage due to laundering and carboxymethylation

The difference in shrinkage between the warp and the fill directions is due to the yarn construction. The yarn in the fill direction does not shrink. It is a weaker yarn with less tension due to the production process. The yarn in the warp direction does shrink. It is a stronger yarn with a tighter construction. A portion of this tension may still remain after treatment, however it appears that treatment causes additional shrinkage. Shrinkage increases with carboxymethylation. Carboxymethyation decreases the density of the polymer structure. As the fabric is washed the anionic carboxyl groups which are not bound to cationic crosslinking agent repel each other and cause the polymer structure to swell. This swelling causes an increase in tension of the fibers and yarns just as NaOH treatment does. Treatments with higher carboxymethylation exhibit higher shrinkage. Since pad-dry-cure carboxymethylation methods produce higher carboxymethylation, they shrink more.

Almost all shrinkage occurs after the first washing. Almost all of the tension is released after one wash cycle. Additionally, the anionic groups on the cellulose chain become bound to cations in the wash water so that they no longer repel each other.

4.5 Basis Weight

4.5.1 Analysis of Basis Weight

Basis weight was evaluated for series 7, 8, 9, 10, and 11, as well as for DMDHEU and untreated fabric. Basis weight data are summarized in Table 4.10 and Figure 4.10. Untreated fabric has a basis weight of 111 g/m^2. DMDHEU treated fabric has a basis weight of 129 g/m^2. Carboxymethylation and ionic crosslinking produce fabrics with basis weights ranging from 114 to 191 g/m^2. All treatments produced an increase in basis weight above that of the untreated fabric.

Table 4.10 Basis weight for series 7, 8, 9, 10, and 11 trials

Sample	Basis Weight – Average (g/cm^2)	Basis Weight - Std. Dev.
BLANK	111	2
7.A	167	4
7.B	151	6
7.C	145	3
7.D	144	4
7.E	154	3
7.F	155	2
8.A	145	5
8.B	128	3
8.C	142	5
8.D	140	1
8.E	139	2
8.F	114	2
8.G	131	2
8.H	117	2
9.A	126	2
9.B	124	3
10.A	187	6
10.B	191	4
10.C	151	3
10.D	185	8
11.A	162	4
11.B	185	3
11.C	142	3
11.D	154	2
11.E	177	5
DMDHEU	129	2

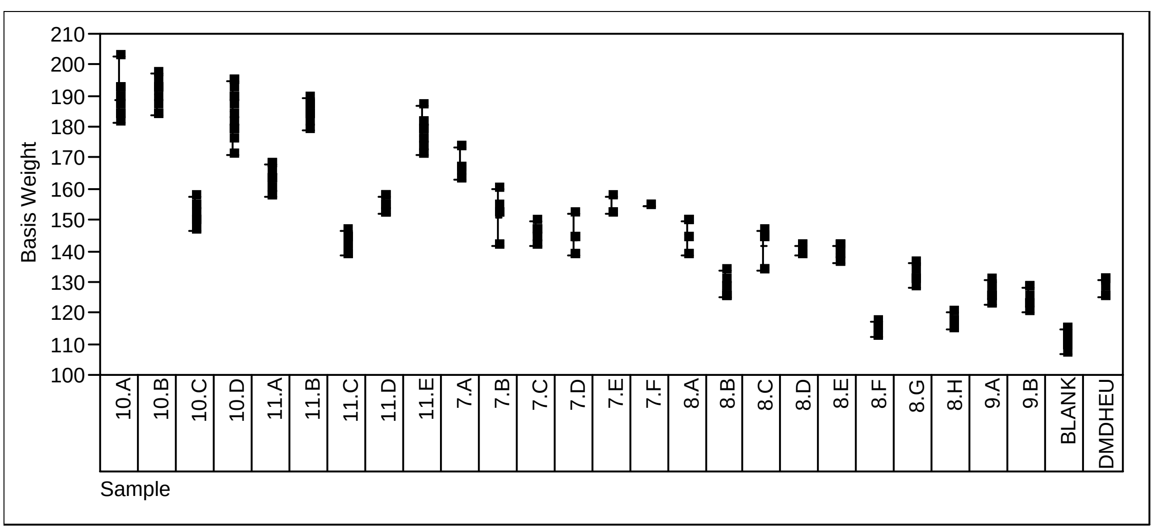


Figure 4.10 Basis weight for series 7, 8, 9, 10, and 11 trials

A model was fit to the basis weight data. The analysis is summarized in Figure 8.10. The analysis indicated that all of the parameters which were varied had a significant effect on basis weight. These parameters included NaOH concentration, chloroacetate concentration, the number of steps in the process, carboxymethylation method, soak time, crosslinking concentration and method, and whether the process was batch or continuous/semi-continuous. Basis weight increases with NaOH concentration and chloroacetate concentration. A one step process has a lower basis weight than a two step process which has a lower basis weight than a three step process. Pad-batch is lower than pad-dry-cure and pad-cure is higher than pad-dry-cure. Long soak times yield lower basis weight than short soak times. Crosslinking with higher concentrations of crosslinking agent yield higher basis weight than lower concentrations of crosslinking agent. The R^2 value for a regression of actual versus predicted values is 0.91.

4.5.2 Summary of Basis Weight

There are many factors which affect basis weight. This is because basis weight is affected by shrinkage, reaction efficiency, and absorption of the crosslinking agent. Any parameters which affect these factors will also affect the basis weight. The Pareto graph in Figure 8.10 shows the most significant factors.

Figure 4.11 shows that there is a correlation between shrinkage during the process and basis weight. As the fabric shrinks, there are more fibers in one unit area. This accounts for the majority of the basis weight increase. There is also a small increase due to the additional functional groups on the cellulose chain and the addition of cationic glycerin.

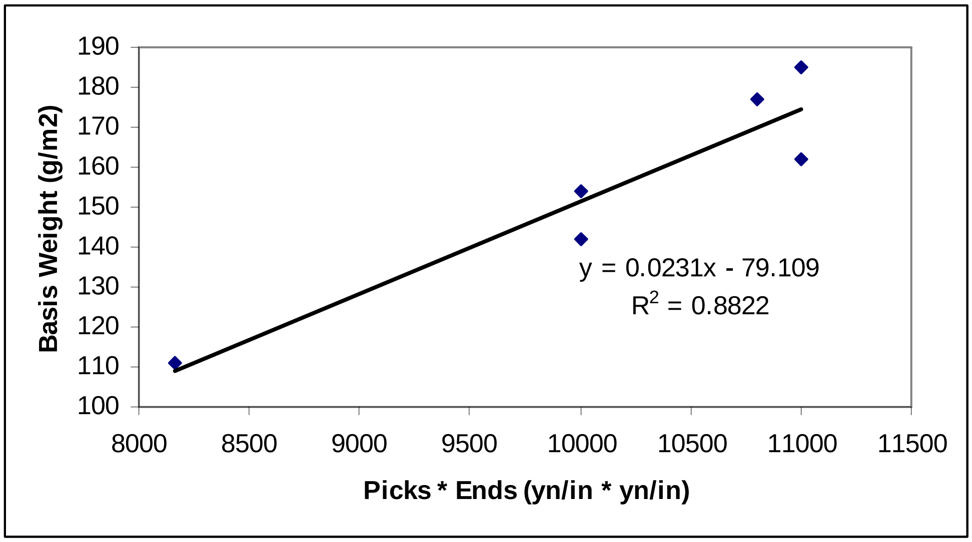


Figure 4.11 Correlation between shrinkage during the process and basis weight

4.6 Bending Rigidity

4.6.1 Analysis of Bending Rigidity

Bending rigidity was analyzed for series 7, 8, 9, 10, and 11, for the DMDHEU treated fabric, and the untreated fabric. The bending rigidity was determined in the warp and fill direction. The warp and fill directions were analyzed separately to verify that the same trends were observed in both sets of data.

4.6.1.1 Bending Rigidity in the Warp Direction

Bending rigidity data in the warp direction is summarized in Table 4.11 and Figure 4.12. The untreated fabric has a bending rigidity of 348 μNm with a standard deviation of 31 μNm and the DMDHEU treated fabric has a bending rigidity of 952 μNm with a standard deviation of 75 μNm. DMDHEU produces a 170% increase in bending rigidity. The carboxymethylated and crosslinked samples exhibited a wide range of bending rigidities from 343 to 3280 μNm. This is a range from no increase to 840% increase. All of these treatment procedures resulted in bending rigidity equal to or greater than the untreated fabric.

Table 4.11 Bending rigidity in the warp direction for series 7, 8, 9, 10, and 11 trials

Sample	Bending Rigidity – Average (μNm)	Bending Rigidity - Std. Dev.
BLANK	348	31
7.A	2267	187
7.B	1329	403
7.C	1694	90
7.D	1830	165
7.E	1413	20
7.F	1349	21
8.A	1137	99
8.B	673	29
8.C	1353	116
8.D	939	82
8.E	1282	84
8.F	343	21
8.G	714	62
8.H	371	31
9.A	945	86
9.B	806	61
10.A	2658	290
10.B	3063	207
10.C	916	91
10.D	2165	233
11.A	1711	122
11.B	3280	118
11.C	759	34
11.D	1331	60
11.E	2593	697
DMDHEU	952	75

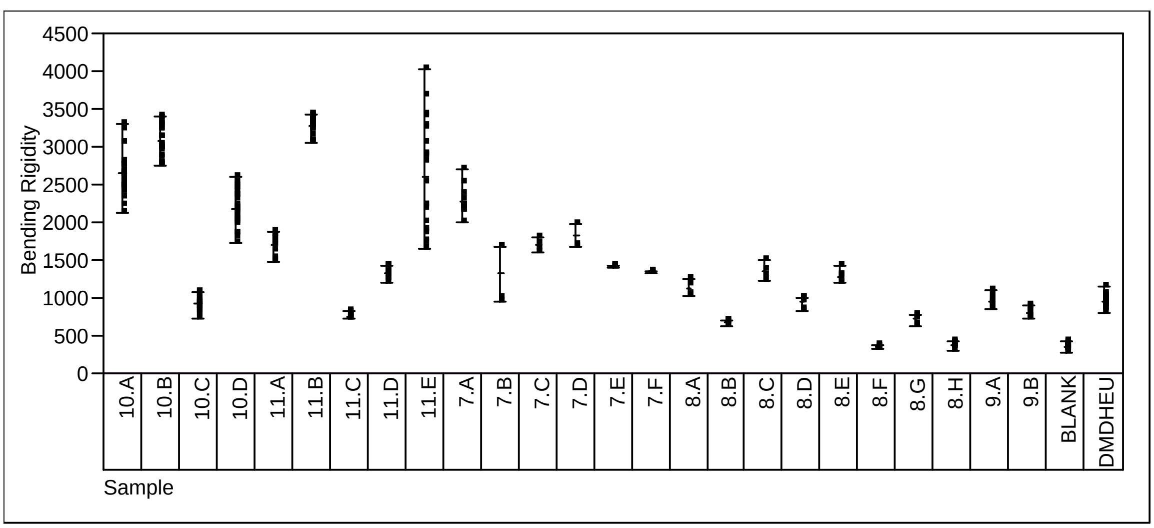


Figure 4.12 Bending rigidity in the warp direction for series 7, 8, 9, 10, and 11 trials

A number of parameters were varied in the procedures to produce these samples. NaOH concentration was varied from 20 to 40% and chloroacetate concentration was varied from 1.0 to 2.0M. The procedure was performed in either one, two, or three steps. Carboxymethylation was performed using pad-batch (indicated as B in the analysis), pad-dry-cure (indicated as D in the analysis), or pad-cure (indicated as C in the analysis) methods. Long and short soak times were evaluated. The cationic glycerin crosslinking procedure was performed with 3, 6 and 9% cationic glycerin solutions using exhaustion and pad-dry-cure procedures.

The analysis summarized in Figure 8.11 shows which parameters do not have an effect on bending rigidity. Bending rigidity is not effected by NaOH concentration or soak time. There is no significant difference between two and three step procedures. There is also no significant difference between batch and semi-continuous/continuous processes.

The analysis of variance and fit to model was performed with only the significant parameters. It is summarized in Figure 8.12. A Pareto plot is included in Figure 8.12 to show the most important parameters. The chloroacetate concentration is one of the most important parameters. 2.0M chloroacetate produces approximately 731 μNm higher bending rigidity than 1.0M chloroacetate. Carboxymethylation method also has a dramatic effect. The pad-cure method produces approximately 743 μNm higher bending rigidity than the pad-dry-cure method and the pad-batch method produces 622 μNm lower bending rigidity than the pad-dry-cure method. Pad-dry-cure methods for crosslinking produce higher bending rigidity than exhaustion methods. Higher cationic glycerin concentrations produce higher bending rigidity. Two and three step processes produce higher bending rigidity than one step processes.

Hand or fabric feel is important for apparel applications. Hand is typically better when bending rigidity is low. Therefore, bending rigidity is optimized at a low value. Low bending rigidity is achieved with 1.0M chloroacetate, pad-batch carboxymethylation, exhaustion and 3% cationic glycerin for crosslinking.

4.6.1.2 Bending Rigidity in the Fill Direction

Bending rigidity data in the fill direction is summarized in Table 4.12 and Figure 4.13. Untreated fabric has a bending rigidity of 220 μNm with a standard deviation of 12 μNm. DMDHEU treated fabric has a bending rigidity of 564 μNm with a standard deviation of 66 μNm. Carboxymethylated and ionically crosslinked fabrics had bending rigidities ranging from 229 to 2694 μNm.

Table 4.12 Bending rigidity in the fill direction for series 7, 8, 9, 10, and 11 trials

Sample	Bending Rigidity – Average (μNm)	Bending Rigidity - Std. Dev.
BLANK	220	12
7.A	1733	152
7.B	921	98
7.C	1049	81
7.D	854	81
7.E	902	10
7.F	998	18
8.A	843	115
8.B	449	20
8.C	951	139
8.D	757	63
8.E	881	72
8.F	229	17
8.G	543	39
8.H	257	11
9.A	492	72
9.B	392	47
10.A	2191	160
10.B	2694	183
10.C	727	48
10.D	2384	322
11.A	1253	56
11.B	2559	121
11.C	513	36
11.D	994	79
11.E	2197	115
DMDHEU	564	66

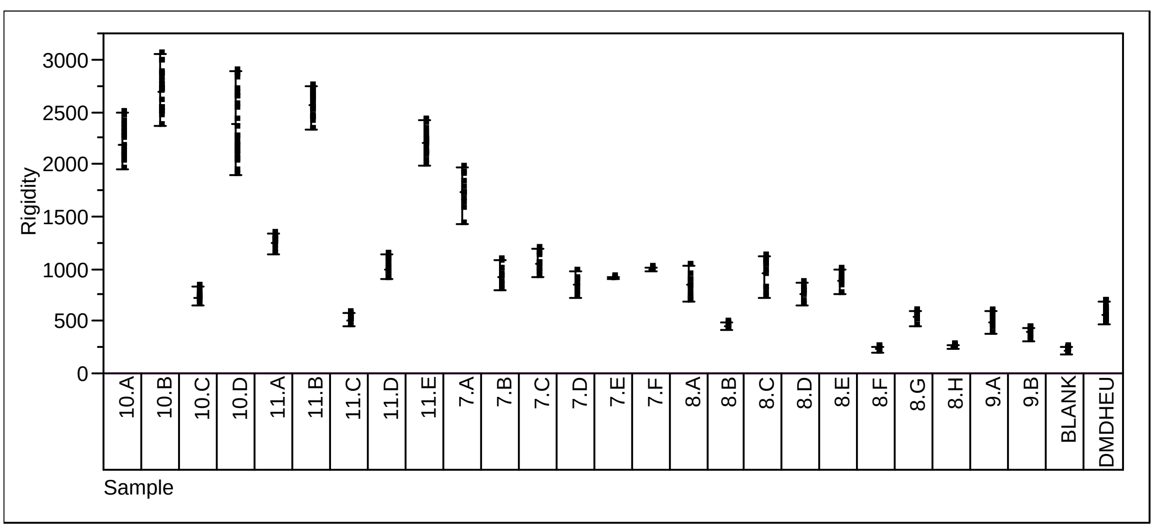


Figure 4.13 Bending rigidity in the fill direction for series 7, 8, 9, 10, and 11 trials

Bending rigidity was analyzed in the fill direction in the same manner that it was analyzed in the warp direction. Figure 8.13 shows that the same parameters are insignificant. Figure 8.14 summarizes the analysis of variance and the fit to model with only the significant parameters. 2.0M chloroacetate produces approximately 592 μNm higher bending rigidity than 1.0M chloroacetate. The pad-cure method produces approximately 521 μNm higher bending rigidity than the pad-dry-cure method and the pad-batch method produces 426 μNm lower bending rigidity than the pad-dry-cure method. Pad-dry-cure methods for crosslinking produce higher bending rigidity than exhaustion methods. Higher cationic glycerin concentrations produce higher bending rigidity. Two and three step processes produce higher bending rigidity than one step processes. These trends are identical to those observed in the warp direction.

4.6.2 Summary of Bending Rigidity

Warp and fill data analysis yields the same results in regards to which variables influence bending rigidity, in what direction they affect it, and their relative magnitude of influence. Both warp and fill data produce models which result in lines of actual versus predicted bending rigidities with R^2 values of around 0.80. This is very good, since error in the test method with this data limits the model to a maximum of about 0.88.

The bending rigidity of carboxymethylated and ionically crosslinked fabrics is heavily influenced by the procedures used to treat the fabric. Process variations can produce no increase in stiffness to almost 10 times the stiffness of untreated fabric. The bending rigidity of the fabric is influenced by both carboxymethylation and crosslinking. The chloroacetate concentrations and the carboxymethylation method influence this property.

They indicate that the extent of carboxymethylation and the geometry of carboxymethylation influence bending rigidity. The relation between carboxymethylation and bending rigidity is shown in Figure 4.14. Bending rigidity increases with extent of carboxymethylation. Crosslinking method and concentration also influence bending rigidity. Bending rigidity increases with an increase in crosslinking agent on the fabric as shown in Figure 4.15.

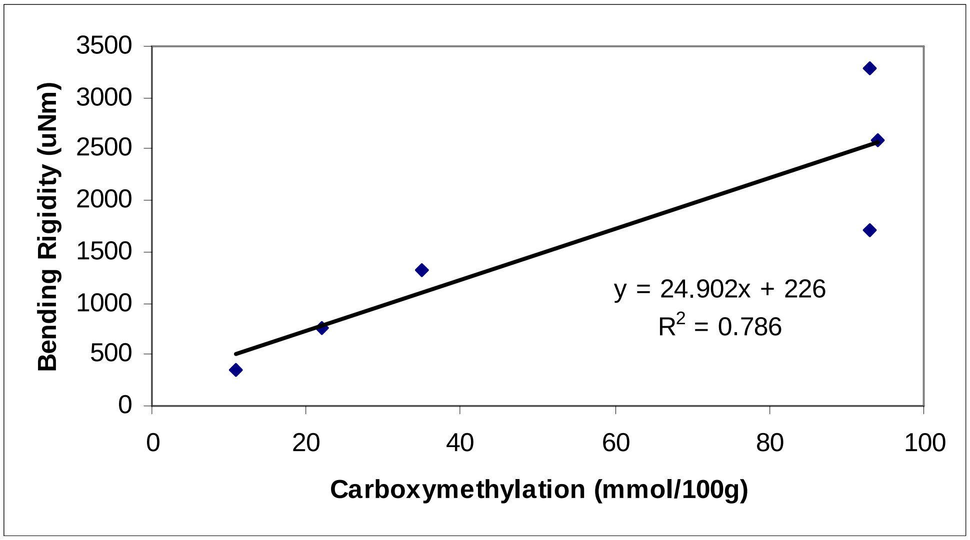


Figure 4.14 Correlation between bending rigidity and carboxymethylation

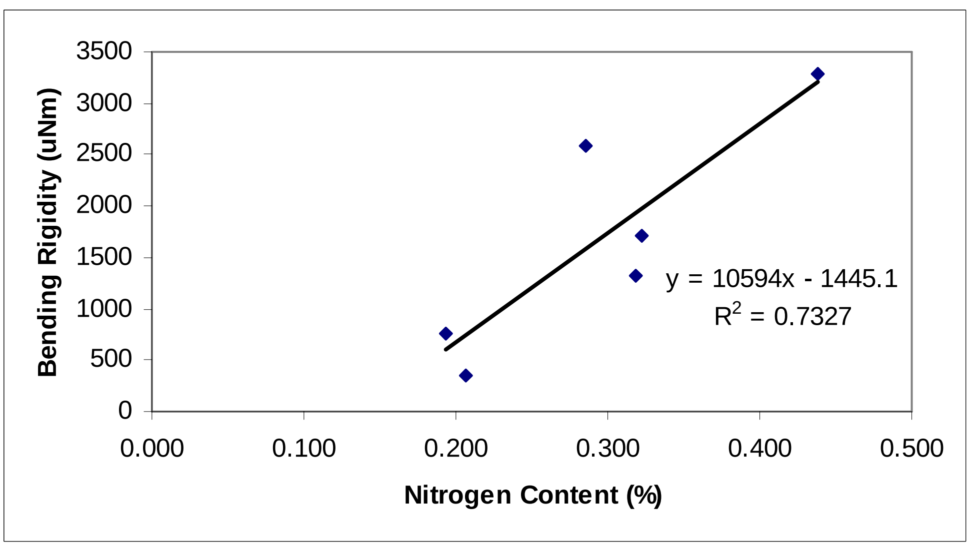


Figure 4.15 Correlation between bending rigidity and nitrogen content

Optimally, bending rigidity would not be increased for most DP applications. Bending rigidity is best with 1.0M chloroacetate and pad-batch carboxymethylation methods. It is better when exhaustion methods are used for crosslinking and the lowest concentration of crosslinking agent 3% is used.

Bending rigidity and basis weight are highly correlated. This is shown in Figure 4.16. Bending rigidity increases when the fabric shrinks during processing, because a larger number of yarns must be bent during testing. It is higher with increased crosslinking, because the crosslinks increase the intermolecular bonding. Bending rigidity is measured using small amounts of force. The effects of ionic crosslinking are quite clear at these forces. The crosslinks are strong enough to hold the fibers in place and increase the forces required to alter the shape of the structure.

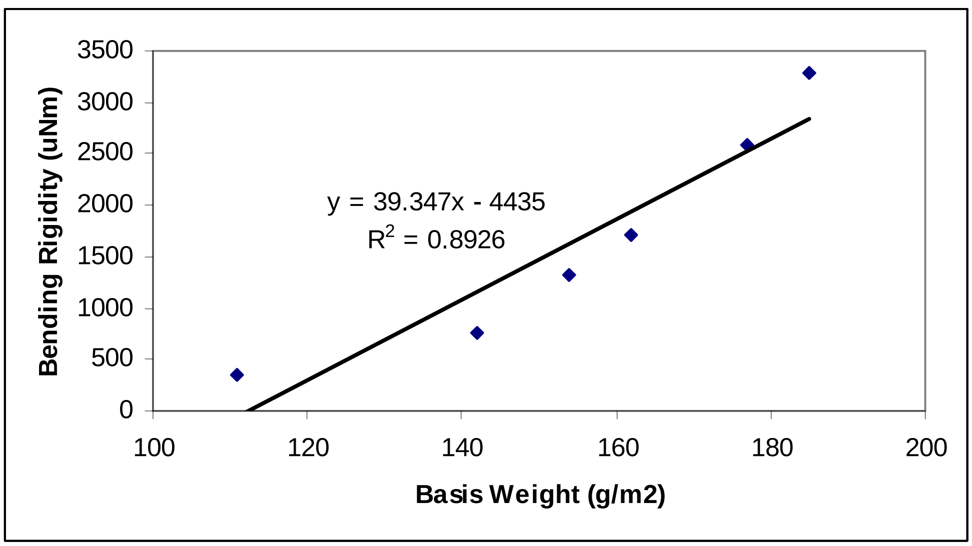


Figure 4.16 Correlation between bending rigidity and basis weight

4.7 Tear Strength

4.7.1 Analysis of Tear Strength

Series 11 and 12 were tested for tear strength in both the warp and fill direction. Warp and fill data are analyzed separately.

4.7.1.1 Tear Strength in the Warp Direction

Tear strength data for the warp direction are summarized in Table 4.13 and Figure 4.17. The untreated fabric has a peak load of 4.1 lb_f with a standard deviation of 0.3 lb_f. DMDHEU treated fabric samples has a tear strength in the warp direction of 0.7 lb_f with a standard deviation of 0.1 lb_f. This is an 83% decrease in tear strength. Carboxymethylated and crosslinked fabrics demonstrate an increase in tear strength. They range from 4.9 to 7.4 lb_f. This shows as much as an 80% increase in tear strength.

Table 4.13 Tear strength in the warp direction for series 10 and 11 trials

Warp Tear Strength by ASTM D 5587-03						
	Peak Load (lb_f)					
Sample	1	2	3	4	Average	Std. Dev.
Blank	3.74	4.49	4.03	4.13	4.1	0.3
10.A	7.34	6.93	7.27	8.03	7.4	0.5
10.B	6.43	6.72	6.63	6.78	6.6	0.2
10.C	6.11	5.75	6.14	5.66	5.9	0.2
10.D	6.33	6.72	6.50	7.06	6.7	0.3
11.A	6.00	5.62	6.08	5.74	5.9	0.2
11.B	6.30	6.12	6.76	6.04	6.3	0.3
11.C	4.96	4.93	4.72	5.10	4.9	0.2
11.D	5.01	5.77	5.52	5.96	5.6	0.4
11.E	5.48	5.82	5.61	5.48	5.6	0.2
DMDHEU	0.74	0.66	0.84	0.69	0.7	0.1

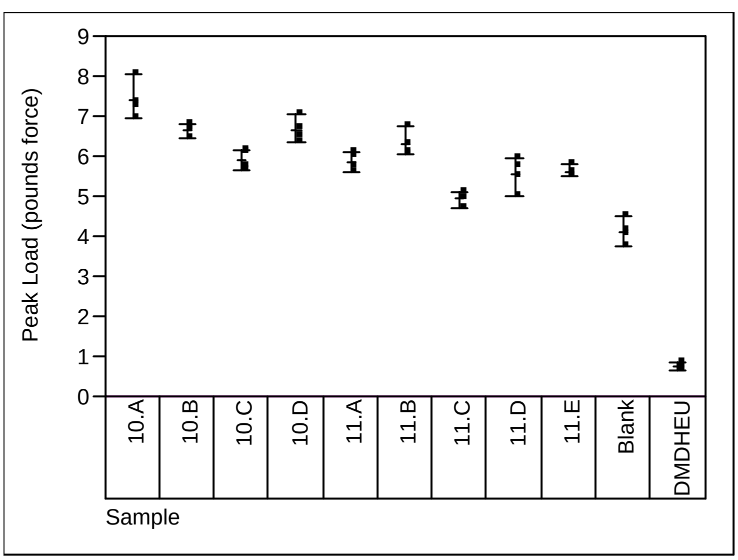


Figure 4.17 Tear strength in the warp direction for series 10 and 11 trials

Tear strength in the warp direction was first analyzed using paired student's t-test to determine the effect of carboxymethylation conditions. This is summarized in Figure 8.15. In the analysis, pad-cure carboxymethylation with 2.0M chloroacetate is indicated as A, pad-dry-cure carboxymethylation with 2.0M chloroacetate is indicated as B, pad-batch carboxymethylation with 1.0M chloroacetate is indicated as C, and pad-batch carboxymethylation with 2.0M chloroacetate is indicated as D. Only C is significantly different from A, B, and D. Therefore carboxymethylation method does not affect tear strength, but the concentration of chloroacetate does have a significant effect on tear strength. Tear strength is higher when 2.0M chloroacetatehloroacetate is used than when 1.0M chloroacetate is used.

A second paired student's t-test is performed to determine the effect of crosslinking conditions which is shown in Figure 8.16. In this analysis pad-dry-cure method with 3% cationic glycerin is indicated as A, exhaustion with 3% cationic glycerin is indicated as B, and pad-batch-dry-cure method with 9% cationic glycerin is indicated as C. A is significantly different from B and C. Therefore, pad-dry-cure crosslinking produces a greater tear strength increase than exhaustion or pad-batch-dry-cure procedures.

4.7.1.2 Tear Strength in the Fill Direction

Tear strength data for the fill direction is summarized in Table 4.14 and Figure 4.18. Tear strength in the fill direction is approximately 50% of that observed in the warp direction.

Table 4.14 Tear strength in the fill direction for series 10 and 11 trials

Fill Tear Strength by ASTM D 5587-03						
	Peak Load (lb_f)					
Sample	1	2	3	4	Average	Std. Dev.
Blank	2.64	2.82	2.85	2.77	2.77	0.09
10.A	3.46	3.90	3.84	4.34	3.9	0.4
10.B	3.86	3.84	3.89	3.87	3.87	0.02
10.C	3.20	3.31	2.95	2.86	3.1	0.2
10.D	3.39	3.01	3.49	3.43	3.3	0.2
11.A	2.96	2.70	2.81	2.93	2.9	0.1
11.B	3.30	3.21	3.43	3.32	3.32	0.09
11.C	2.87	2.73	2.60	2.70	2.7	0.1
11.D	3.01	2.67	2.77	2.64	2.8	0.2
11.E	3.06	3.23	2.98	3.26	3.1	0.1
DMDHEU	0.34	0.32	0.32	0.29	0.32	0.02

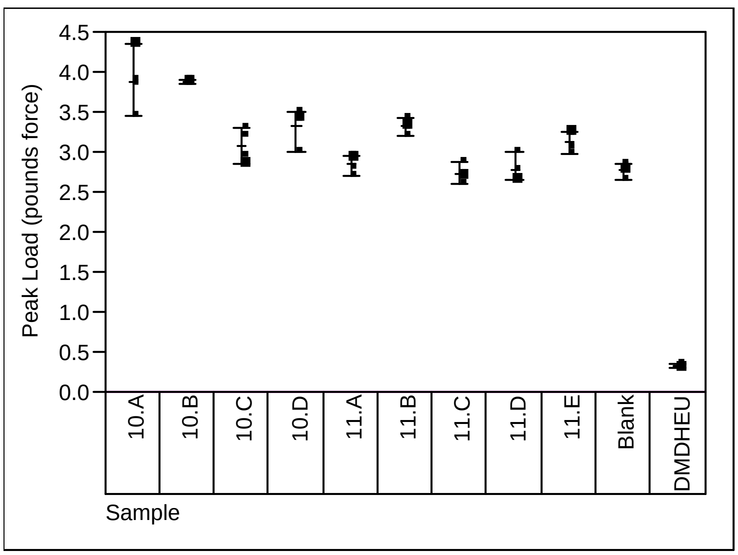


Figure 4.18 Tear strength in the fill direction for series 10 and 11 trials

A paired student's t-test of data in the fill direction is summarized in Figure 8.17. The same letters are used to indicate carboxymethylation conditions. The results in the fill direction differ from those in the warp direction. B is significantly different from C and D, and A is significantly different than C. This suggests that pad-cure and pad-dry-cure methods produce slightly higher tear strength increases than the pad-batch method. There is no significant difference between chloroacetate concentrations.

A fill direction tear strength paired student's t-test is performed in Figure 8.18, which indicates the effect of crosslinking conditions. The same letters indicate crosslink conditions as used previously. These results are the same as those seen for the warp direction. A is significantly different from B and C. Therefore, pad-dry-cure crosslinking produces a greater tear strength increase than exhaustion or pad-batch-dry-cure procedures.

4.7.2 Summary of Tear Strength

Analysis of both warp and fill data indicate that tear strength is influenced by both carboxymethylation and crosslinking. The relationship between carboxymethylation and tear strength is shown in Figure 4.19. Tear strength increases with extent of carboxymethylation. It appears to be affected by both extent of carboxymethylation and carboxymethylation geometry. The relationship between nitrogen content and tear strength is shown in Figure 4.20. Tear strength increases with nitrogen content on the fabric.

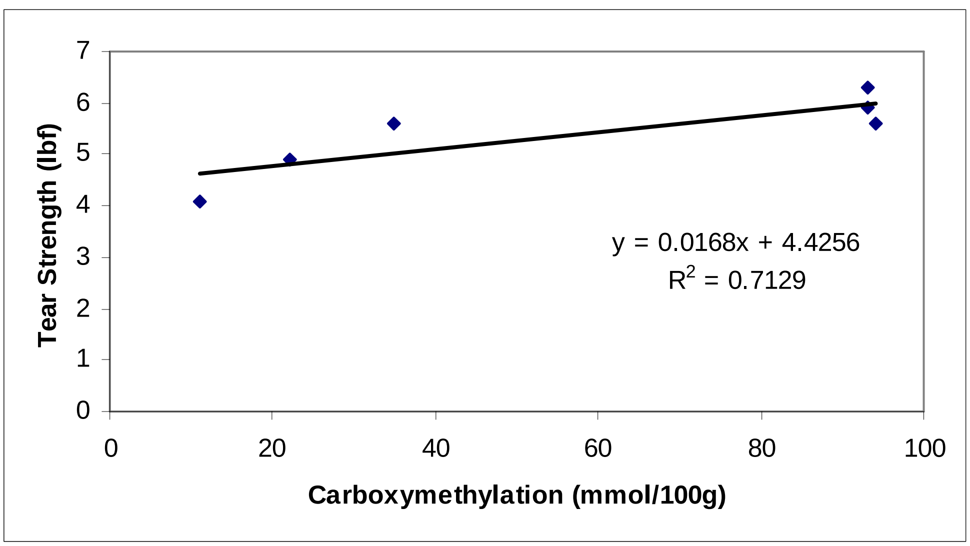


Figure 4.19 Correlation between tear strength and carboxymethylation

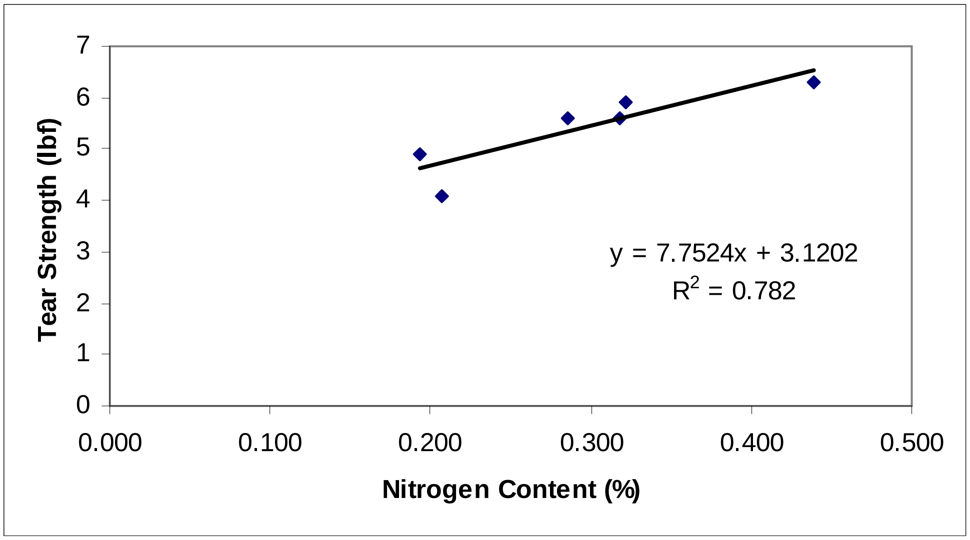


Figure 4.20 Correlation between tear strength and nitrogen content

There is a difference between results for carboxymethylation. Warp data indicates that 2.0 M sodium salt produces higher tear strength than 1.0M. Fill data indicates that pad-dry-cure and pad-cure carboxymethylation methods produce higher tear strength than pad-batch. The effects are not large and there is a relatively small amount of tear strength data. When compared to other physical properties, it appears that both of these parameters have a small effect of tear strength. The difference in results is likely due to the relatively small number of samples compared with the small effect of the parameters and the error in the test method.

The results for crosslinking analysis are the same for both warp and fill data. Pad-dry-cure methods produce higher tear strength than pad-batch and pad-batch-dry-cure methods.

Tear strength increases with basis weight as shown in Figure 4.21. Tear strength increases due to a larger number of yarns per unit length. It also increases due to the effects of ionic crosslinking which both increases bond strength between fibers and allows the bonds to break and reform as the fiber is stretched. (The increase in strength due to ionic crosslinking is further elaborated in the summary section of strain at break.)

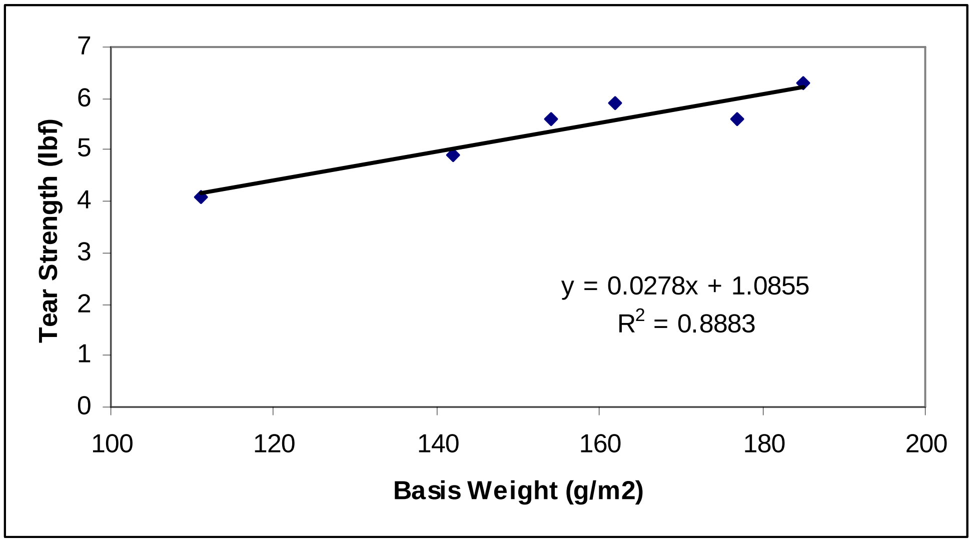


Figure 4.21 Correlation between tear strength and basis weight

4.8 Tensile Strength

4.8.1 Analysis of Tensile Strength

Tensile strength was measured for both warp and fill directions. Data for the warp direction are summarized in Table 4.15 and Figure 4.22. Untreated fabric has a tensile strength of 48 lb_f with a standard deviation of 6 lb_f. DMDHEU treated fabric has a tensile strength of 20 lb_f with a standard deviation of 2 lb_f. DMDHEU reduces the tensile strength of this fabric by 58%. Carboxymethylation and ionic crosslinking produces fabric with a tensile strength in the range from 47 to 60 lb_f. This ranges from no change to an increase of 25%.

Table 4.15 Tensile strength in the warp direction for series 7, 8, 9, 10, and 11 trials

Sample	Peak Load – Average (lb_f)	Peak Load - Std. Dev.
BLANK	48	6
7.A	54	3
7.B	54	2
7.C	50	2
7.D	53	1
7.E	56	1
7.F	55	2
8.A	52	1
8.B	51	1
8.C	53	1
8.D	50	1
8.E	53	2
8.F	48	1
8.G	48	1
8.H	47	1
9.A	51	2
9.B	51	1
10.A	61	1
10.B	59	2
10.C	57	1
10.D	57	2
11.A	60	1
11.B	59	1
11.C	54	2
11.D	56	2
11.E	58	3
DMDHEU	20	2

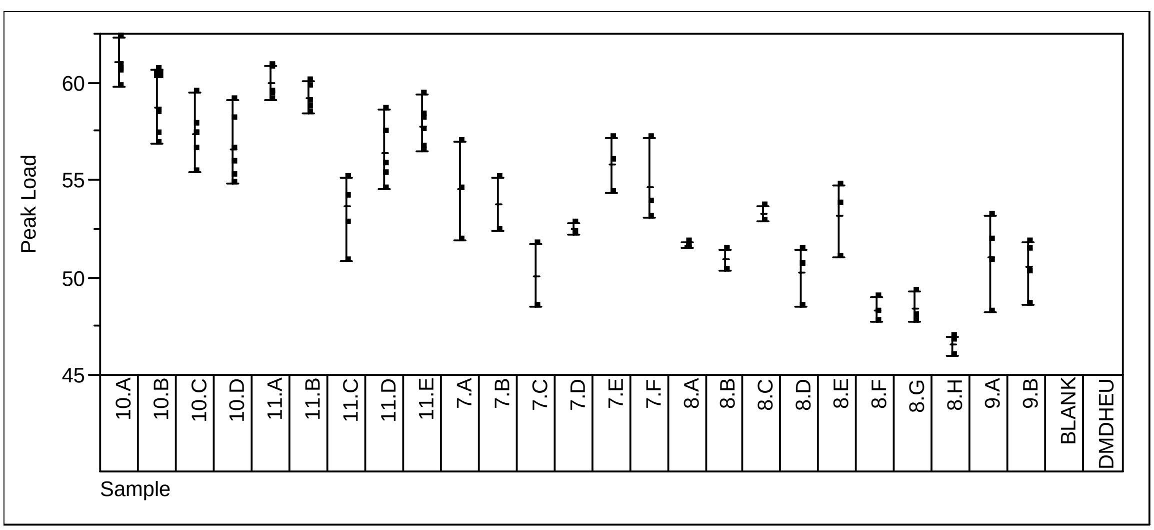


Figure 4.22 Tensile strength in the warp direction for series 7, 8, 9, 10, and 11 trials

There were a number of parameters which were varied in the procedures to produce these samples. NaOH concentration was varied from 20 to 40% and chloroacetate concentration was varied from 1.0 to 2.0M. The procedure was performed in either one, two, or three steps. Carboxymethylation was performed using pad-batch (indicated as B in the analysis), pad-dry-cure (indicated as D in the analysis), or pad-cure (indicated as C in the analysis) methods. Long and short soak times were used. The cationic glycerin crosslinking procedure was performed with 3, 6 and 9% cationic glycerin solutions using exhaustion and pad-dry-cure procedures.

The results of modeling analysis show which parameters do not have a significant effect on tensile strength in Figure 8.19. Soak times and NaOH concentration do not have a significant effect on tensile strength. There is no difference between pad-dry-cure and pad-cure carboxymethylation methods. The transition from batch to semi-continuous / continuous processes did not affect tensile strength.

The analysis was repeated with only significant parameters. This analysis is summarized in Figure 8.20. The R^2 value for a regression line of actual versus predicted values is 0.82. The R^2 value can be no greater than 0.86 due to error in the test method. Tensile strength is about 2.6 lb_f higher for 2.0M chloroacetate concentrations than 1.0M concentrations. The strength increases with the number of steps in the process. Pad-batch carboxymethylation methods produce about 1.1 lb_f lower strength than pad-dry-cure or pad-cure methods. Crosslinking method also affects tensile strength. Pad-dry-cure methods with 9% cationic glycerin (indicated as A in this analysis) yield the highest strength, followed by exhaustion with 6% cationic glycerin (indicated as D in this analysis) , and finally exhaustion with 3% cationic glycerin (indicated by B in this analysis).

The results for analysis of fill direction tensile strength showed the same trends as seen with warp direction data. The fill tensile strength was lower and had a higher standard deviation. However, when the data were analyzed, the same parameters were determined to be significant and affect the tensile strength in the same manner. The magnitudes of these effects were lower, but their relative magnitudes were comparable to those seen in the warp direction.

4.8.2 Summary of Tensile Strength

Carboxymethylation and ionic crosslinking improve the tensile strength of treated fabric. There are effects of both carboxymethylation and crosslinking. Tensile strength increases with degree of carboxymethylation as shown in Figure 4.23. Tensile strength also increases with nitrogen content and thus crosslinking agent content as shown in Figure 4.24.

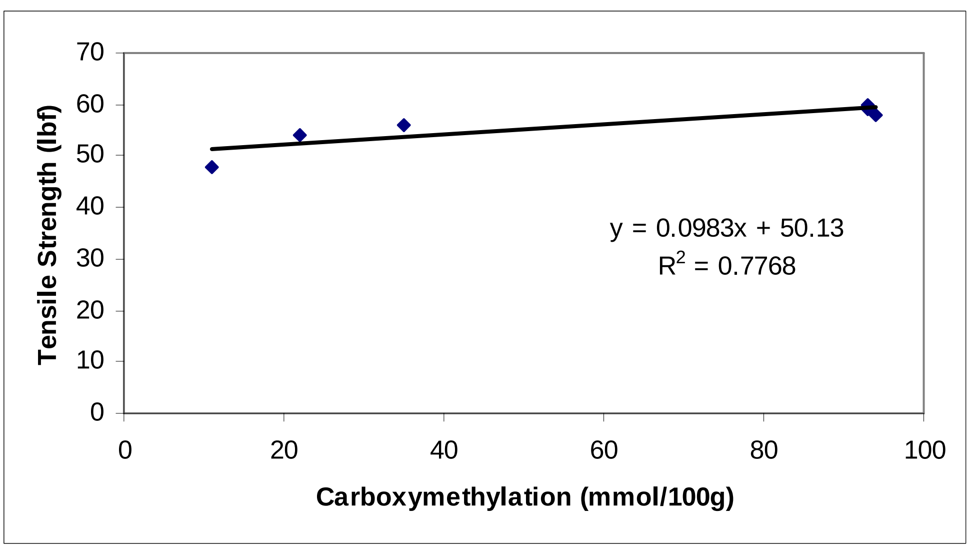


Figure 4.23 Correlation between tensile strength and carboxymethylation

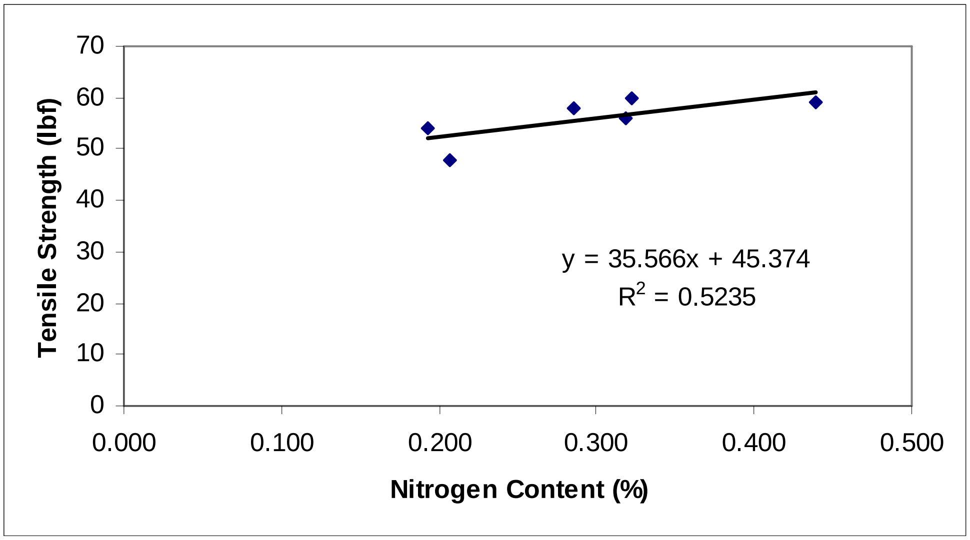


Figure 4.24 Correlation between tensile strength and nitrogen content

Tensile strength increases with basis weight as shown in Figure 4.25. Tensile strength increases due to a larger number of yarns per unit length. The larger number of yarns must be broken before the fiber breaks. It also increases due to the effects of ionic crosslinking which both increases bond strength between fibers and allows the bonds to break and reform as the fiber is stretched. (The increase in strength due to ionic crosslinking is further elaborated in the summary section of strain at break.)

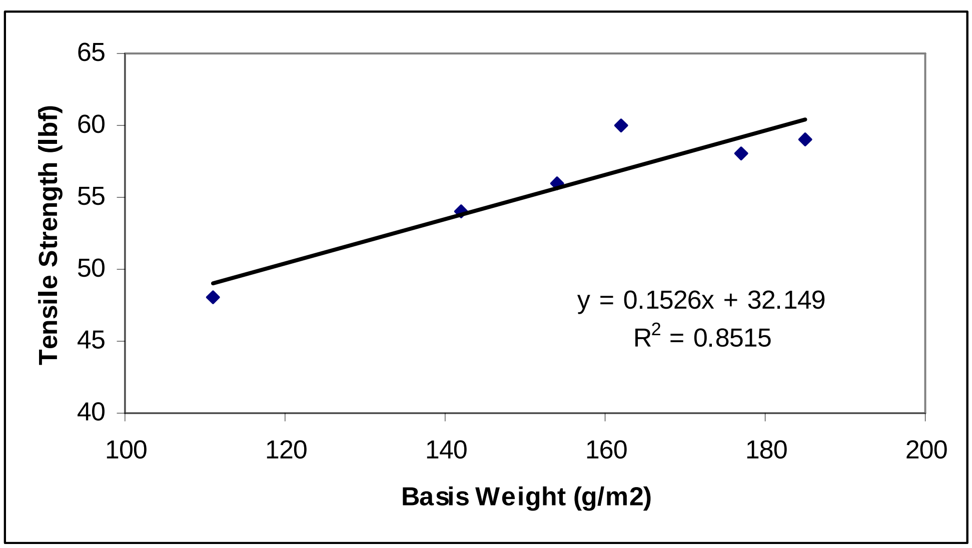


Figure 4.25 Correlation between tensile strength and basis weight

4.9 Strain at Break

4.9.1 Analysis of Strain at Break

Strain at break was recorded for warp and fill samples while measuring tensile strength. Stain at break in the warp direction is summarized in Table 4.16 and Figure 4.26. Untreated fabrics had a breaking strain of 9% with a standard deviation of 1%. DMDHEU treated fabrics had a breaking strain of 3% with a standard deviation of 0.3%. DMDHEU reduces the breaking stain by 67%. Carboxymethylated and ionically crosslinked samples had breaking strains ranging from 11 to 40%. This treatment increases breaking strain from 22 to 340%.

Table 4.16 Strain at break in the warp direction for series 7, 8, 9, 10, and 11 trials

Sample	Strain at Break – Average (%)	Strain at Break - Std. Dev.
BLANK	9	1
7.A	24	2
7.B	23	1
7.C	17	2
7.D	21	1
7.E	21	1
7.F	21	1
8.A	19	0
8.B	14	1
8.C	19	0
8.D	19	1
8.E	15	1
8.F	11	1
8.G	15	1
8.H	11	1
9.A	13	1
9.B	14	1
10.A	40	1
10.B	40	1
10.C	24	1
10.D	31	1
11.A	21	1
11.B	27	1
11.C	16	1
11.D	21	1
11.E	25	1
DMDHEU	3	0.3

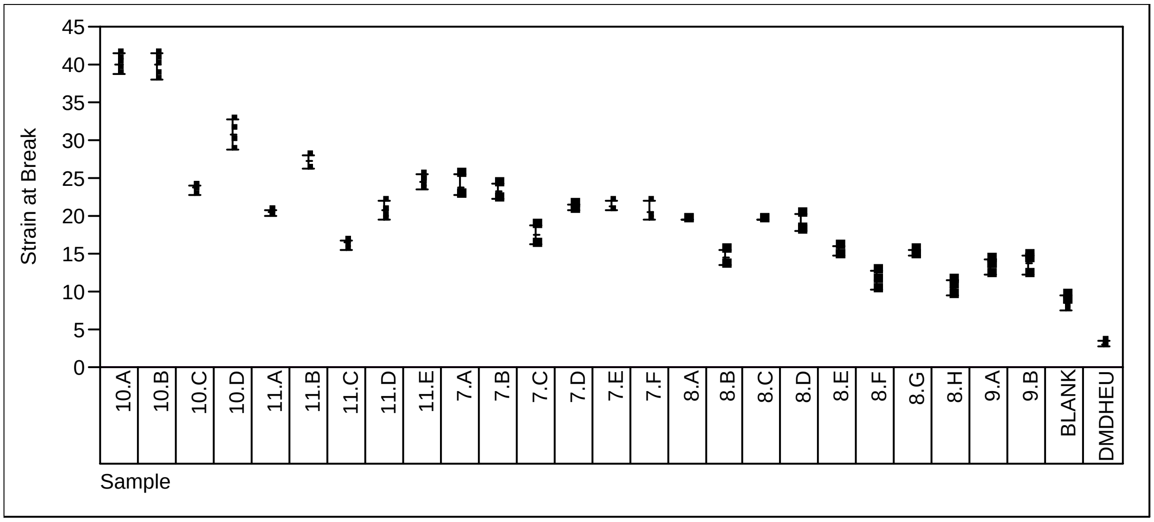


Figure 4.26 Strain at break in the warp direction for series 7, 8, 9, 10, and 11 trials

The same parameters were evaluated as with tensile strength. NaOH concentration was varied from 20 to 40% and chloroacetate concentration was varied from 1.0 to 2.0M. The procedure was performed in either one, two, or three steps. Carboxymethylation was performed using pad-batch (indicated as B in the analysis), pad-dry-cure (indicated as D in the analysis), or pad-cure (indicated as C in the analysis) methods. Long and short soak times were used. The cationic glycerin crosslinking procedure was performed with 3, 6 and 9% cationic glycerin solutions using exhaustion and pad-dry-cure procedures.

The first analysis to determine which factors do not have a significant effect on elongation is summarized in Figure 8.21. It shows that soak time does not affect elongation. Whether the process is batch or semi-continuous / continuous does not affect the elongation either. There is no significant difference between using a two step and a three step process.

Analysis is repeated without the insignificant parameters determined in Figure 8.21. The next analysis showed that NaOH concentration was not significant either. A third analysis without NaOH concentration is shown in Figure 8.22. 2.0M chloroacetate produces about 6% higher breaking strain than 1.0M chloroacetate. A one step process produces about

4% higher breaking strain than a two or three step process. Pad-dry-cure and pad-cure carboxymethylation methods produce 2 to 3% higher breaking strain than pad-batch methods. Pad-dry-cure crosslinking methods with 9% cationic glycerin (indicated as A in this analysis) yield the highest breaking strain, followed by exhaustion with 6% cationic glycerin (indicated as D in this analysis) , and finally exhaustion with 3% cationic glycerin (indicated by B in this analysis). A Pareto graph is included in Figure 8.22 to show the relative significance of each parameter.

Specimens were tested in the fill direction as well. The results in the fill direction show the same trends as seen with warp specimen. Increases in the fill direction are not as large, but still dramatic. The same variables affect the fill direction as the warp direction. Their relative significance is the same as well.

4.9.2 Summary of Strain at Break

Carboxymethylation and ionic crosslinking produce dramatic changes in the strain at break for fabrics. Strain at break is related to both carboxymethylation and nitrogen content. Figure 4.27 shows that breaking strain increases with carboxymethylation. Figure 4.28 shows that breaking elongation increases with nitrogen content and thus crosslinking agent present on the fabric.

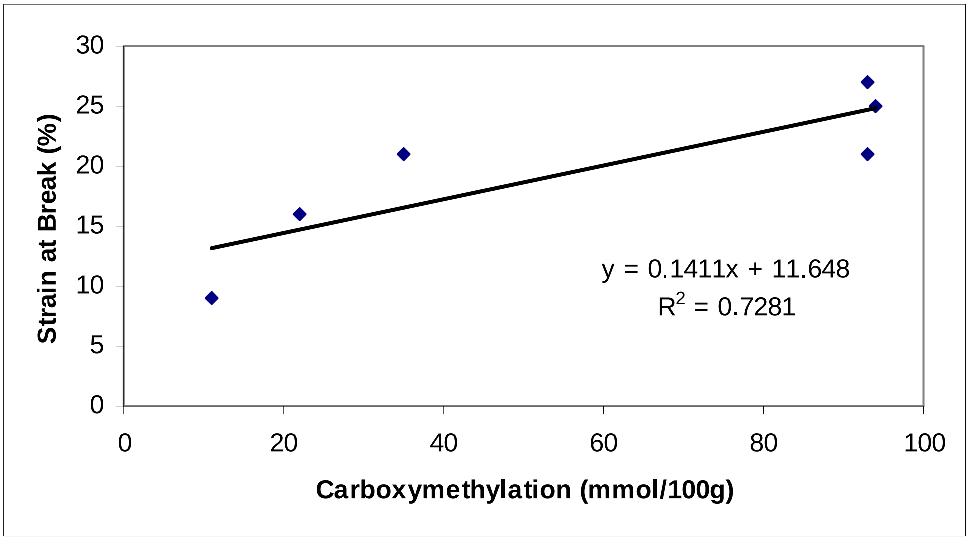


Figure 4.27 Correlation between strain at break and carboxymethylation

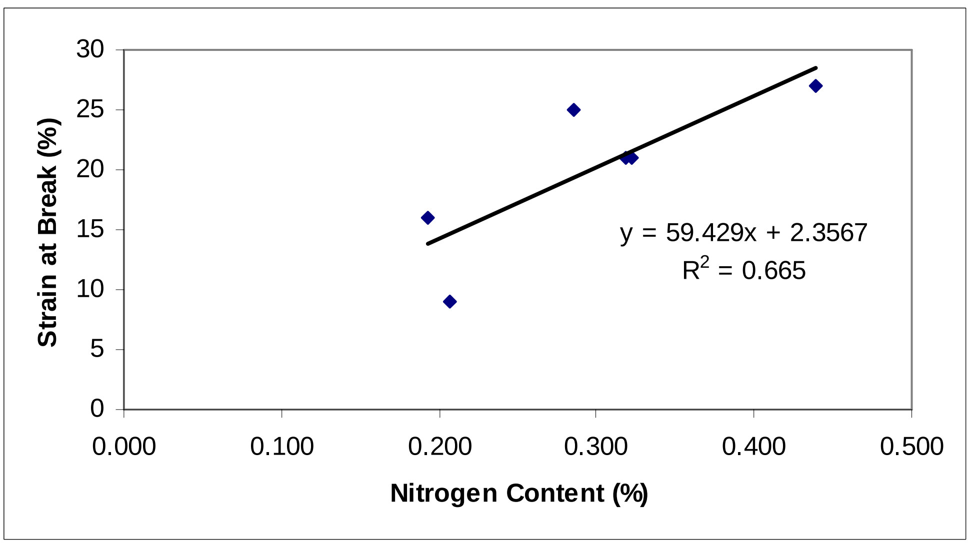


Figure 4.28 Correlation between strain at break and nitrogen content

Increase in elongation is a large factor in the increases in tensile strength and tear strength that have been observed. Increases in bond strength increase the tear and tensile strength somewhat, but the increase in elongation has a much larger effect. Since the polymers and fibers can elongate, they can share a force over a larger area between more fibers and yarns. Figure 4.29 shows that tear strength increases with breaking strain. Figure 4.30 shows that tensile strength increases with breaking strain.

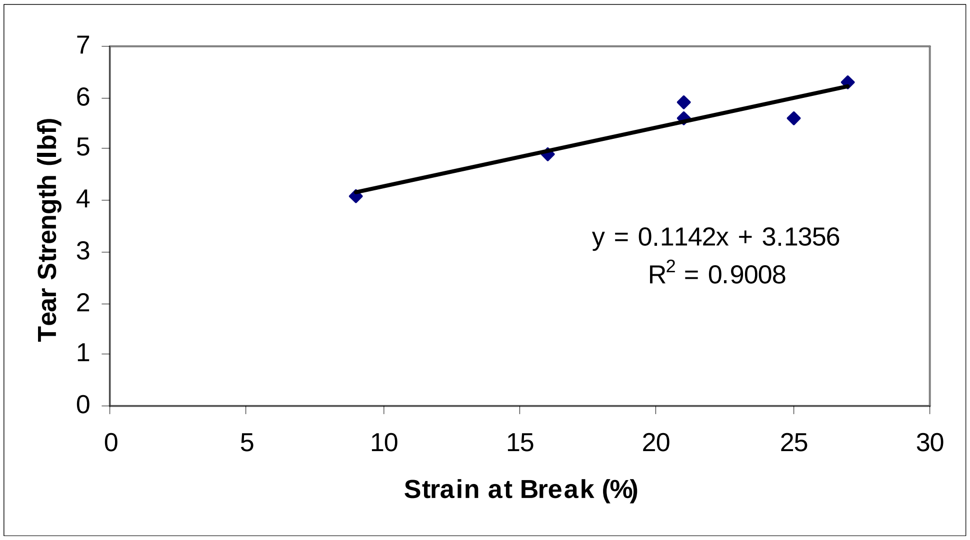


Figure 4.29 Correlation between tear strength and strain at break

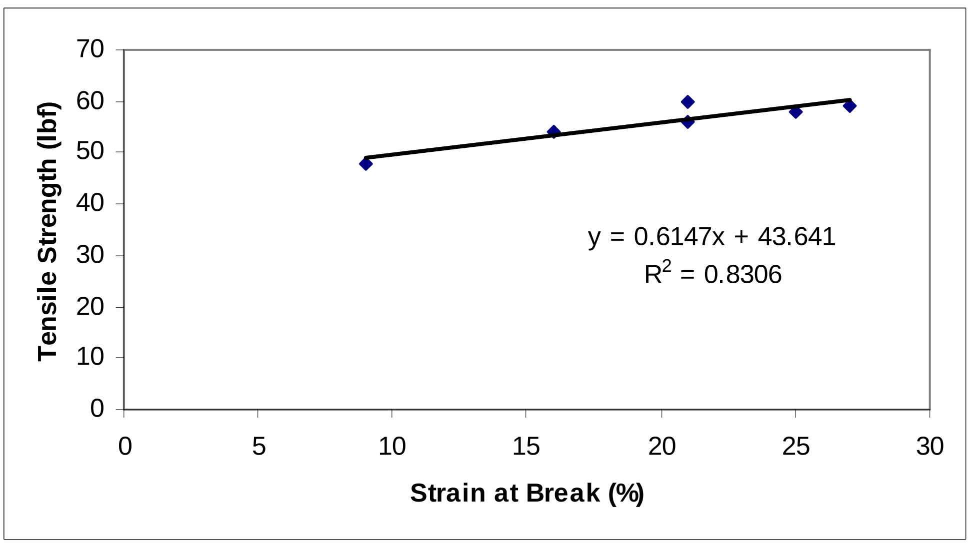


Figure 4.30 Correlation between tensile strength and strain at break

The increase in strain is due to the nature of the ionic crosslinks. With DMDHEU the crosslinks are rigid. They prevent the load from being shared between a larger number of fibers and yarns. With ionic crosslinking, the crosslinks can break and reform. The ionic bonds are stronger than hydrogen bonds but weaker than the covalent bonds of the polymer chain. When they are pulled with sufficient force, they will break. They can then reform with the next crosslink. They increase the intermolecular forces, but still allow the structure to stretch so that the load is shared. Because they can break and reform, they increase the strength of the fibers as they are stretched.

4.10 Dry WRA

4.10.1 Analysis of Dry WRA

Dry WRA was measured for all fabric treatments. It was the primary metric used to determine the significant parameters for the statistical experimentation performed in series 7, 8, and 9 and the scale up to 10 yard trials in series 10 and 11. A number of conclusions were drawn from series 3, 4, 5, and 6. Tension during treatment was shown to have no significant effect on WRA performance. It was also shown that the first wash, which removes excess cationic glycerin, does not significantly impact WRA. Crosslinking using exhaustion applications of the crosslinking agent were attempted for time periods between 5 and 30 minutes. These shorter soak times produced significantly lower WRA than the one hour exhaustion which was used for all subsequent treatment. Washing of the carboxymethylated fabric prior to crosslinking was performed with both tap water and deionized water. Deionized water produced better results than tap water.

Dry WRA data are summarized in Table 4.17 and Figure 4.31 for series 7, 8, 9, 10, and 11, untreated fabric, and DMDHEU treated fabric. Untreated fabric has a dry WRA of 184° with a standard deviation of 12°. DMDHEU treated fabric has a dry WRA of 281° with a standard deviation of 4°. Carboxymethylated and ionically crosslinked samples have dry WRA that range from 97° to 216°. DMDHEU increases dry WRA by 53%. Carboxymethylation and ionic crosslinking can decrease the dry WRA by 47% or increase it by 19%.

Table 4.17 Dry WRA for series 7, 8, 9, 10, and 11 trials

Sample	Dry WRA – Average (°)	Dry WRA - Std. Dev.
BLANK	184	12
7.A	162	6
7.B	158	6
7.C	121	6
7.D	139	5
7.E	191	5
7.F	191	4
8.A	176	8
8.B	202	7
8.C	151	6
8.D	176	5
8.E	143	8
8.F	180	4
8.G	161	6
8.H	180	6
9.A	143	7
9.B	148	7
10.A	99	6
10.B	97	3
10.C	157	7
10.D	131	3
11.A	180	4
11.B	147	4
11.C	216	1
11.D	191	4
11.E	150	5
DMDHEU	281	4

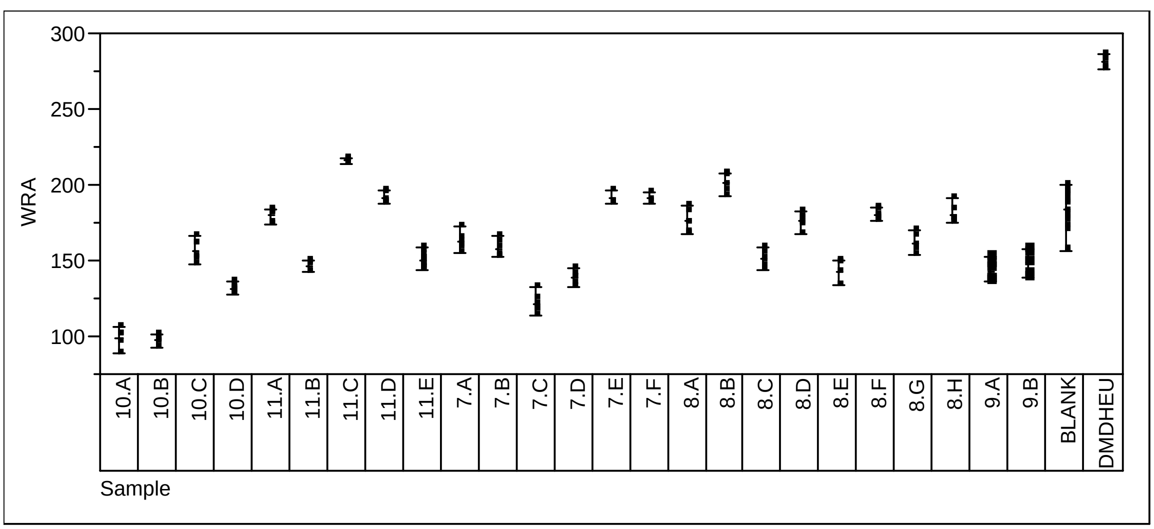


Figure 4.31 Dry WRA for series 7, 8, 9, 10, and 11 trials

Figure 8.23 shows the analysis used to determine which parameters do not have a significant effect on dry WRA. NaOH concentration, soak time, and whether the process is batch or semi-continuous/continuous do not affect the dry WRA. The concentration of crosslinking agent does not affect the dry WRA in the range from 3 to 9%.

Figure 8.24 summarizes analysis of variance and fit to model for the significant parameters on dry WRA. Carboxymethylation using the pad-batch method produces 23° higher dry WRA than the pad-dry-cure method. The pad-cure method produces 19° lower dry WRA than the pad-dry-cure method. 1.0M chloroacetate produces 13° higher dry WRA than 2.0M chloroacetate. A three step process yields 11° higher WRA than a two step process. Exhaustion methods of crosslinking produce 30° higher dry WRA than pad-dry-cure methods.

4.10.2 Summary of Dry WRA

Dry WRA can be increased or decreased with carboxymethylation and crosslinking relative to untreated fabrics. Dry WRA tends to trend in the opposite direction from most other properties with respect to process parameters. Dry WRA is higher with pad-batch carboxymethylation than pad-dry-cure and with 1.0M chloroacetate than with 2.0M chloroacetate. Dry WRA does not trend well with carboxymethylation or nitrogen content. It does tend to decrease as many other physical properties evaluated increase. For example, as stiffness increases dry WRA decreases as seen in Figure 4.32.

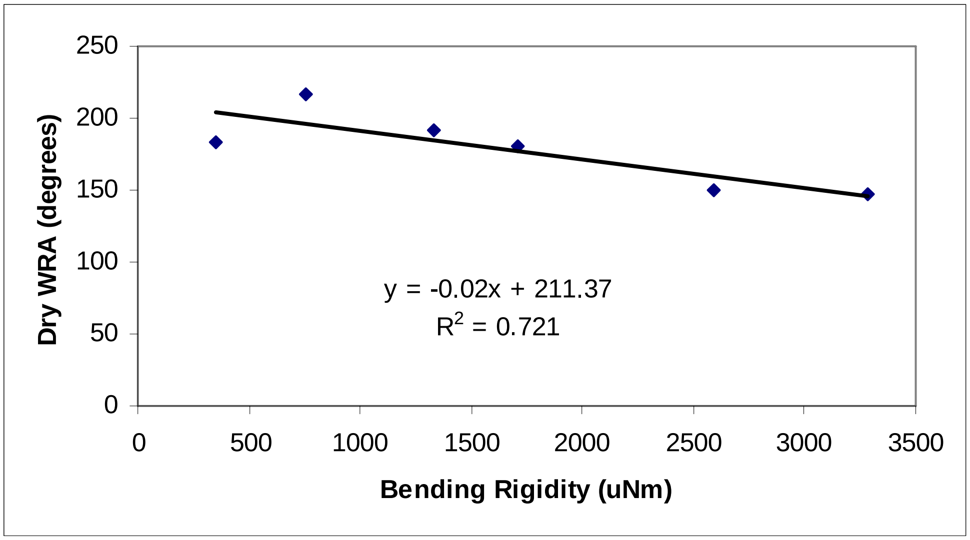


Figure 4.32 Correlation between dry WRA and bending rigidity

The poor correlations between dry WRA and most other properties is due to the test method. With most test methods the forces are small enough to see the effects of the ionic bonds or measuring the property involves breaking the bonds. Dry WRA requires that the bonds be broken, but then measures a property after the bonds are broken. The weight which is placed on the sample when it is bent is heavy enough that the ionic bonds are broken. Dry WRA actually measures the effects of the small number of bonds which were not broken which provide a restoring force combined with the effects of the small number of bonds which reform in the new orientation after being broken which offset the restoring force. The result is that the dry WRA can be increased or decreased with this treatment depending on the quantity and arrangement of the ionic bonds.

4.11 Wet WRA

4.11.1 Analysis of Wet WRA

Wet WRA data for series 7, 8, 10, and 11, untreated fabric, and DMDHEU treated fabric are summarized in Table 4.18 and Figure 4.33. Untreated fabric has a wet WRA of 115° with a standard deviation of 15°. DMDHEU treated fabric has a wet WRA of 270° with a standard deviation of 4°. DMDHEU increases wet WRA by 135%. Carboxymethylated and ionically crosslinked fabrics have wet WRA ranging from 162° to 210°. Wet WRA increases significantly with all procedures ranging from 41% to 83%.

Table 4.18 Wet WRA for series 7, 8, 9, 10, and 11 trials

Sample	Wet WRA - Average	Wet WRA - Std. Dev.
BLANK	115	15
7.A	210	11
7.B	183	12
7.C	176	16
7.D	185	11
7.E	190	3
7.F	190	6
8.A	173	8
8.B	193	6
8.C	180	8
8.D	182	8
8.E	208	11
8.F	180	5
8.G	162	6
8.H	181	6
10.A	195	10
10.B	206	12
10.C	165	5
10.D	193	5
11.A	172	4
11.B	180	3
11.C	180	9
11.D	190	4
11.E	193	7
DMDHEU	270	4

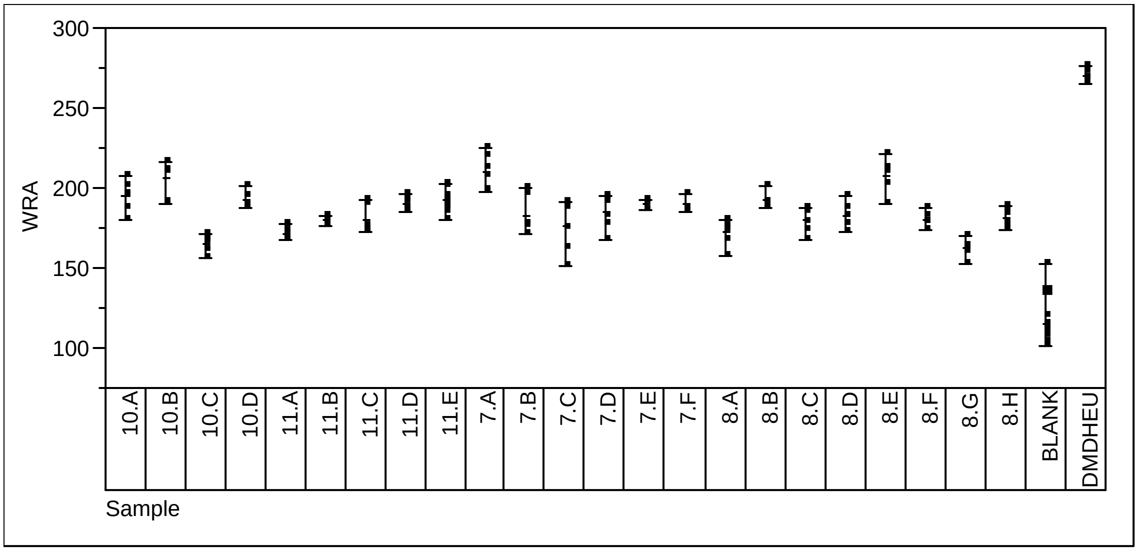


Figure 4.33 Wet WRA for series 7, 8, 10, and 11 trials

Wet WRA data were analyzed to determine which parameters do not significantly affect the value. The analysis is summarized in Figure 8.25. The only parameter which appears to have a significant effect is the concentration of CAA.

The data are then analyzed as a function of the chloroacetate concentration. This analysis is summarized in Figure 8.26. Wet WRA increases with increases in chloroacetate concentration. 2.0M chloroacetate produces 13° higher wet WRA than 1.0M chloroacetate.

4.11.2 Summary of Wet WRA

Wet WRA increases when fabrics are treated through carboxymethylation and ionic crosslinking. Higher concentrations of chloroacetate solution used for carboxymethylation produce higher wet WRA. From this data, no other variables are significant. Wet WRA does not show good correlation with carboxymethylation or nitrogen content.

Wet WRA test methods easily show the differences between untreated fabric, carboxymethylated and ionically crosslinked fabric, and DMDHEU treated fabric. However, this test method is not sensitive enough to show differences between the different carboxymethylation and ionic crosslinking procedures which were used in this work. The maximum R^2 value can be no higher than 0.61 due to error in the test method alone. It has been demonstrated qualitatively that very slight variations in testing technique will result in changes in the results. Since the fabric is wet, it is more lubricated than with dry WRA. Very slight force variations in how the sample is handled can impact the test results.

The dramatic increase in wet WRA compared to dry WRA is due to the water lubrication between hydrogen bonds. They allow for the molecules to slip past each other and adjust to the bent orientation without breaking the ionic bonds. When the load is removed, the ionic bonds provide a restoring force. The lubricated molecules will easily slide by each other back into the original orientation.

4.12 Durable Press Performance

4.12.1 Analysis of DP Performance

Durable Press ratings were determined for series 10 and 11, untreated fabric, and DMDHEU treated fabric. The results are summarized in Table 4.19. They are shown using two preparation techniques.

Table 4.19 DP rating for series 10 and 11 trails

Sample	Line Dry DP Rating	Tumble Dry DP Rating
10.A	<1	<1
10.B	<1	<1
10.C	2.5	1.4
10.D	<1	1.5
11.A	<1	<1
11.B	<1	<1
11.C	2.6	1.3
11.D	<1	1.4
11.E	<1	<1
BLANK	1.1	1.7
DMDHEU	3.7	3.8

When line drying was used, the untreated fabric has a DP rating of 1.1 and the DMDHEU treated fabric has a DP rating of 3.7. Fabrics prepared using a pad-batch carboxymethylation method with 1.0M chloroacetate have DP ratings of 2.5 and 2.6. All other carboxymethylated and ionically crosslinked samples have a DP rating below 1.0 which is below the range of the test.

When tumble drying was used, the untreated fabric has a DP rating of 1.7 and the DMDHEU treated fabric has a DP rating of 3.8. Fabrics prepared using the pad-batch method for carboxymethylation have DP ratings in the range of the test method, all other carboxymethylation methods yield samples with DP ratings less than 1.0 below the range of the test.

The best DP ratings were obtained with the traditional DMDHEU treatment. Using the line dry method, samples prepared using the pad-batch carboxymethylation method with 1.0M CAA produced a slight improvement in DP performance. All other carboxymethylated and ionically crosslinked samples showed poorer DP performance than the untreated fabric. Using the tumble dry method, all carboxymethylated and ionically crosslinked samples demonstrated worse performance than the untreated fabric. Samples produced using pad-batch procedures for carboxymethylation showed the best performance which was slightly worst than the blank.

4.12.2 Summary of DP Rating

There were no carboxymethylated and ionically crosslinked samples with DP performance approaching that of DMDHEU. This fabric generally showed poorer DP performance after carboxymethylation and ionic crosslinking. There was one treatment which did increase performance. This treatment involved 1.0M chloroacetate and a pad-batch carboxymethylation method. This treatment also produced the best dry WRA compared to other carboxymethylation and ionic crosslinking procedures. The second best DP performance was seen from the second best dry WRA performance. This involved 2.0M chloroacetate and a pad-batch carboxymethylation method. The DP rating appears to correlate with dry WRA. It difficult to verify this correlation since most treatments resulted in DP ratings below the range of the test method.

The same factors influence DP rating that influence WRA. The bonds must be unbroken when force is applied in order to provide a restoring force after it is removed. The fabric is wet during washing which lubricates the molecules as in wet WRA and then dry during drying as in dry WRA. The forces in home laundering are higher than in the WRA test. They are high enough to break the ionic bonds. The behavior is more similar to that of dry WRA where the ionic bonds are broken. The bonds are broken and a portion of them reform in new orientations when the fabric is dried. Because the fabric is wet, the bonds can reform more easily than with dry WRA. As a result, the bonds are likely to reform in a new wrinkled orientation and DP rating is generally much worse after carboxymethylation and ionic crosslinking.

4.13 Whiteness Index

4.13.1 Analysis of Whiteness Index

Whiteness index was measured for Series 7, 8, 9, 10, and 11, untreated fabric, and DMDHEU treated fabric. Whiteness index results are summarized in Table 4.20 and Figure 4.34. The blank fabric has a CIE whiteness index of 83.8 with a standard deviation of 0.2. The DMDHEU treated fabric has a CIE whiteness index of 60.2. Fabric which was carboxymethylated and ionically crosslinked varies between 72.1 and 83.2. DMDHEU reduces the whiteness index by 28%. Carboxymethylation and ionic crosslinking ranges from having no effect on whiteness index to decreasing it by 14%.

Table 4.20 WI for series 7, 8, 9, 10, and 11 trials

Sample	ASTM WI	CIE WI
BLANK	82.33	83.58
BLANK	82.35	83.61
BLANK	82.89	83.97
BLANK	82.61	83.91
7.A	72.64	74.30
7.B	71.18	73.28
7.C	75.66	77.32
7.D	77.26	78.79
7.E	76.70	78.53
7.F	76.74	78.53
8.A	72.88	74.84
8.B	75.29	77.14
8.C	71.92	73.98
8.D	69.98	72.07
8.E	76.06	77.68
8.F	78.73	80.53
8.G	75.60	77.37
8.H	76.64	78.82
9.A	81.74	82.90
9.B	81.94	83.21
10.A	73.20	75.25
10.B	75.77	77.60
10.C	72.67	75.11
10.D	76.73	78.56
11.A	71.84	74.16
11.B	72.23	74.40
11.C	73.77	76.06
11.D	73.26	75.56
11.E	75.33	77.16
DMDHEU	55.91	60.19

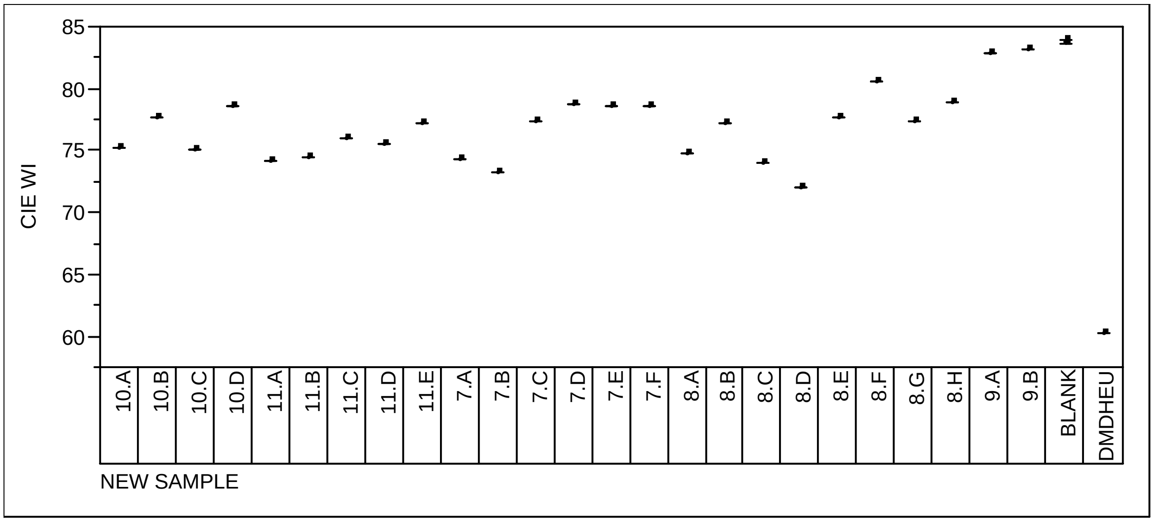


Figure 4.34 CIE WI for series 7, 8, 9, 10, and 11 trials

Analysis was performed to determine which factors in the process had an affect on CIE whiteness index. Carboxymethylation methods including pad-batch, pad-cure, and pad-dry-cure were compared. Chloroacetate concentrations of 1.0M and 2.0M and NaOH concentrations of 20% and 40% were compared. Cationic glycerin methods were compared including 3% exhaustion-pad-dry-cure, 9% exhaustion-pad-dry-cure, 6% pad-dry-cure. The number of steps (one, two, and three), length of soak time, and whether batch or continuous application and drying were utilized were also compared.

A model was generated with all parameters to show which ones are not significant. This model is summarized in Figure 8.27. This analysis shows that the chloroacetate concentration, the crosslink method, the soak time, and whether it is batch or continuous do not have significant effects on the whiteness index. There is also no difference between two and three steps and between pad-dry-cure and pad-cure carboxymethylation techniques.

Repeating the analysis without the insignificant parameters showed that carboxymethylation was not significant either. Another model, summarized in Figure 8.28, was generated using the significant factors. This model shows that NaOH concentration and the number of steps have a significant effect on the whiteness index. 20% NaOH produces a higher whiteness index than 40% NaOH. A 1 step process produces a higher whiteness index than a two or three step process. Two and three step processes are not significantly different. Pad-batch processes are not significantly different from pad-dry-cure or pad-cure processes. Pad-dry-cure and pad-cure processes are not significantly different.

4.13.2 Summary of Whiteness Index

DMDHEU produces at least twice as much yellowing as carboxymethylation and ionic crosslinking. While the one step process is significantly different, this is probably because the reaction efficiency is low with only one step. The one step process produces very little change for all properties tested. NaOH is probably the only significant factor in yellowing with this treatment. Since NaOH in the concentration range used for this work does not appear to have a large effect on any of the properties measured, this treatment can be performed with low NaOH concentrations and virtually no yellowing.

5 Conclusions

Carboxymethylation and ionic crosslinking with cationic glycerin significantly increases the intermolecular forces between cellulose chains. These increased forces result in increased tear strength, tensile strength, and elongation. While these ionic bonds are stronger than hydrogen bonding, they can still be easily broken by common forces such as in home laundering. When these bonds reform they will maintain their new configuration just like hydrogen bonds. As a result, fabric may actually have lower DP performance and increased wrinkling over untreated fabrics.

The fabric used for this work showed significant increases in physical properties after treatment by carboxymethylation and ionic crosslinking with glycerin. This is in sharp contrast to the decreases in physical properties observed with DMDHEU treatment. Every carboxymethylation and ionic crosslinking procedure evaluated produced tensile strength, elongation, and tear strength properties which were equal to or better than the untreated fabric. In the best cases, tensile strength was increased by 25%, breaking strain was increased by 340%, and tear strength was increased by 80%. Treatment with DMDHEU produced a 58% decrease in tensile strength, a 67% decrease in breaking strain, and an 83% decrease in tear strength.

Dry WRA can be increased or decreased through carboxymethylation and ionic crosslinking. Under different conditions the fabric's dry WRA was increased as much at 19% or decreased as much as 47%. This performance is considerably lower than the 53% increase observed with DMDHEU.

Wet WRA is improved significantly with this treatment. Wet WRA was increased from 41 to 83%. This is not close to DMDHEU. However, this is a significant improvement, compared to DMDHEU treatment which increases wet WRA by 135%.

DP rating is generally decreased with this treatment. Most treatments produce a dramatic decrease in DP performance. One set of treatment conditions shows a slight increase in DP rating over the untreated fabric. None come anywhere close to the DP rating of DMDHEU treated fabrics.

The wrinkle resistance and durable press performance depend on the forces used to measure this performance. With the better treatments in this work, these properties are improved, but most treatments make DP performance worse. When the forces between molecules are strengthened significantly relative to the forces of the test method, the properties improve. However, when the bonds can be broken by the test method used, they can reform in a new conformation. Without restoring forces, they will be locked into the new conformation. The strength of the intermolecular forces seems to straddle the range which is produced during dry WRA. With wet WRA, the hydrogen bonds are disrupted and the fibers are lubricated. Lubricated hydrogen bonds can shift, transferring most of the stress away from the ionic crosslinks, and allowing the ionic bonds to act as crosslinks just as covalent bonds. The hydrogen bound regions can shift with the force, while the ionic bonds remain in place to provide a restoring force.

DP rating evaluation involves multiple washing and drying cycles. It produces higher forces which can break ionic bonds. It also puts force on the structure during drying, when the ionic bonds are more easily broken. When the ionic bonds reform, they lock in the wrinkles produced during the laundering cycles. Crosslinking agent is also removed from the fabric during laundering. The divalent crosslinking agent is removed and replaced with a monovalent ion which will no longer form a crosslink.

Crosslinking fabrics for DP performance generally produces an increase in stiffness. This is an undesirable property for most applications. DMDHEU treatment increased fabric bending rigidity by 170%. Carboxymethylation and ionic crosslinking with cationic glycerin process allow for the stiffness of the fabric to be controlled. Bending rigidity for treated fabrics ranged from no increase to 840% increase. Thus the process can be run with little to no increase in stiffness as required for the application.

Carboxymethylation and ionic crosslinking with cationic glycerin can be performed without discoloring the fabric. DMDHEU has a significant yellowing effect on white fabrics. This treatment was performed under conditions which did not increase the whiteness index of the fabric at all. The worst discoloration observed was 14% with carboxymethylation and ionic crosslinking. DMDHEU treatment reduces whiteness index by 28% or twice as much as carboxymethylation and ionic crosslinking.

This treatment does not provide satisfactory DP performance. However, optimal treatments do provide a slight increase in wrinkle resistance and DP performance. They increase performance without any of the adverse effects which have been problems with conventional DP treatments. There is no discoloration, no reduction in strength, and no formaldehyde release. Furthermore, there is an increase in tensile strength, tear strength, and elongation, and stiffness increases can be avoided.

The optimal treatment evaluated with this work will provide the largest increase in dry WRA, the second largest increase in wet WRA, the best DP rating, no increase in stiffness, no discoloration, and moderate increases in strength and elongation as compared to the other treatments. This method involves carboxymethylation in two steps. The first step is NaOH treatment with 20% NaOH solution using a pad-dry procedure. The second step is a pad-batch treatment of the fabric with 1.0M chloroacetate. A third step is used to crosslink the fabric. It is performed through exhaustion of 3% cationic glycerin in a bath, followed by a pad-dry-cure sequence.

6 Future Work

6.1 Durable Press Applications

This work indicates that carboxymethylation and ionic crosslinking with cationic glycerin are not likely to produce acceptable durable press performance for the fabric tested. This does not show that ionic crosslinking cannot produce acceptable durable press treatment using other chemistries or fabrics. Alternative crosslinking agents can be easily evaluated based on the results of this work and previous research. Cationic glycerin was selected because it produced the greatest improvement in wet and dry WRA in previous work. (*2*) Several other chemistries produced very similar WRA results. Cationic chitosan has shown very similar WRA performance with superior durability. (*1*) Durable press evaluation requires multiple washing and drying cycles of the treated fabric. Improved durability may provide a considerable advantage to cationic chitosan over cationic glycerin in DP rating.

A variety of other chemistries have been evaluated to both produce ionic cellulose and ionically crosslink it. Many of these methods have increased the WRA performance of the fabric. (*1,2*) They may produce better or worse results as durable press treatments as compared to the chemistry used for this work. For example, a crosslinking agent which is more hydrophobic than cationic glycerin may produce similar performance for WRA, but could produce superior DP performance because it is less likely to be displaced during laundering. If other chemistries will produce slightly stronger intermolecular forces and demonstrate higher durability, they should exhibit better wrinkle resistance and superior DP performance.

There are questions about treatment uniformity. Wet and dry WRA of samples has shown considerable variation between different specimens of the same sample. This may be attributable to test methods and variations in fabric construction, but it also calls treatment variation into question. Analysis with confocal microscopy has indicated that the carboxymethylation is uniform over a small scale. Analysis with mass spectroscopy has indicated that the carboxymethylation and cationic glycerin are not uniform over a larger scale. Further evaluation of uniformity may suggest other ways in which this treatment can be improved.

6.2 Other Applications of Ionic Cellulose

This work also shows that there are significant modifications to a variety of other properties which may yield other products. This treatment does increase the intermolecular forces between cellulose chains. It produces increased tensile strength, tear strength, and elongation. Abrasion resistance is improved as well. There may be a number of applications for ionically crosslinked cellulose or ionic cellulose. Simply ionizing the polymer will likely result in improved dyeability and antimicrobial properties.

7 References

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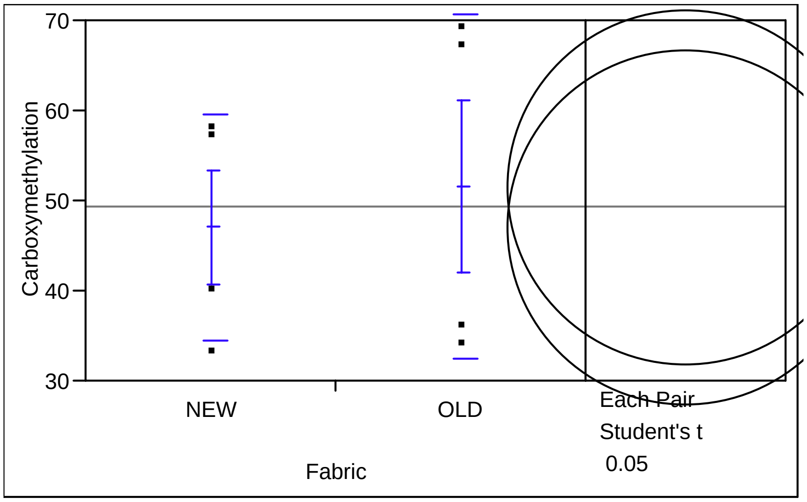
Appendix

8 Appendix

Statistical analysis was performed using SAS JMP software.



Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean
NEW	4	47.0000	12.4633	6.2316
OLD	4	51.5000	19.0875	9.5438

Means Comparisons

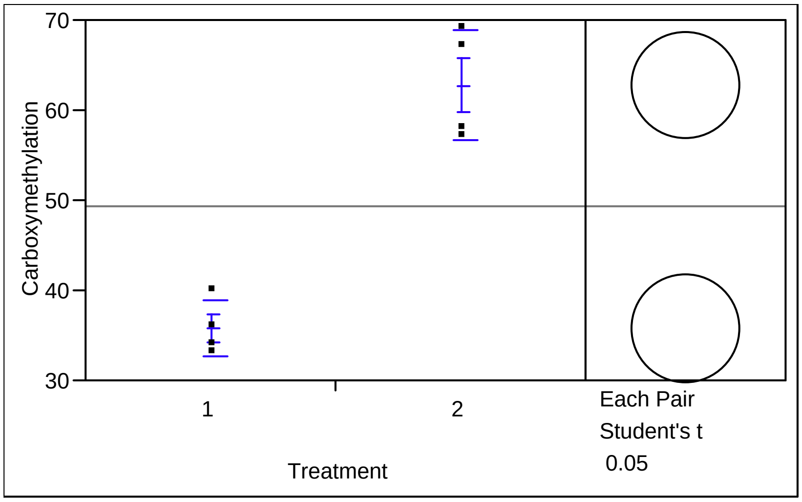
Comparisons for each pair using Student's t

t	Alpha
2.44691	0.05

Abs(Dif)-LSD	OLD	NEW
OLD	-27.890	-23.390
NEW	-23.390	-27.890

Positive values show pairs of means that are significantly different.

Figure 8.1 Analysis of the effect of fabric type on degree of carboxymethylation



Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean
1	4	35.7500	3.09570	1.5478
2	4	62.7500	6.13052	3.0653

Means Comparisons

Comparisons for each pair using Student's t

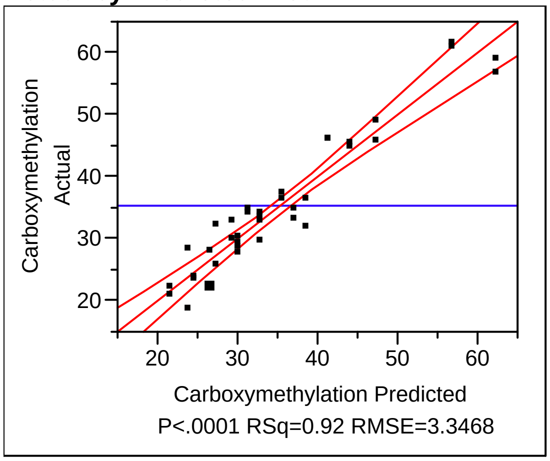
t	Alpha
2.44691	0.05

Abs(Dif)-LSD	2	1
2	-8.402	18.598
1	18.598	-8.402

Positive values show pairs of means that are significantly different.

Figure 8.2 Analysis of the effect of double treatment on degree of carboxymethylation

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	4312.2461	862.449	76.9955
Error	32	358.4414	11.201	Prob > F
C. Total	37	4670.6875		<.0001

Lack Of Fit

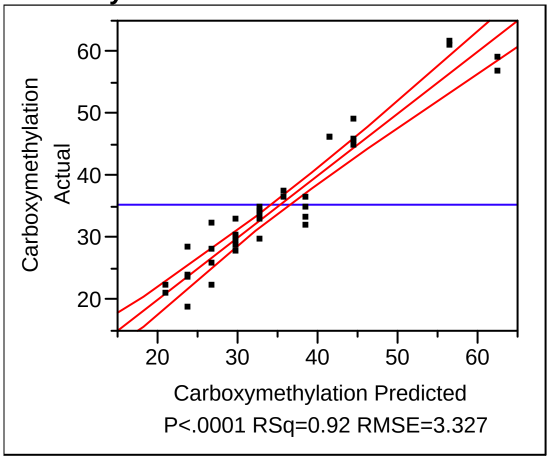
Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	11	230.02174	20.9111	3.4195
Pure Error	21	128.41963	6.1152	Prob > F
Total Error	32	358.44137		0.0075
				Max RSq
				0.9725

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	27.354264	3.090002	8.85	<.0001
CAA	11.205264	1.157275	9.68	<.0001
Day[1]	0.3581286	0.818704	0.44	0.6647
CM Method[B]	-11.27729	1.192094	-9.46	<.0001
NaOH	0.2391099	0.151281	1.58	0.1238
Steps[2]	-0.389144	1.164104	-0.33	0.7403

Figure 8.3 Initial analysis of the effects of process parameters on degree of carboxymethylation using series 3 and 4 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	4283.2673	2141.63	193.4777
Error	35	387.4202	11.07	Prob > F
C. Total	37	4670.6875		<.0001

Lack Of Fit

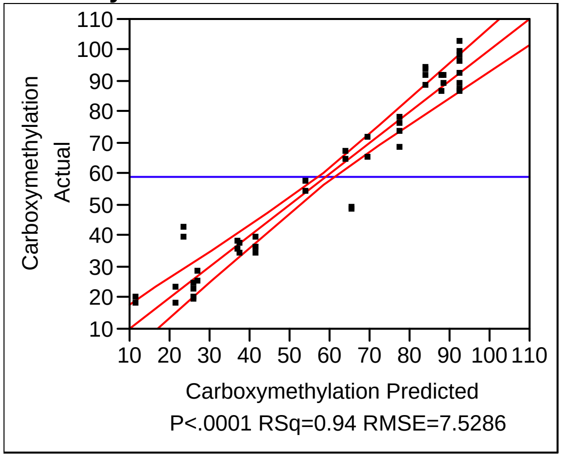
Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	8	224.97311	28.1216	4.6740
Pure Error	27	162.44711	6.0166	Prob > F
Total Error	35	387.42022		0.0011
				Max RSq
				0.9652

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	31.346245	1.477759	21.21	<.0001
CAA	11.797385	0.955758	12.34	<.0001
CM Method[B]	-10.43205	0.913079	-11.43	<.0001

Figure 8.4 Final analysis of the effects of process parameters on degree of carboxymethylation using series 3 and 4 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	7	35851.616	5121.66	90.3611
Error	40	2267.196	56.68	Prob > F
C. Total	47	38118.813		<.0001

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	10	1879.8212	187.982	14.5582
Pure Error	30	387.3750	12.913	Prob > F
Total Error	40	2267.1962		<.0001
				Max RSq
				0.9898

Parameter Estimates

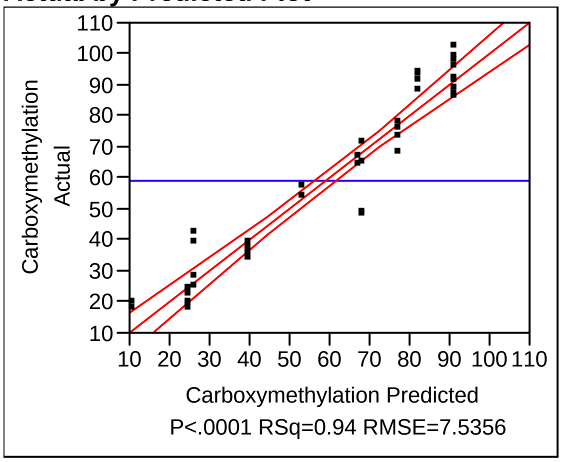
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	37.703243	6.295507	5.99	<.0001
NaOH	-0.181443	0.231805	-0.78	0.4384
CAA	15.518049	2.950944	5.26	<.0001
Steps[2]	-5.287357	1.814631	-2.91	0.0058
CM Method[B]	-31.01351	1.574881	-19.69	<.0001
CM Method[C]	19.713757	1.814103	10.87	<.0001
Soak[L]	-0.18917	1.848866	-0.10	0.9190
Batch or Continuous[B]	-2.026553	1.845371	-1.10	0.2787

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH	1	1	34.727	0.6127	0.4384
CAA	1	1	1567.406	27.6536	<.0001
Steps	1	1	481.205	8.4899	0.0058
CM Method	2	2	22172.754	195.5963	<.0001
Soak	1	1	0.593	0.0105	0.9190
Batch or Continuous	1	1	68.356	1.2060	0.2787

Figure 8.5 Initial analysis of the effects of process parameters on degree of carboxymethylation using series 7, 8, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	4	35677.072	8919.27	157.0718
Error	43	2441.740	56.78	Prob > F
C. Total	47	38118.813		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	5	1380.6985	276.140	9.8896
Pure Error	38	1061.0417	27.922	Prob > F
Total Error	43	2441.7401		<.0001
				Max RSq
				0.9722

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	33.275219	5.000656	6.65	<.0001
CAA	15.361842	2.760634	5.56	<.0001
Steps[2]	-6.960526	1.180979	-5.89	<.0001
CM Method[B]	-31.28838	1.541335	-20.30	<.0001
CM Method[C]	20.083333	1.715922	11.70	<.0001

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
CAA	1	1	1758.328	30.9649	<.0001
Steps	1	1	1972.563	34.7376	<.0001
CM Method	2	2	23960.065	210.9731	<.0001

Effect Screening

	Lenth PSE
t-Test Scale	18.772359
Coded Scale	20.418025

Pareto Plot of Transformed Estimates

Term	Orthog Estimate
CM Method[B]	-18.36060
CAA	14.49390
CM Method[C]	12.73014
Steps[2]	-5.83363

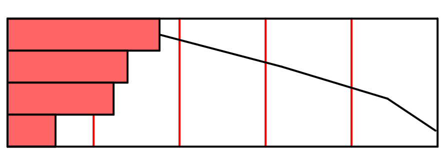
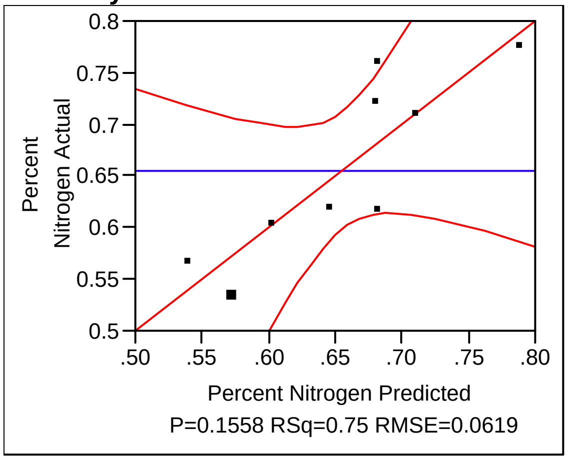


Figure 8.6 Final analysis of the effects of process parameters on degree of carboxymethylation using series 7, 8, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	4	0.04602503	0.011506	3.0059
Error	4	0.01531140	0.003828	Prob > F
C. Total	8	0.06133643		0.1558

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	3	0.00503392	0.001678	0.1633
Pure Error	1	0.01027748	0.010277	Prob > F
Total Error	4	0.01531140		0.9103
				Max RSq
				0.8324

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.5436213	0.115464	4.71	0.0093
CAA	0.064425	0.06187	1.04	0.3565
CM Method[B]	-0.016236	0.034792	-0.47	0.6650
CM Method[C]	0.0624876	0.031847	1.96	0.1213
Crosslink Method[A]	-0.053497	0.021016	-2.55	0.0636

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
CAA	1	1	0.00415058	1.0843	0.3565
CM Method	2	2	0.01563798	2.0427	0.2448
Crosslink Method	1	1	0.02480296	6.4796	0.0636

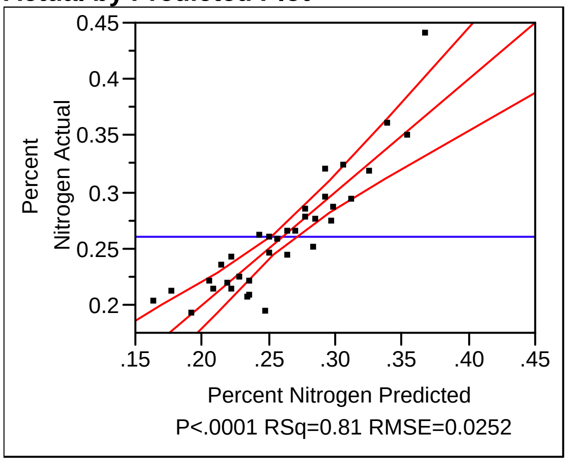
Figure 8.7 Analysis of the effects of process parameters on nitrogen content prior to washing using series 10 and 11 data

Parameter Estimates

Term	Estimate
Intercept	0.0326667
CAA	0.125
CM Method[B]	-0.041667
CM Method[C]	0.0793333
Crosslink Method[B]	-0.077

Figure 8.8 Analysis of the effects of process parameters on nitrogen content after washing using series 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	0.07905069	0.015810	24.8150
Error	29	0.01847646	0.000637	Prob > F
C. Total	34	0.09752714		<.0001

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.2131143	0.026928	7.91	<.0001
CAA	0.0441429	0.013492	3.27	0.0028
Carboxymethylation Method[B]	-0.029857	0.00779	-3.83	0.0006
Carboxymethylation Method[C]	0.0457143	0.00779	5.87	<.0001
Crosslink Method[B]	-0.034429	0.006746	-5.10	<.0001
Wash	-0.014029	0.002133	-6.58	<.0001

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
CAA	1	1	0.00682007	10.7045	0.0028
Carboxymethylation Method	2	2	0.02262886	17.7587	<.0001
Crosslink Method	1	1	0.01659457	26.0463	<.0001
Wash	1	1	0.02755211	43.2448	<.0001

Effect Screening

	Lenth PSE
t-Test Scale	7.6553302
Coded Scale	0.0326618

Pareto Plot of Transformed Estimates

Term	Orthog Estimate
Wash	-0.0280571
CAA	0.0272857
Crosslink Method[B]	-0.0217745
Carboxymethylation Method[C]	0.0152691
Carboxymethylation Method[B]	-0.0044272

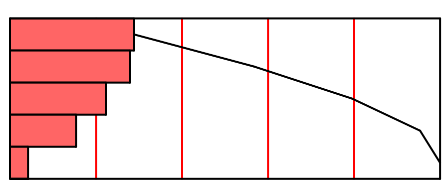
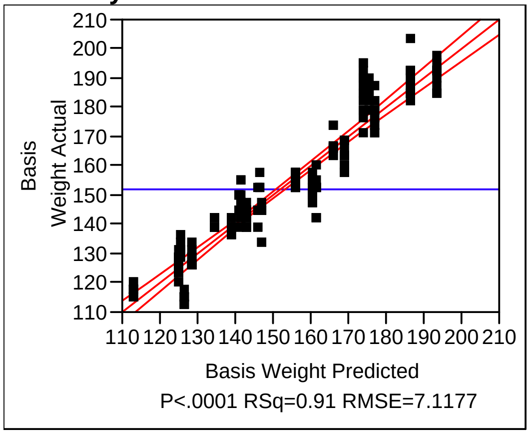


Figure 8.9 Analysis of the effects of process parameters on nitrogen content as an indication of durability to laundering using series 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	10	118766.96	11876.7	234.4349
Error	224	11348.05	50.7	Prob > F
C. Total	234	130115.01		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	13	8091.039	622.388	40.3203
Pure Error	211	3257.014	15.436	Prob > F
Total Error	224	11348.053		<.0001
				Max RSq
				0.9750

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	114.18244	2.962884	38.54	<.0001
NaOH	0.3990801	0.10833	3.68	0.0003
CAA	13.3753	1.321433	10.12	<.0001
Steps[1]	-12.92797	1.579754	-8.18	<.0001
Steps[2]	-3.560092	1.298273	-2.74	0.0066
CM Method[B]	-10.73128	0.766418	-14.00	<.0001
CM Method[C]	8.8453322	0.897457	9.86	<.0001
Soak[L]	-2.34623	0.932955	-2.51	0.0126
CG Method[A]	11.444986	1.070405	10.69	<.0001
CG Method[B]	-5.038101	1.573074	-3.20	0.0016
Batch or Continuous[B]	-5.554945	1.388228	-4.00	<.0001

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH	1	1	687.543	13.5714	0.0003
CAA	1	1	5190.270	102.4511	<.0001
Steps	2	2	11566.612	114.1571	<.0001
CM Method	2	2	10146.146	100.1377	<.0001
Soak	1	1	320.400	6.3244	0.0126
CG Method	2	2	8100.797	79.9511	<.0001
Batch or Continuous	1	1	811.168	16.0117	<.0001

Pareto Plot of Transformed Estimates

Term	Orthog Estimate
Steps[1]	-16.59437
CAA	10.12335
CG Method[A]	5.68693
Soak[L]	-5.35676
CG Method[B]	-4.32684
CM Method[B]	-4.23218
Steps[2]	-2.99677
NaOH	-2.98114
CM Method[C]	2.92359
Batch or Continuous[B]	-1.85790

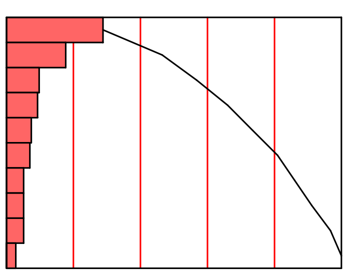
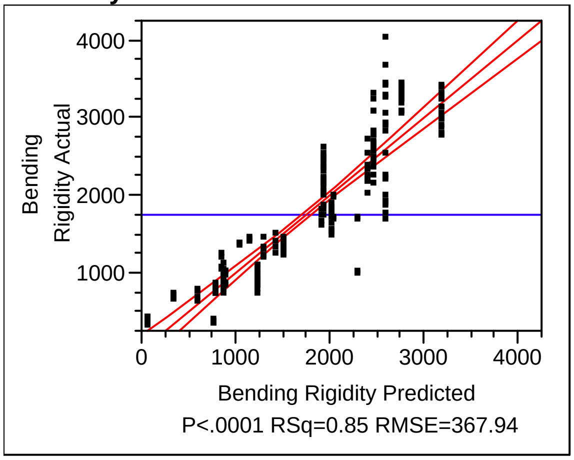


Figure 8.10 Analysis of the effects of process parameters on basis weight using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	10	222536892	22253689	164.3754
Error	287	38855022	135383.35	Prob > F
C. Total	297	261391914		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	13	21384726	1644979	25.7995
Pure Error	274	17470296	63760	Prob > F
Total Error	287	38855022		<.0001
				Max RSq
				0.9332

Parameter Estimates

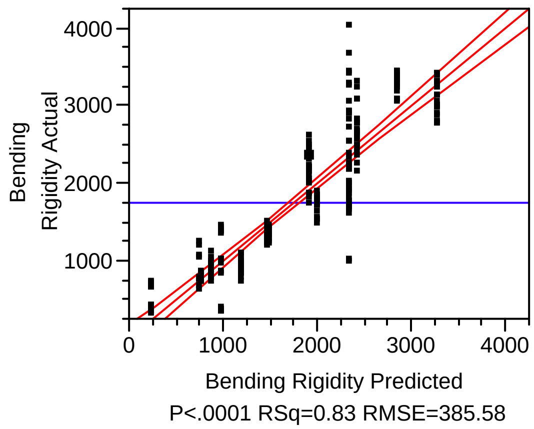
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	150.59354	166.0247	0.91	0.3651
NaOH	6.1847409	6.791148	0.91	0.3632
CAA	702.90807	61.48568	11.43	<.0001
Steps[1]	-330.6815	89.11036	-3.71	0.0002
Steps[2]	-22.96756	74.61844	-0.31	0.7585
CM Method[B]	-596.547	35.57407	-16.77	<.0001
CM Method[C]	666.0341	39.06476	17.05	<.0001
Soak[L]	-56.78859	53.7682	-1.06	0.2918
CG Method[A]	342.77568	40.26495	8.51	<.0001
CG Method[B]	-255.3201	59.75418	-4.27	<.0001
Batch or Continuous[B]	-92.07721	58.59328	-1.57	0.1172

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH	1	1	112285	0.8294	0.3632
CAA	1	1	17693526	130.6920	<.0001
Steps	2	2	4794840	17.7084	<.0001
CM Method	2	2	50766026	187.4899	<.0001
Soak	1	1	151021	1.1155	0.2918
CG Method	2	2	10809810	39.9230	<.0001
Batch or Continuous	1	1	334329	2.4695	0.1172

Figure 8.11 Initial analysis of the effects of process parameters on bending rigidity in the warp direction using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	218128650	36354775	244.5317
Error	291	43263263	148671.01	Prob > F
C. Total	297	261391914		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	7	13512902	1930415	18.4279
Pure Error	284	29750362	104755	Prob > F
Total Error	291	43263263		<.0001
				Max RSq
				0.8862

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	320.02444	129.8409	2.46	0.0143
CAA	730.98139	61.72407	11.84	<.0001
Steps[1]	-298.2353	56.88328	-5.24	<.0001
CM Method[B]	-622.2229	36.18417	-17.20	<.0001
CM Method[C]	743.2365	37.04542	20.06	<.0001
CG Method[A]	458.60977	32.68297	14.03	<.0001
CG Method[B]	-486.9883	32.74371	-14.87	<.0001

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
CAA	1	1	20851139	140.2502	<.0001
Steps	1	1	4086723	27.4884	<.0001
CM Method	2	2	70420190	236.8323	<.0001
CG Method	2	2	42848595	144.1054	<.0001

Pareto Plot of Transformed Estimates

Term	Orthog Estimate
CAA	576.3863
CM Method[C]	375.8695
CG Method[B]	-332.1969
Steps[1]	-291.4588
CG Method[A]	182.8454
CM Method[B]	-172.4552

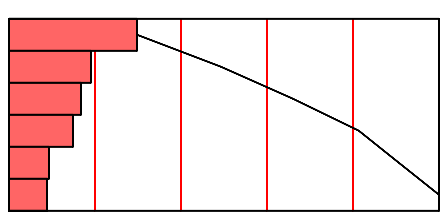
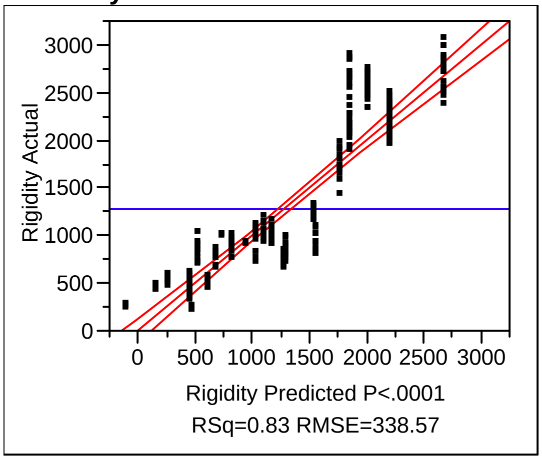


Figure 8.12 Final analysis of the effects of process parameters on bending rigidity in the warp direction using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	10	216088590	21608859	188.5054
Error	379	43445746	114632.58	Prob > F
C. Total	389	259534337		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	13	37631600	2894738	182.2235
Pure Error	366	5814146	15886	Prob > F
Total Error	379	43445746		<.0001
				Max RSq
				0.9776

Parameter Estimates

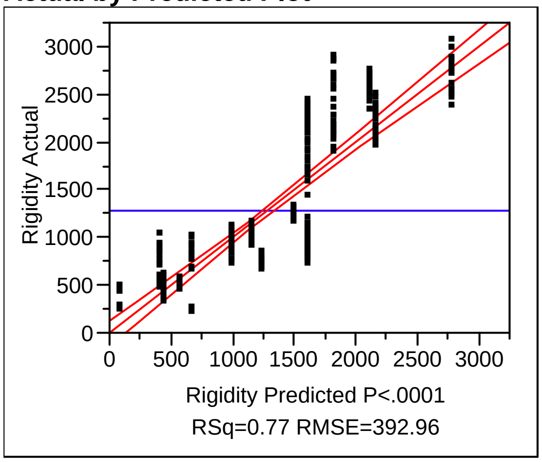
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-187.8698	116.1435	-1.62	0.1066
NaOH	10.467498	4.240365	2.47	0.0140
CAA	573.00416	49.32082	11.62	<.0001
Steps[1]	-275.9834	63.73448	-4.33	<.0001
Steps[2]	-97.7361	52.84935	-1.85	0.0652
CM Method[B]	-395.6278	28.19853	-14.03	<.0001
CM Method[C]	432.33722	31.86136	13.57	<.0001
Soak[L]	-101.6601	37.49218	-2.71	0.0070
CG Method[A]	382.05396	36.17223	10.56	<.0001
CG Method[B]	-94.79542	53.34362	-1.78	0.0764
Batch or Continuous[B]	-216.2151	51.26917	-4.22	<.0001

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH	1	1	698534	6.0937	0.0140
CAA	1	1	15472592	134.9755	<.0001
Steps	2	2	8236799	35.9270	<.0001
CM Method	2	2	27720320	120.9094	<.0001
Soak	1	1	842807	7.3522	0.0070
CG Method	2	2	21865010	95.3700	<.0001
Batch or Continuous	1	1	2038767	17.7852	<.0001

Figure 8.13 Initial analysis of the effects of process parameters on bending rigidity in the fill direction using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	200391807	33398635	216.2856
Error	383	59142530	154419.14	Prob > F
C. Total	389	259534337		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	7	26095664	3727952	42.4158
Pure Error	376	33046865	87891	Prob > F
Total Error	383	59142530		<.0001
				Max RSq
				0.8727

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	181.6549	113.0303	1.61	0.1088
CAA	591.94983	53.33876	11.10	<.0001
Steps[1]	-278.4962	46.78119	-5.95	<.0001
CM Method[B]	-425.7262	31.4205	-13.55	<.0001
CM Method[C]	521.27721	32.78394	15.90	<.0001
CG Method[A]	609.34743	31.69979	19.22	<.0001
CG Method[B]	-549.3824	28.32742	-19.39	<.0001

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
CAA	1	1	19018884	123.1640	<.0001
Steps	1	1	5472642	35.4402	<.0001
CM Method	2	2	44707106	144.7590	<.0001
CG Method	2	2	79584336	257.6894	<.0001

Pareto Plot of Transformed Estimates

Term	Orthog Estimate
CAA	409.1759
CG Method[B]	-385.9100
Steps[1]	-279.3930
CM Method[C]	242.6920
CG Method[A]	234.8104
CM Method[B]	-73.3345

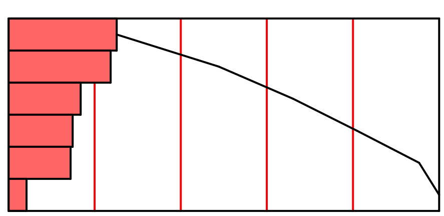
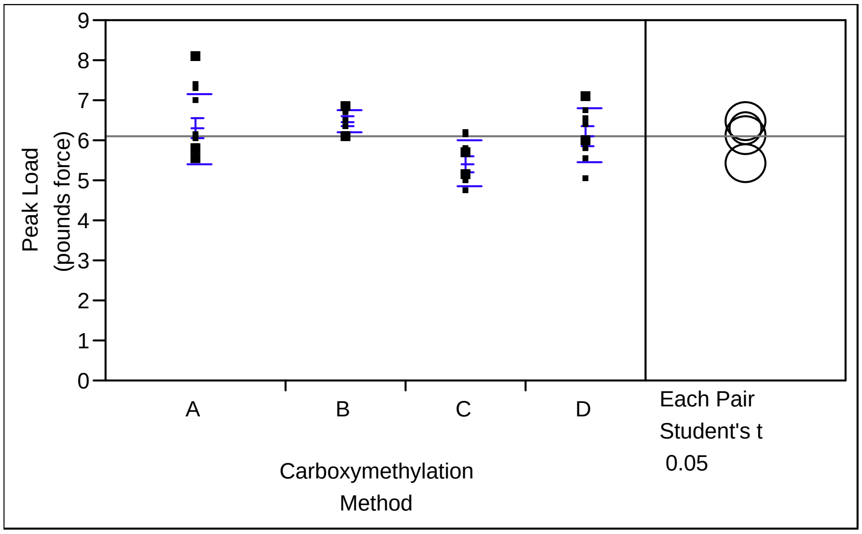


Figure 8.14 Final analysis of the effects of process parameters on bending rigidity in the fill direction using series 7, 8, 9, 10, and 11 data



Missing Rows
8

Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean
A	12	6.28333	0.872544	0.25188
B	8	6.47250	0.294267	0.10404
C	8	5.42125	0.561260	0.19844
D	8	6.10875	0.673083	0.23797

Means Comparisons
Comparisons for each pair using Student's t

t	Alpha
2.03693	0.05

Abs(Dif)-LSD	B	A	D	C
B	-0.68219	-0.43359	-0.31844	0.36906
A	-0.43359	-0.55701	-0.44817	0.23933
D	-0.31844	-0.44817	-0.68219	0.00531
C	0.36906	0.23933	0.00531	-0.68219

Positive values show pairs of means that are significantly different.

Level			Mean
B	A		6.4725000
A	A		6.2833333
D	A		6.1087500
C		B	5.4212500

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL	p-Value
B	C	1.051250	0.369058	1.733442	0.0036
A	C	0.862083	0.239330	1.484837	0.0082
D	C	0.687500	0.005308	1.369692	0.0483
B	D	0.363750	-0.318442	1.045942	0.2855
B	A	0.189167	-0.433587	0.811920	0.5405
A	D	0.174583	-0.448170	0.797337	0.5720

Difference

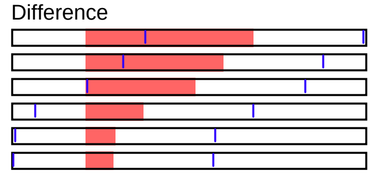
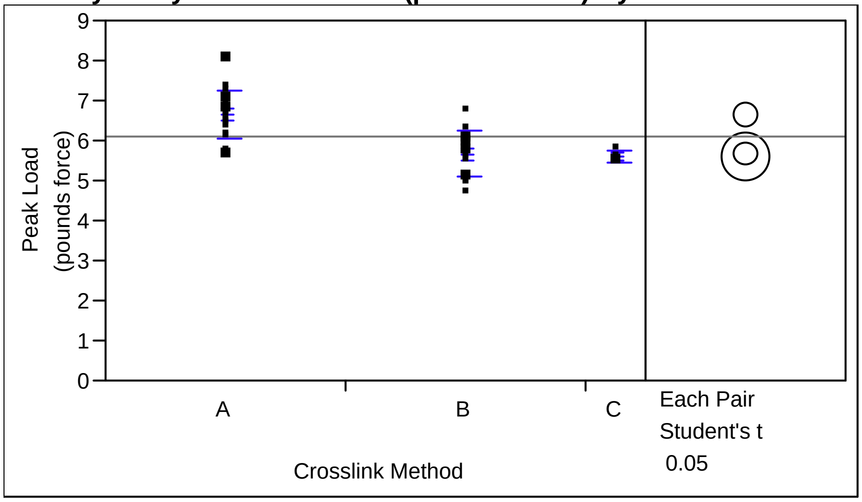


Figure 8.15 Analysis of the effect of carboxymethylation on tear strength in the warp direction

Oneway Analysis of Peak Load (pounds force) By Crosslink Method



Missing Rows
8

Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
A	16	6.65000	0.608473	0.15212	6.3258	6.9742
B	16	5.66438	0.579632	0.14491	5.3555	5.9732
C	4	5.59750	0.160494	0.08025	5.3421	5.8529

Means Comparisons

Comparisons for each pair using Student's t

t	Alpha
2.03452	0.05

Abs(Dif)-LSD	A	B	C
A	-0.40903	0.57660	0.40577
B	0.57660	-0.40903	-0.57985
C	0.40577	-0.57985	-0.81805

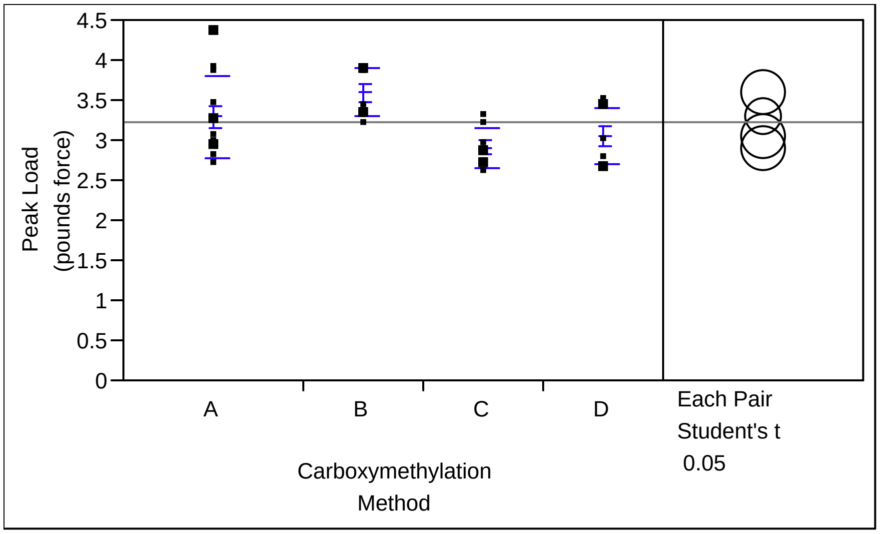
Positive values show pairs of means that are significantly different.

Level			Mean
A	A		6.6500000
B		B	5.6643750
C		B	5.5975000

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL	p-Value
A	C	1.052500	0.405773	1.699227	0.0023
A	B	0.985625	0.576599	1.394651	<.0001
B	C	0.066875	-0.579852	0.713602	0.8347

Figure 8.16 Analysis of the effect of crosslinking on tear strength in the warp direction



Missing Rows
8

Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean
A	12	3.28917	0.502403	0.14503
B	8	3.59000	0.300190	0.10613
C	8	2.90250	0.245517	0.08680
D	8	3.05125	0.347992	0.12303

Means Comparisons

Comparisons for each pair using Student's t

t	Alpha
2.03693	0.05

Abs(Dif)-LSD	B	A	D	C
B	-0.38936	-0.05460	0.14939	0.29814
A	-0.05460	-0.31791	-0.11752	0.03123
D	0.14939	-0.11752	-0.38936	-0.24061
C	0.29814	0.03123	-0.24061	-0.38936

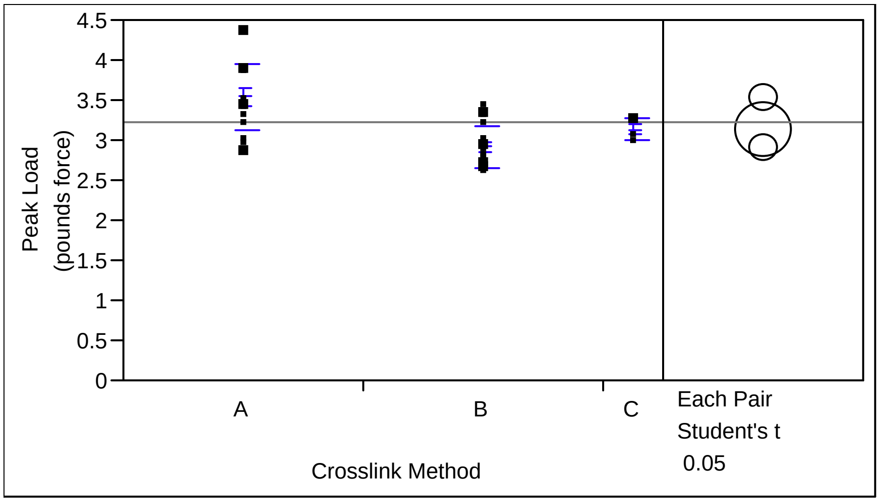
Positive values show pairs of means that are significantly different.

Level				Mean
B	A			3.5900000
A	A	B		3.2891667
D		B	C	3.0512500
C			C	2.9025000

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL	p-Value	Difference
B	C	0.6875000	0.298139	1.076861	0.0011	
B	D	0.5387500	0.149389	0.928111	0.0082	
A	C	0.3866667	0.031231	0.742103	0.0339	
B	A	0.3008333	-0.054603	0.656269	0.0944	
A	D	0.2379167	-0.117519	0.593353	0.1823	
D	C	0.1487500	-0.240611	0.538111	0.4422	

Figure 8.17 Analysis of the effect of carboxymethylation on tear strength in the fill direction



Missing Rows
8

Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean
A	16	3.54000	0.415275	0.10382
B	16	2.91563	0.267257	0.06681
C	4	3.13250	0.134505	0.06725

Means Comparisons

Comparisons for each pair using Student's t

t	Alpha
2.03452	0.05

Abs(Dif)-LSD	A	C	B
A	-0.24126	0.02603	0.38311
C	0.02603	-0.48253	-0.16460
B	0.38311	-0.16460	-0.24126

Positive values show pairs of means that are significantly different.

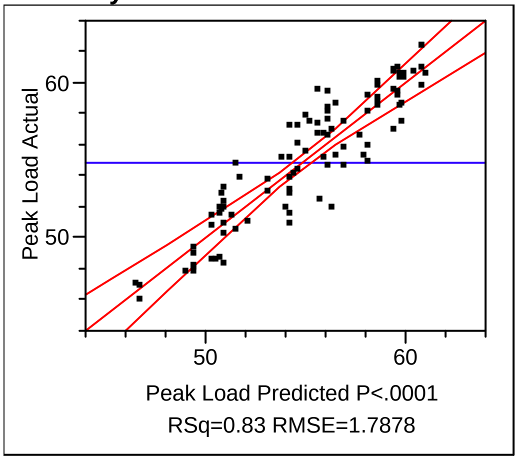
Level			Mean
A	A		3.5400000
C		B	3.1325000
B		B	2.9156250

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL	p-Value	Difference
A	B	0.6243750	0.383112	0.8656378	<.0001	
A	C	0.4075000	0.026030	0.7889700	0.0370	
C	B	0.2168750	-0.164595	0.5983450	0.2557	

Figure 8.18 Analysis of the effect of crosslinking on tear strength in the fill direction

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	10	1335.3397	133.534	41.7793
Error	83	265.2824	3.196	Prob > F
C. Total	93	1600.6221		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	34	137.72227	4.05066	1.5560
Pure Error	49	127.56017	2.60327	Prob > F
Total Error	83	265.28245		0.0772
				Max RSq
				0.9203

Parameter Estimates

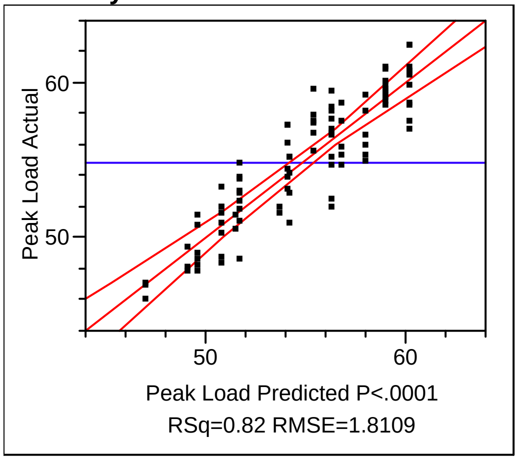
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	47.790476	1.27199	37.57	<.0001
NaOH	0.0480002	0.048792	0.98	0.3281
CAA	2.6767567	0.509382	5.25	<.0001
Steps[1]	-2.290436	0.556985	-4.11	<.0001
Steps[2]	-1.444545	0.415788	-3.47	0.0008
CM Method[B]	-1.502859	0.28579	-5.26	<.0001
CM Method[C]	0.2631058	0.331607	0.79	0.4298
Soak Time[L]	-0.195293	0.210666	-0.93	0.3566
Crosslink Method[A]	1.6374091	0.310863	5.27	<.0001
Crosslink Method[B]	-2.085701	0.352907	-5.91	<.0001
Batch or Continuous[B]	0.1107284	0.2247	0.49	0.6235

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH	1	1	3.09331	0.9678	0.3281
CAA	1	1	88.25948	27.6141	<.0001
Steps	2	2	276.61545	43.2729	<.0001
CM Method	2	2	102.23813	15.9938	<.0001
Soak Time	1	1	2.74671	0.8594	0.3566
Crosslink Method	2	2	135.87980	21.2566	<.0001
Batch or Continuous	1	1	0.77614	0.2428	0.6235

Figure 8.19 Initial analysis of the effects of process parameters on tensile strength in the warp direction using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	1315.3309	219.222	66.8520
Error	87	285.2913	3.279	Prob > F
C. Total	93	1600.6221		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	8	64.63291	8.07911	2.8925
Pure Error	79	220.65837	2.79314	Prob > F
Total Error	87	285.29128		0.0070
				Max RSq
				0.8621

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	48.829162	0.920972	53.02	<.0001
CAA	2.6176059	0.486951	5.38	<.0001
Steps[1]	-2.138763	0.479162	-4.46	<.0001
Steps[2]	-1.196411	0.371059	-3.22	0.0018
CM Method[B]	-1.080764	0.210538	-5.13	<.0001
Crosslink Method[A]	1.6890211	0.310731	5.44	<.0001
Crosslink Method[B]	-2.206375	0.322238	-6.85	<.0001

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
CAA	1	1	94.75608	28.8960	<.0001
Steps	2	2	282.75226	43.1129	<.0001
CM Method	1	1	86.41084	26.3511	<.0001
Crosslink Method	2	2	174.12231	26.5494	<.0001

Pareto Plot of Transformed Estimates

Term	Orthog Estimate
Steps[1]	-2.901209
CAA	1.293677
Crosslink Method[B]	-1.278861
Steps[2]	-1.149152
CM Method[B]	-0.854023
Crosslink Method[A]	0.465704

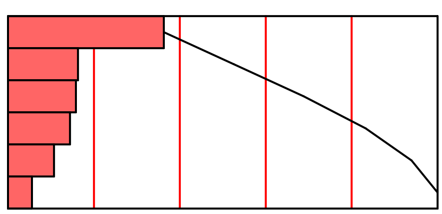
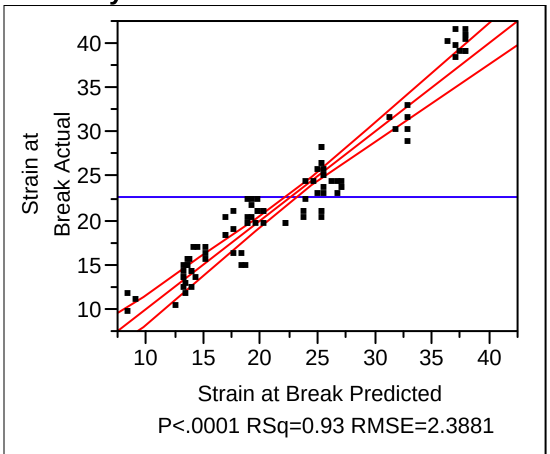


Figure 8.20 Final analysis of the effects of process parameters on tensile strength in the warp direction using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	6075.7768	675.086	118.3722
Error	84	479.0588	5.703	Prob > F
C. Total	93	6554.8356		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	30	322.71337	10.7571	3.7154
Pure Error	54	156.34546	2.8953	Prob > F
Total Error	84	479.05883		<.0001
				Max RSq
				0.9761

Parameter Estimates

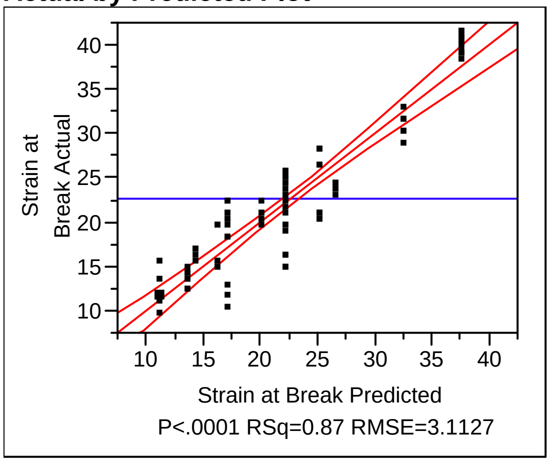
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	7.0180982	1.657951	4.23	<.0001
NaOH	0.1743826	0.064735	2.69	0.0085
CAA	5.0612137	0.663694	7.63	<.0001
Steps[1]	-5.019793	0.676392	-7.42	<.0001
Steps[2]	-0.623707	0.550868	-1.13	0.2608
CM Method[B]	-2.598231	0.285544	-9.10	<.0001
Soak Time[L]	-0.48535	0.281272	-1.73	0.0881
Crosslink Method[A]	8.3422531	0.411084	20.29	<.0001
Crosslink Method[B]	-4.100745	0.451722	-9.08	<.0001
Batch or Continuous[B]	-0.297082	0.29525	-1.01	0.3172

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH	1	1	41.3847	7.2565	0.0085
CAA	1	1	331.6529	58.1533	<.0001
Steps	2	2	720.7388	63.1885	<.0001
CM Method	1	1	472.1930	82.7961	<.0001
Soak Time	1	1	16.9812	2.9775	0.0881
Crosslink Method	2	2	2349.7782	206.0095	<.0001
Batch or Continuous	1	1	5.7741	1.0125	0.3172

Figure 8.21 Initial analysis of the effects of process parameters on strain at break in the warp direction using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	5702.1920	1140.44	117.7028
Error	88	852.6436	9.69	Prob > F
C. Total	93	6554.8356		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	5	208.31912	41.6638	5.3670
Pure Error	83	644.32449	7.7629	Prob > F
Total Error	88	852.64361		0.0003
				Max RSq
				0.9017

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	9.6640232	1.64183	5.89	<.0001
CAA	5.9092109	0.834971	7.08	<.0001
Steps[1]	-4.328507	0.617683	-7.01	<.0001
CM Method[B]	-2.534264	0.361892	-7.00	<.0001
Crosslink Method[A]	9.2601009	0.509288	18.18	<.0001
Crosslink Method[B]	-6.141952	0.45073	-13.63	<.0001

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
CAA	1	1	485.2902	50.0860	<.0001
Steps	1	1	475.8062	49.1072	<.0001
CM Method	1	1	475.1488	49.0394	<.0001
Crosslink Method	2	2	3705.2728	191.2077	<.0001

Pareto Plot of Transformed Estimates

Term	Orthog Estimate
Crosslink Method[A]	4.503108
Crosslink Method[B]	-4.374907
Steps[1]	-3.255617
CAA	2.717362
CM Method[B]	-1.805748

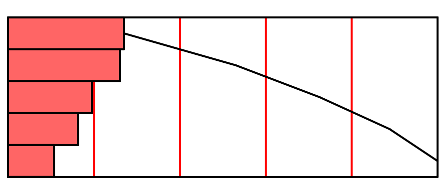
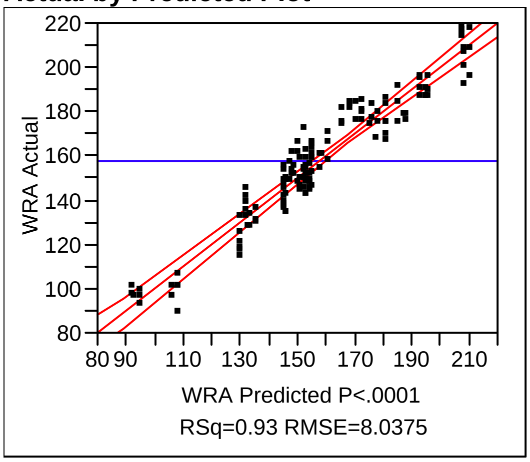


Figure 8.22 Final analysis of the effects of process parameters on strain at break in the warp direction using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	115061.77	12784.6	197.8984
Error	140	9044.29	64.6	Prob > F
C. Total	149	124106.06		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	43	5636.3065	131.077	3.7308
Pure Error	97	3407.9786	35.134	Prob > F
Total Error	140	9044.2851		<.0001
				Max RSq
				0.9725

Parameter Estimates

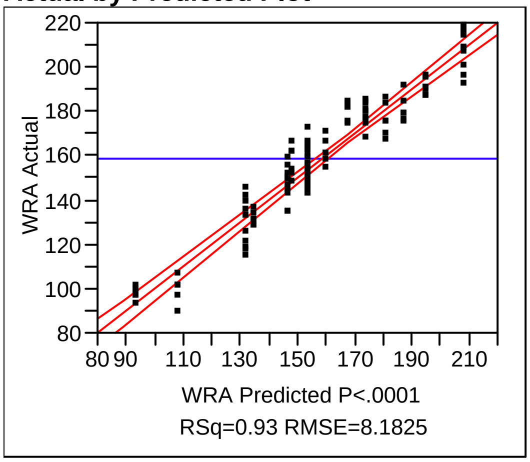
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	151.50856	4.129277	36.69	<.0001
NaOH	0.270148	0.144053	1.88	0.0628
CAA	-14.95209	1.907853	-7.84	<.0001
Steps[1]	-6.246548	1.9598	-3.19	0.0018
Steps[2]	-8.257979	1.342766	-6.15	<.0001
CM Method[B]	22.528713	1.017951	22.13	<.0001
CM Method[C]	-17.95316	1.172427	-15.31	<.0001
Soak Time[L]	-1.167603	0.695841	-1.68	0.0956
CG Method[A]	-29.97129	1.009616	-29.69	<.0001
Batch or Continuous[B]	0.1828223	0.730785	0.25	0.8028

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH	1	1	227.197	3.5169	0.0628
CAA	1	1	3967.895	61.4206	<.0001
Steps	2	2	12246.071	94.7808	<.0001
CM Method	2	2	33058.651	255.8638	<.0001
Soak Time	1	1	181.894	2.8156	0.0956
CG Method	1	1	56930.408	881.2479	<.0001
Batch or Continuous	1	1	4.043	0.0626	0.8028

Figure 8.23 Initial analysis of the effects of process parameters on dry WRA using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	112688.52	22537.7	336.6159
Error	132	8837.90	67.0	Prob > F
C. Total	137	121526.41		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	8	2861.4473	357.681	7.4212
Pure Error	124	5976.4500	48.197	Prob > F
Total Error	132	8837.8973		<.0001
				Max RSq
				0.9508

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	157.67545	3.361433	46.91	<.0001
CAA	-13.17748	1.786007	-7.38	<.0001
Steps[2]	-10.60973	0.8024	-13.22	<.0001
CM Method[B]	22.930441	1.017103	22.54	<.0001
CM Method[C]	-18.80157	1.121248	-16.77	<.0001
CG Method[A]	-30.04052	0.99214	-30.28	<.0001

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
CAA	1	1	3644.799	54.4375	<.0001
Steps	1	1	11705.824	174.8344	<.0001
CM Method	2	2	37060.061	276.7586	<.0001
CG Method	1	1	61382.470	916.7889	<.0001

Pareto Plot of Transformed Estimates

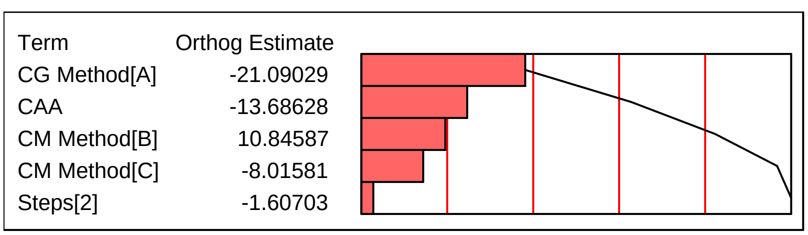
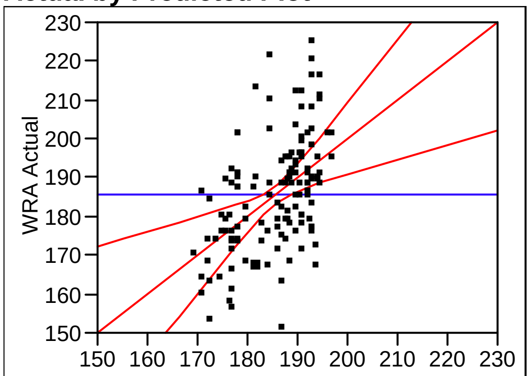


Figure 8.24 Final analysis of the effects of process parameters on dry WRA using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	8	7017.505	877.188	5.2116
Error	129	21712.640	168.315	Prob > F
C. Total	137	28730.145		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	39	10552.197	270.569	2.1819
Pure Error	90	11160.443	124.005	Prob > F
Total Error	129	21712.640		0.0013
				Max RSq
				0.6115

Parameter Estimates

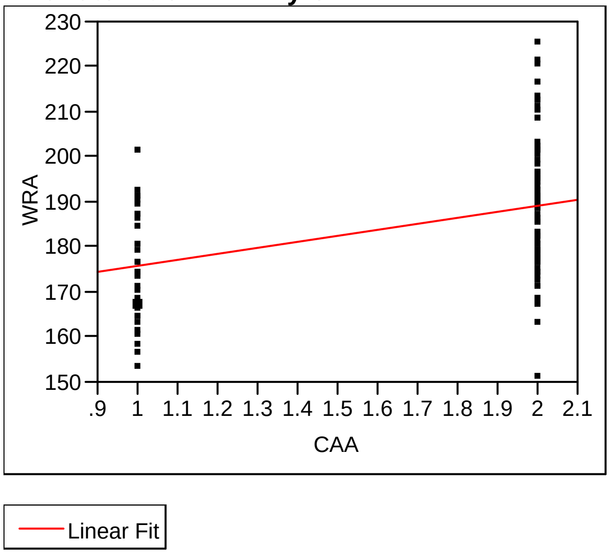
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	169.54942	6.653725	25.48	<.0001
NaOH	-0.245633	0.231829	-1.06	0.2913
CAA	12.238576	3.12545	3.92	0.0001
Steps[2]	-2.118611	1.399701	-1.51	0.1326
CM Method[B]	0.8136663	1.629976	0.50	0.6185
CM Method[C]	1.519705	1.916173	0.79	0.4292
Soak Time[L]	-0.843345	1.205173	-0.70	0.4853
CG Method[A]	2.4390191	1.451617	1.68	0.0953
Batch or Continuous[B]	1.5034212	1.233373	1.22	0.2251

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH	1	1	188.9558	1.1226	0.2913
CAA	1	1	2580.8318	15.3333	0.0001
Steps	1	1	385.6159	2.2910	0.1326
CM Method	2	2	281.2438	0.8355	0.4360
Soak Time	1	1	82.4203	0.4897	0.4853
CG Method	1	1	475.1705	2.8231	0.0953
Batch or Continuous	1	1	250.0894	1.4858	0.2251

Figure 8.25 Initial analysis of the effects of process parameters on wet WRA using series 7, 8, 10, and 11 data

Bivariate Fit of WRA By CAA



Linear Fit

WRA = 162.1634 + 13.447712 CAA

Summary of Fit

RSquare	0.167488
RSquare Adj	0.161366
Root Mean Square Error	13.26157
Mean of Response	185.5507
Observations (or Sum Wgts)	138

Analysis of Variance

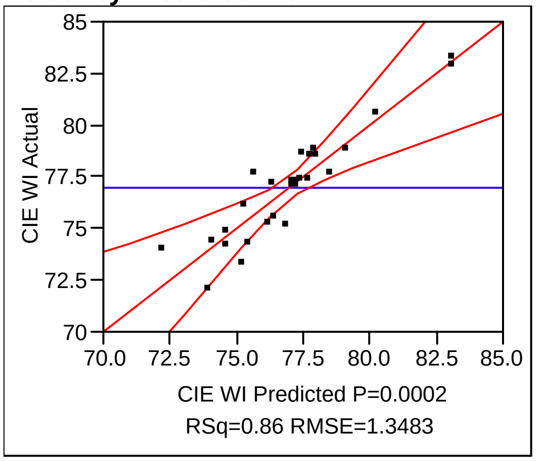
Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	4811.942	4811.94	27.3609
Error	136	23918.203	175.87	Prob > F
C. Total	137	28730.145		<.0001

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	162.1634	4.611423	35.17	<.0001
CAA	13.447712	2.570887	5.23	<.0001

Figure 8.26 Final analysis of the effects of process parameters on wet WRA using series 7, 8, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	10	158.75384	15.8754	8.7332
Error	14	25.44962	1.8178	Prob > F
C. Total	24	184.20346		0.0002

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	13	25.401569	1.95397	40.6653
Pure Error	1	0.048050	0.04805	Prob > F
Total Error	14	25.449619		0.1222
				Max RSq
				0.9997

Parameter Estimates

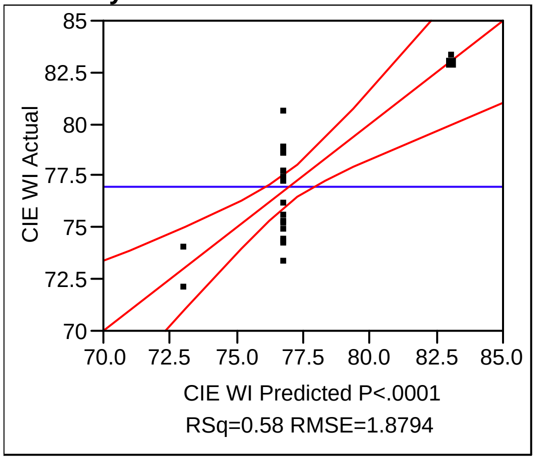
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	73.438081	1.750397	41.96	<.0001
NaOH[20]	3.1447227	0.589471	5.33	0.0001
CAA	1.120276	0.748728	1.50	0.1568
STEPS[1]	4.0722107	0.893373	4.56	0.0004
STEPS[2]	-0.801664	0.700916	-1.14	0.2719
CM METHOD[B]	1.3518931	0.41274	3.28	0.0055
CM METHOD[C]	-0.958484	0.501081	-1.91	0.0764
SOAK[L]	-0.130334	0.469033	-0.28	0.7852
CG METHOD[A]	0.0128707	0.694733	0.02	0.9855
CG METHOD[B]	1.5592587	1.010791	1.54	0.1452
BATCH OR CONTINUOUS[B]	-0.876081	0.832263	-1.05	0.3103

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH	1	1	51.735938	28.4603	0.0001
CAA	1	1	4.069629	2.2387	0.1568
STEPS	2	2	61.940122	17.0368	0.0002
CM METHOD	2	2	19.617068	5.3957	0.0183
SOAK	1	1	0.140367	0.0772	0.7852
CG METHOD	2	2	9.350254	2.5718	0.1119
BATCH OR CONTINUOUS	1	1	2.014286	1.1081	0.3103

Figure 8.27 Initial analysis of the effects of process parameters on WI using series 7, 8, 9, 10, and 11 data

Actual by Predicted Plot



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	106.49344	53.2467	15.0743
Error	22	77.71001	3.5323	Prob > F
C. Total	24	184.20346		<.0001

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	78.04	0.939717	83.05	<.0001
NaOH[20]	1.8453571	0.695403	2.65	0.0145
STEPS[1]	3.1696429	0.695403	4.56	0.0002

Figure 8.28 Final analysis of the effects of process parameters on WI using series 7, 8, 9, 10, and 11 data