ABSTRACT

VARGANTWAR, PRUTHESH HARIHARRAO. Preparation of Ionic Cellulose for Wrinkle Resistant Fabrics. (Under the direction of Dr. Brent Smith and Dr. Peter Hauser.)

Conventional treatment of cellulosic fabrics by formaldehyde-based cross-linkers provides improved wrinkle recovery angles (WRA) and durable press (DP) performance. But these treatments suffer from strength loss and later release of formaldehyde, a known carcinogen. Ionic crosslinking offers a potential solution to these problems, and has shown improved wrinkle recovery performance in previous studies. In the current novel method of ionic crosslinking for wrinkle resistant fabrics, the cellulosic fabric is treated with salt of mono chloroacetic acid and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) sequentially or in mixture to form covalently bonded anionic and cationic sites on cellulose, which are durable to washing, and which form inter/intra molecular ionic cross-links. There is no later release of hazardous chemicals involved with this treatment and improved wet WRA are obtained. Fabric treated by this method gains tensile strength and breaking strain compared to the untreated fabric. Different routes for chloroacetate treatment are presented. The pad-dry-pad-cure is the most efficient route and a functional relationship between the anionic content and the process parameters is established. Analytical techniques like confocal microscopy and scanning electron microscopy are used to confirm the morphological changes and occurrence of carboxymethylation reaction in the fiber interior.

PREPARATION OF IONIC CELLULOSE FOR WRINKLE RESISTANT FABRICS

by
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DEDICATION

This work is dedicated to my family for their loving support and inspiration in all my endeavors and to Dr. Brent Smith for the honor of being his last masters' student before his retirement.

BIOGRAPHY

I was born in Pusad located in Maharashtra state of India. I completed my high school education from Phulsing Naik Mahavidyalaya, Pusad in 2000 to join the Bachelor of Technology program in Fiber and Textile Processing in University Institute of Chemical Technology, Mumbai and graduated in 2004. I joined North Carolina State University in August 2005 to pursue a dual M.S. program in Textile Chemistry and Chemical Engineering and started my research in Textile Chemistry under the direction of Dr. Brent Smith and Dr. Peter Hauser.

ACKNOWLEDGEMENTS

I would like to thank the National Textile Center and North Carolina state University for their financial support and research facilities for this work. I am thankful to Dr. Brent Smith and Dr. Peter Hauser for their advice and help during my research and thesis preparation. I also wish to thank all my friends and collogues who have been very helpful and supportive in my work.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1 Introduction

Easy care, wrinkle resistant cellulosic fabric is in demand in today's market. Due to the disruption of inter and intra chain hydrogen bonds in cotton cellulose by moisture, the wrinkle recovery performance of cellulosic fabric is often poor. When exposed to moisture and external stresses, hydrogen bonds break and reform, stabilizing creases. Formaldehyde-based cross-linkers, which replace some of the hydrogen bonds with covalent bonds between the fibers and the finishing agent, have been used to improve durable press (DP) properties of cellulosic fabric. The covalent bonds are stronger than the hydrogen bonds, and can resist external stresses and survive bond breakage due to moisture. When external stress is applied the bonds store energy and on release of the external stress, the energy stored in the covalent bonds helps in the return of fabric to its original state. Urea-formaldehyde derivatives, melamine-formaldehyde derivatives and methylol derivatives were the original formaldehyde based finishing agents. These finishes suffered from poor stability of the finishing agent, poor durability and chlorine retention of the fabric, which caused yellowing and degraded the fabric.[1,2] Although these treatments improved performance, they typically suffered from later release of formaldehyde, a known carcinogen[3,4], as well as loss of tensile strength, tear strength, and abrasion resistance in the fabric. Polycarboxylic acid anhydrides were also used on the similar principle of covalent bond formation. This finish was expensive and yellowed the product.[2] These disadvantages compelled the search for a non-formaldehyde based wrinkle resistant finish at an affordable cost.

In the work reported here, fabric stabilization for wrinkle resistant fabrics was achieved by formation of ionic bonds instead of covalent bonds. The process involved production of zwitter ionic cellulosic fabric. The step of producing anionic cellulose was studied in detail

with the optimization of the process parameters. The cationization treatment was adopted from previous research.[2] The routes for ionic crosslinked wrinkle resistant fabric involved, (1) treatment of cellulosic fabric with anionic material followed by reaction with cationic reactant, (2) treatment of cellulosic fabric with cationic material followed by treatment with anionic reactant and (3) treatment of cellulosic fabric with a mixture of oppositely charged ionic materials. The treatment used existing equipment and common industrial reactants with no associated safety or environmental issues. There was no release of hazardous chemicals involved with these treatments. The success of the process was evaluated by measuring the wet wrinkle recovery angles (WRA), dry WRA and tensile strength. The wet WRA, important for applications like bedding, showed an improvement and the strength of the fabric increased after the treatment.

2 Literature review

2.1 Cellulose and its chemistry

Chemical and physical properties of cotton cellulose can best be understood by knowing the chemical structure of its molecules and their structural and morphological arrangements in the fibrous form. Cotton grows as a natural fiber from the surface of the cotton plant seeds and has impurities of wax, protein, etc. Once these impurities are removed during scouring and bleaching processes, cotton is almost 99% pure cellulose.[5] Cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units often called anhydroglucose joined together by β- 1, 4- glucosidic bonds. The repeat unit is the anhydro-beta-cellobiose. Figure 2.1 shows the cellulose polymer. The number of repeat units bound together gives the degree of polymerization, which is between 1000 and 15000 in native cotton.[6] The cellulose molecule has three hydroxyl groups, one primary and two secondary, in each anhydroglucose unit. The chemical reactivity of cellulose is strongly influenced by these hydroxyl groups. The primary hydroxyl group is the most reactive due to its greater acidity compared to the secondary hydroxyls forming ionized cellulosate which is a good nucleophile for attack on moieties like vinyl group (Michael addition), or for nucleophilic substitution.[7] These hydroxyl groups serve as principal sites for reactions like etherification and esterification and are responsible for dyeing and finishing applications.

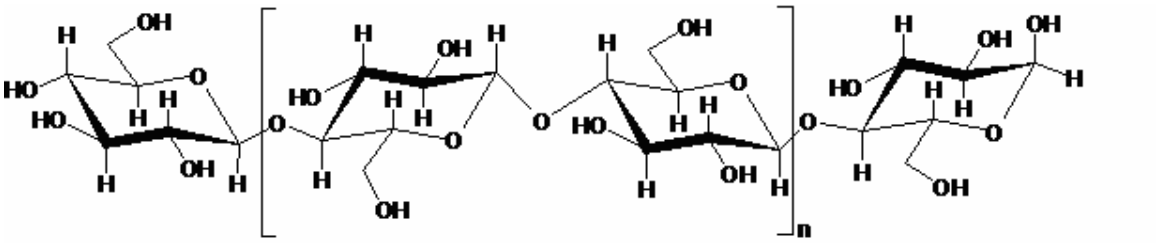


Figure 2.1 Cellulose polymer chain

Approximately 65 to 70% of cotton cellulose is crystalline in nature with the rest being amorphous.[8] Polymeric chains are held in place by inter-chain hydrogen bonds.[9] The molecules are parallel and loosely packed in the crystalline areas. The hydrogen bonding is more prominent in crystalline areas than in the amorphous regions. The hydroxyl groups of cellulose serve as adsorption sites for water molecules. Cotton shows improved strength as its moisture content increases, which is explained by the increased hydrogen bonding due to the adsorbed moisture.[9]

2.2 Wrinkling of cellulosic fabrics

Wrinkling is very prominently shown by cellulosic fabrics. This is due to the frequent breaking of the hydrogen bonds in the stressed condition and reforming of new bonds. When the stress is released the newly formed hydrogen bonds do not break and the fabric is incapable of recovering to its previous shape, thus forming creases.[10] Wrinkles are typically set into the fibers when the fabric moisture content decreases from 25% to 5%. In the wet state, water molecules attach to the polymer chains and disrupt hydrogen bonding. Water molecules act as lubricant thereby helping the chains to slide past each other when forces are applied. As the fabric loses its moisture, the lubrication is lost and the wrinkles are set due to reformation of hydrogen bonds. This is the reason why washing and drying results in wrinkling of the fabric. Thicker fabrics wrinkle more due to the large variation of stresses from the inside to the outside of the fibers in the bent state. Similarly, highly twisted yarns wrinkle more easily than low twist yarns.

In the chemical treatment of cellulosic fabrics for wrinkle resistance, often termed as DP finishing, some of the hydrogen bonds are replaced by the covalent bonds between the fibers and the finishing agent. The covalent bonds are stronger than the hydrogen bonds. In

the stressed condition, these covalent bonds resist the external stress, and thus provide the driving force for returning the fibers to their previous orientation.

2.3 Conventional DP finishing of cellulosic fabric

In DP finishing, cellulosic fabric is treated so that it returns to its previous shape after washing and drying. The original process was developed in 1928.[11] The treatment removes the problem of wrinkling by replacing a few of the hydrogen bonds with covalent bonds between the fibers and the finishing agent.[12] The usual method of treatment involves padding through a cross-linking agent with a catalyst, drying at 100-110°C and then curing at 150-175°C for 2-3 min.[13] Many different cross-linkers are available. The most common ones are urea formaldehyde (UF) derivatives, melamine-formaldehyde (MF) derivatives and N-methylol compounds. These cross-linkers produce DP performance of varying degrees.

2.3.1 Urea formaldehyde derivatives

UF derivatives were the first widely used cross-linkers for DP finishing. They are formed by the reaction of urea and formaldehyde (Figure 2.2). One mole of urea and two moles of formaldehyde react to form one mole of dimethylol urea (DMU). Methylol groups form the crosslinks by reacting with the hydroxyl group on cellulose chains in the presence of suitable temperature and catalysts.

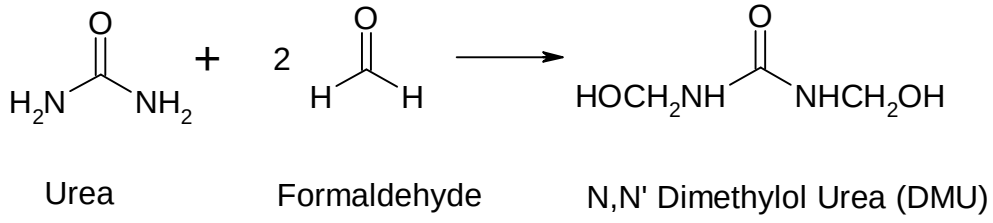


Figure 2.2 Urea/formaldehyde reaction to form dimethylol urea[1]

The finish is applied by padding the fabric through the urea-formaldehyde precondensate with the Lewis acid catalyst, drying, curing and then washing. The treatment gives excellent crease recovery. The chemicals are inexpensive and highly efficient. The finishing bath has a limited shelf life once the chemicals are mixed. The fabric becomes stiff after treatment due to self-crosslinking of the finishing agent. It releases formaldehyde, and shows chlorine retention due to the presence of –NH groups that can react with the bleach to form chloramines that produce hydrochloric acid, which eventually degrades the fabric and causes yellowing.[14-16]

2.3.2 Melamine-formaldehyde derivatives

Melamine and formaldehyde react to form a MF derivative. One mole of melamine (2, 4, 6-triamino-1,3,5-triazine) reacts with three moles of formaldehyde to produce one mole of trimethylol melamine (TMM). Reaction of one mole of melamine with six moles of formaldehyde gives one mole of hexamethylol melamine. Trimethylol melamine and hexamethylol melamine are reacted further with methanol for stability giving trimethoxymethyl and hexamethoxymethyl melamines respectively (Figure 2.3).They either form self-crosslinks or react with the cellulose hydroxyl groups in the presence of suitable temperature and Lewis acid catalyst forming covalent bonds. MF derivatives are more durable and expensive than UF derivatives. The fabric becomes stiffer on treatment with trismethyloxymethylol melamine treatment, whereas hexamethoxymethylol melamine gives a softer hand. The finished fabric releases formaldehyde and has poor chlorine resistance that eventually leads to fabric degradation due to formation of hydrochloric acid.[17, 18]

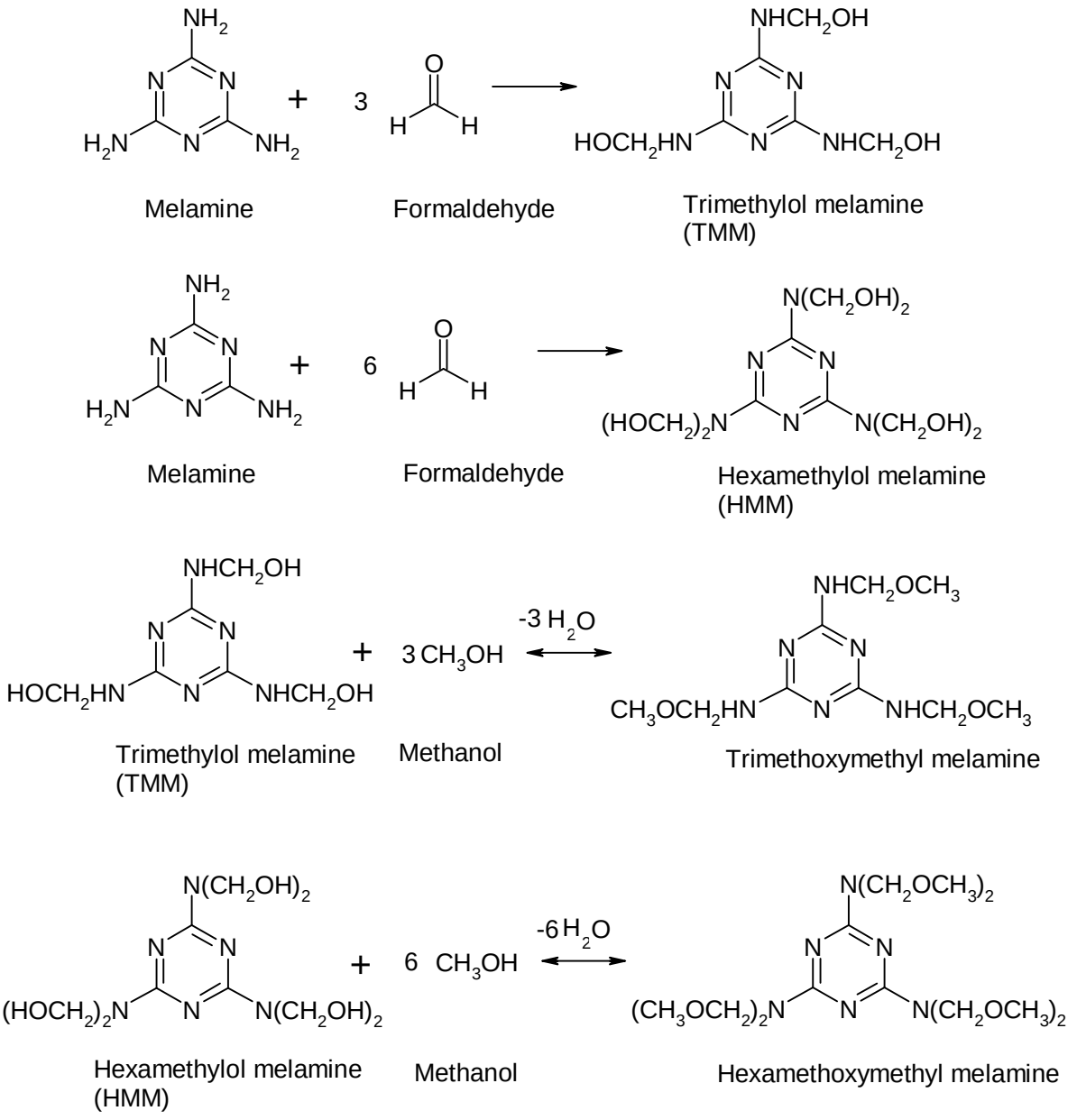
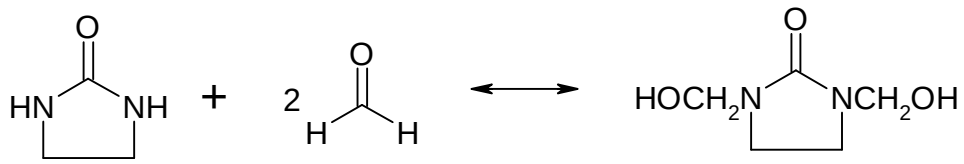


Figure 2.3 Melamine-formaldehyde reactions[1]

2.3.3 Cyclic urea methylol derivatives

Unlike UF and MF, cyclic urea methylol derivatives react with cellulose only to form crosslinks and do not react with themselves to form stiff films. The main cross-linkers from this group are dimethylol ethylene urea (DMEU), dimethylol propylene urea (DMPU) and dimethylol dihydroxy ethylene urea (DMDHEU).

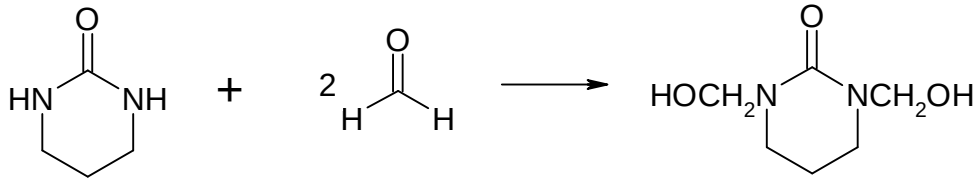
DMEU is formed by the reaction of one mole of ethylene urea with two moles of formaldehyde (Figure 2.4). It is not very expensive and produces high WRA at low add-ons. It is sensitive to acids. In the presences of an acid catalyst, DMEU reacts with cellulose hydroxyl groups.[19]



Ethylene Urea Formaldehyde Dimethylol ethylene urea (DMEU)

Figure 2.4 Ethylene urea-formaldehyde reaction to form dimethylol ethylene urea

DMPU is formed by the reaction of one mole of propylene urea with two moles of formaldehyde (Figure 2.5). The crosslinker shows more stability and durability than DMEU, has less chlorine retention and no odor. It is more expensive than DMEU and especially suitable for white fabrics as no yellowing with heating is involved.[20]

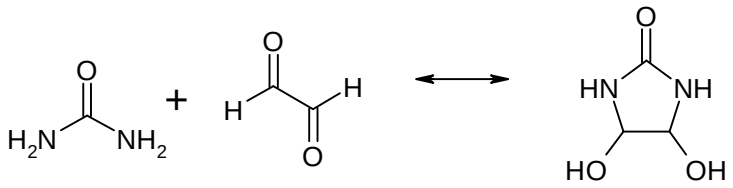


Propylene urea Formaldehyde Dimethylol Propylene Urea (DMPU)

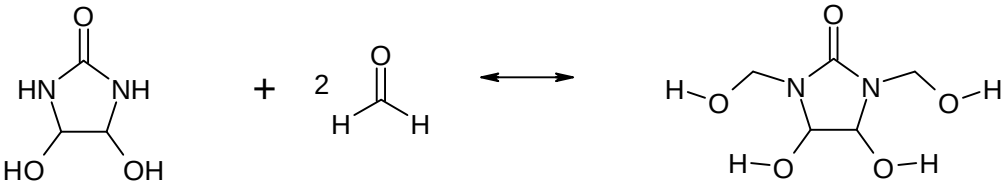
Figure 2.5 Propylene urea-formaldehyde reaction to form dimethylol propylene urea

DMDHEU is the most widely used cross-linker for DP finishing. One mole of 4,5-dihydroxy ethylene urea reacts with two moles of formaldehyde to form one mole of DMDHEU. The synthesis of DMDHEU and its reaction with cellulose are shown in Figure 2.6. Its lower reactivity allows for a delayed curing step. Though the finish has a longer shelf

life and pad bath life than DMU and TMM, better durability than DMEU and reduced release of formaldehyde, it causes fabric yellowing.[10, 21, 22]

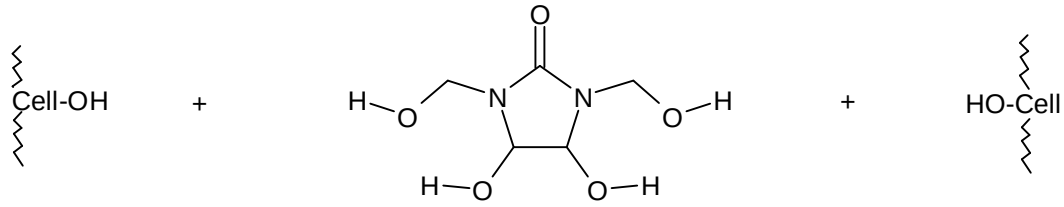


Urea Glyoxal 4,5-Dihydroxyethylene urea

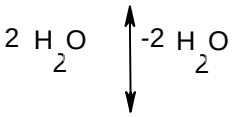


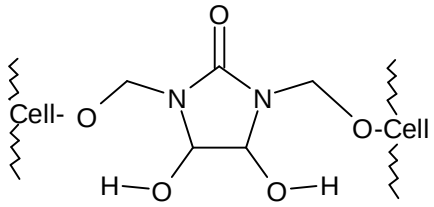
4,5-Dihydroxyethylene urea Formaldehyde 1,3- Dimethylol- 4,5- dihydroxyethylene urea (DMDHEU)

(a) Synthesis of DMDHEU



1,3- Dimethylol- 4,5- dihydroxyethylene urea (DMDHEU)





Cross-linked cellulose

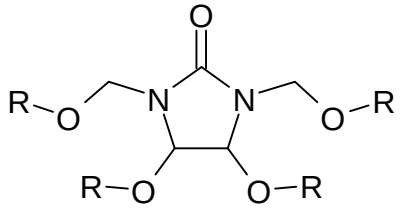
(b) Crosslinking of cellulose with DMDHEU

Figure 2.6 (a) Synthesis of DMDHEU and (b) its reaction with cellulose[1]

2.3.4 Low formaldehyde release DP finishing cross-linkers

The traditional DP finishing cross-linkers suffer from release of formaldehyde, a known carcinogen.[4] Consequently, low formaldehyde or formaldehyde free finishes are widely sought after.

Alkylated DMDHEU (Figure 2.7) shows reduced formaldehyde release.[1] DMDHEU releases about 500mg formaldehyde/kg of fabric, whereas alkylated DMDHEU (fully methylated) releases 300mg/kg of fabric. The formaldehyde release can be lowered to about 50mg/kg of fabric by using the cross-linker obtained by reacting one mole of DMDHEU to two moles of diethylene glycol.[1, 10]



Alkylated dimethylol dihydroxy ethylene urea

Figure 2.7 Alkylated DMDHEU (R is $-CH_3$)

2.3.5 Problems with N-methylol finishes

The N-methylol based finishes have been very successful in imparting wrinkle resistance to the fabric. The process of finishing uses Lewis acid salts such as magnesium chloride and zinc nitrate that create acidic conditions in the bath causing a high degree of depolymerization of cellulose chains. As a result fabric loses its strength.[23] The strength loss is also due to the rigid covalent crosslinks formed by the finish, which does not allow the polymeric chains to slide, share and absorb the stresses. Also, this finishing has an additional problem of formaldehyde release.[4, 12] The presence of formaldehyde in the finished product,

work environment, and in wastewater streams has been a cause of concern for health safety issues. The focus has thus been on formaldehyde free finishes.

2.4 Non formaldehyde based DP finishes

Polycarboxylic anhydrides have been used for DP finishing. These chemicals have carboxylic acid groups, which react with the cellulose hydroxyl groups forming ester linkages. The finish is formaldehyde free, does not produce any odor, and gives a soft hand compared to the N-methylol finishes.

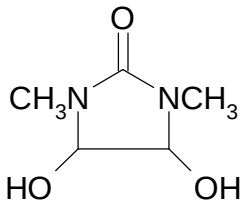
BTCA (1, 2, 3, 4- butane tetra carboxylic acid) was used as a crosslinking agent for DP finishes. It forms an anhydride that reacts with the cellulosic hydroxyl groups in the presence of sodium hypophosphite monohydrate catalyst. The performance of this finish is similar to the DMDHEU finish, but it is less durable due to easier hydrolysis of ester groups. It also leads to strength loss caused by the polymer degradation due to the catalyst.[24, 25] A large amount of catalyst, about 30%, is required for the treatment with BTCA. Also, BTCA is almost four times more expensive than DMDHEU.

The phosphorus containing catalyst has environmental issues and hence alternative catalysts like boric acid, N-heterocyclic compounds like imidazole and its alkyl derivatives are suggested.[26, 27] Mono and disodium fumaric acid, maleic acid and itanoic acid salts are also mentioned as efficient catalyst for BTCA treatment.[27] These catalysts show similar performance as the sodium hypophosphite, but with better mechanical properties.

BTCA being expensive has been replaced with less expensive chemicals like polymaleic and polyacrylic acids. Citric acid, tartaric acid and maleic acid have also been studied. Citric acid shows good DP performance but has a problem of yellowing.[28, 29] Mixtures of citric acid and maleic acid/itaconic acid have been used for wrinkle recovery

performance.[27] The treatment is 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 also been tried. It showed improved performance over most polycarboxylic acids.[27] A treatment of cellulosic fabric with the copolymer of maleic and acrylic acids gives the same wrinkle recovery performance as the BTCA with improved strength properties.[31] The problem with all of the polycarboxylic acids is that they yellow the fabric. The strength loss due to polycarboxylic acid can be improved by using long chain polycarboxylic acids.[24, 25]

Another non-formaldehyde based finish (Figure 2.8), N,N'-Dimethyl-4,5-dihydroxyethylene urea (DMeDHEU)[1] is available commercially.[30] This finish is difficult to cure, requires high level of resin add-on and is less efficient than DMDHEU. It is less expensive than BTCA but costlier than DMDHEU.



N,N'-Dimethyl-4,5-dihydroxyethylene urea
(DMeDHEU)

Figure 2.8 DMeDHEU

Chitosan citrate has been evaluated for DP finishing and antimicrobial performance.[32] The carboxylic acid groups in the reagent react with cellulosic hydroxyl groups. The treatment is done by pad-dry-cure method. Slight improvement in wrinkle recovery performance is observed. An aqueous easy-care finish of BTCA-chitosan with sodium hypophosphite catalyst can be applied by pad-dry-cure method. The treated fabric showed crease recovery comparable to the DP finish.[33]

2.5 Carboxymethylation of cotton cellulose

Cellulose can be made anionic via various routes: treatment with chloroacetic acid, chlorosulphonic acid[34], or sodium, 4-(4,6-dichloro-1,3 5- triazinylamino)-benzenesulfonate.[35] The product of the carboxymethylation of cotton cellulose is carboxymethylcellulose (CMC), anionic cellulose.[36] It is also termed as cellulose glycolate and cellulose glycolic acid. It is formed by the treatment of cellulose with chloroacetic acid and sodium hydroxide. The chemical structure of CMC is shown in Figure 2.9

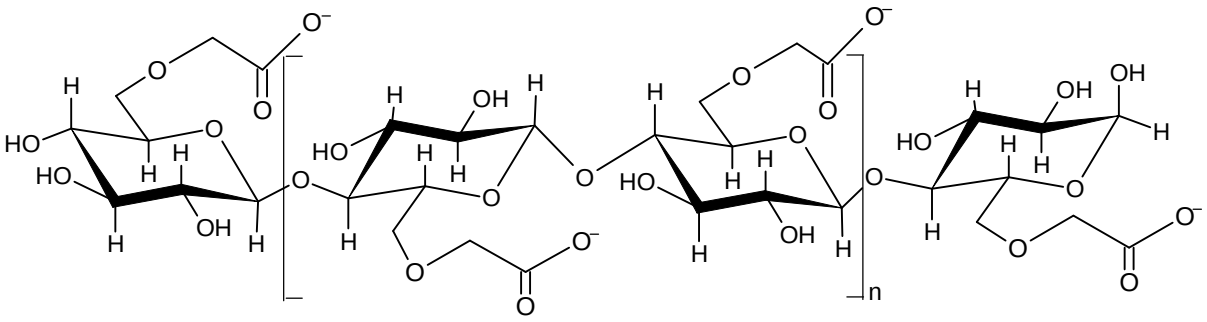


Figure 2.9 Chemical structure of carboxymethylcellulose

Different routes of treatment give different degrees of substitution.[36] The substitution is at the 6-O- position predominantly on the cellulose molecules followed by 2-O, 2, 6- di- O, 3- O, 2, 3- di- O and then 2, 3, 6- tri-O positions. The reaction proceeds unevenly with areas of high and low substitutions.[2]

At low degree of carboxymethylation, CMC molecules are extended and have a rod like structure. As the ionic concentration increases, the molecules overlap and form coils. This is influenced by the degree of substitution and average chain length. CMC molecules cross-link at low pH through the carboxylic acid and free hydroxyl groups.

Previously carboxymethylation has been done by the pad-batch[2, 34], pad-dry-cure[10]and pad-dry-pad-cure[10] methods. In the pad-batch process, the cellulosic fabric is padded through sodium hydroxide, typically dried at 100°C, then padded with sodium chloroacetate and

batched in a polyethylene bag for 1 hr at 70°C. In the pad-dry-pad cure method, the fabric is padded through the mixture of sodium hydroxide and sodium chloroacetate, dried, and then cured at 110°C for 90 seconds. In the pad-dry-pad-cure process, the fabric is soaked in sodium hydroxide, dried at 80°C, soaked in sodium chloroacetate solution, padded and then cured at 80°C for 10 min. There were several parameters in these processes that needed further evaluation to increase the extent of reaction.

2.6 Cationization of cotton cellulose by CHTAC

Cellulose can be cationized by 3- chloro- 2- hydroxypropyl trimethyl ammonium chloride (CHTAC),[37-39] which is commercially available as a 69% aqueous solution under the name of CR-2000 from Dow chemical. CHTAC forms an epoxy intermediate in the presence of sodium hydroxide, which has low affinity for cellulose giving low reaction efficiencies. The intermediate is susceptible to hydrolysis forming a non-reactive product. The cationization has been tried by several methods[37]: pad- batch, pad-steam, exhaust, and pad-dry cure. In the pad-batch process fabric is padded through the sodium hydroxide-CHTAC solution and batched at room temperature for 24 hours. In the exhaust method, fabric is treated for 90 min at 75°C. Different solvents such as water, acetone, ethanol, isopropanol and methanol have been tried. Acetone gave the best reaction efficiency. In the pad-steam method, fabric is padded through the mixture and steamed at 100°C for 30 min. The pad-dry-cure method involves padding the fabric in the mixture of NaOH and CHTAC solution and drying and curing at different temperatures for different times. NaOH to CHTAC mole ratios were varied. The highest cationization was achieved by drying at 35°C for 5 min followed by curing at 110°C for 5 min. All these methods produced different reaction efficiencies. The exhaustion method gave 10% fixations; pad-batch gave 25% substitution, whereas pad-dry-

cure gave 85%. The reaction efficiency went down with increase in CHTAC concentration. The NaOH to CHTAC mole ratio of 1.8 or greater worked the best.[37] The chemical structure of cationic cellulose is shown in Figure 2.10.

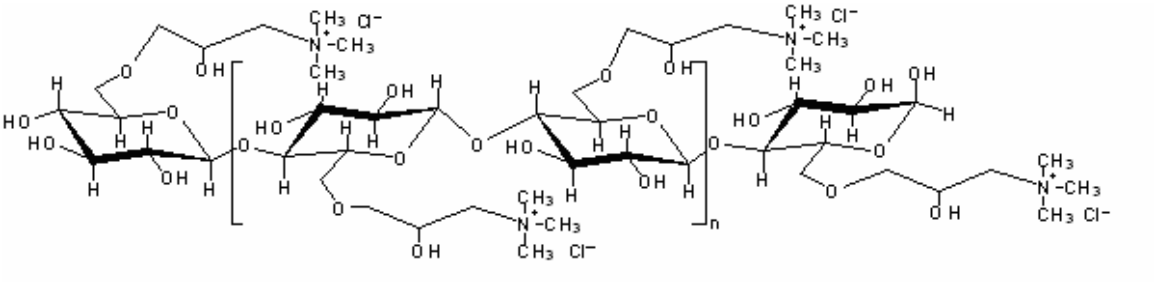


Figure 2.10 Chemical structure of cationic cellulose

2.7 Ionic cross-linking

Ionic cross-linking is an alternative to covalent cross-linking that can be used to improve properties and performance of the materials. A brief discussion of the applicability of ionic crosslinking in polymer industry and the prior work in the development of wrinkle resistant fabric via ionic crosslinking is provided in this section along with the involved chemistries.

2.7.1 Research on ionic cross-linking

Ionic cross-linking can be used to improve the thermal resistance, abrasion resistance, durability and chemical resistance of a polymer. The phenomenon of ionic cross-linking has been successfully employed in the polymer industry for various applications.

Acrylic sizes applied on polyester filaments to improve their weaving properties have calcium and magnesium ions in them.[2, 40] In the absence of these ions, the sizes are not stable to moisture. In high humidity, they absorb moisture causing blockage of weaving beams.

The divalent calcium and magnesium ions form cross-links between the acrylic polymer chains and make the size stable to moisture.

Magnesium compounds have been reported for ionic cross-linking in the copolymer of propylene and maleic anhydride. Maleic anhydride groups get cross-linked by these compounds. Magnesium 12-hydroxy stearate (MgStOH), zinc oxide (ZnO), and zinc sulfide (ZnS) are used. The type and the content of the metal compound can control the viscosity of the polymer melt. Rheologically, the cross-linked compound shows ideal flow processabilities for extrusion.[41, 42]

Synthesis of a series of siloxane- based liquid crystalline elastomers using ionic cross-linking agent like 2,2'-(1,2-ethenediyl)-bis[5-[(4-undecenoyloxy)phenyl]-azo]-benzenesulfonic acid having sulfonic acid groups has been reported.[43] The cross-link densities of the synthesized polymers are studied by the swelling experiments. The variety of cross-linked structures obtained by varying the ionic cross-linking contents showed different swelling properties.

Vulcanized compounds with ionic and covalent bonds can be formed by the vulcanization of the carboxylated rubber by the mixed system of zinc peroxide and sulphur accelerators. The ionic aggregates formed increased the rigidity of the vulcanized compound giving higher stress values at constant deformation, storage modulus and resistance of traction. These properties show reversible disappearance when exposed to saturated ammonia due to the plasticizing action of the vapors.[44]

Cross-linked polyurethanes can be made by ionic cross-linking. Different approaches are employed to make cationic, anionic or zwitter ionic polyurethanes, which can then be

used in coatings, adhesives, shoe soles and in variety of damping materials. The structure, morphology and characteristics of polyurethanes can be tailored by cross-linking networks.[45]

2.7.2 Prior research on ionic cross-linking for crease recovery performance

Ionic cross-linking has been successfully employed in improving wrinkle recovery performance of the fabric. Cotton cellulosic fabric (100%) with a plain weave was used in the studies.[2,34] Several routes were used to produce ionic cross-linked wrinkle resistant fabric. The cellulosic fabric could be made anionic first and then cross-linked with the cationic reagent or it can be made cationic first followed by cross-linking with anionic cross-linker.

In the first case, the fabric was treated with sodium chloroacetate to make anionic cellulose. This anionic cellulosic fabric was then cross-linked using cationic chitosan, cationic glycerin, calcium chloride, magnesium chloride, cationized ethylene glycol, cationized D-cellobiose, cationized dextrose and cationized β-cyclodextrin. Out of all these treatments, cationic glycerin and cationic chitosan showed the best performance. Cationic glycerin showed an edge over the cationic chitosan treatment.[2, 34]

In the second route of treatment, cellulosic fabric was reacted with CHTAC to get cationic cellulose. It was then ionic cross-linked with PCA, BTCA, EDTA, NTA, HEDTA, citric acid, oxalic acid and maleic acid. The best results were seen with PCA and BTCA.[2, 34]

In the above treatments, improvement in WRA performance was seen in all the treatments. The best results seen with cationic glycerin showed improvement of 120° in wet recovery angles and up to 55° in dry recovery angles over the untreated controls. The fabrics gained strength up to 58% in the treatment. However, the cross-linking reagents were not very durable to washing. The untreated cellulosic fabric had %N content of about 0.25 to 0.20 before treatment and 0.62 to 0.78%N after treatment. After the first wash, almost 45 to

70% nitrogen content was lost. After seven washes, almost all the nitrogen due to the cross-linker was lost.[10]

2.7.3 Chemistry for ionic cross-linking

Chemical methods for carboxymethylation and cationization are presented below, with special attention to ionic crosslinking.

2.7.3.1 Chemistry of carboxymethylation of cellulose

The carboxymethylation reaction is responsible for forming anionic cotton cellulose. Carboxymethylation proceeds very easily in the amorphous regions compared to the crystalline regions. At the early stages of the reaction the distribution of the carboxymethyl groups is very uneven. With reaction time, the reactants penetrate to the more highly ordered regions resulting in more even distribution of carboxymethyl groups.[46]

In the carboxymethylation reaction, the cellulosic fabric is soaked and then padded through sodium hydroxide followed by drying. In the process, the hydrogen of the primary hydroxyl groups is removed and negatively charged oxygen remains. The cellulose now is known as soda cellulose. These are the reactive sites for sodium chloroacetate to react. Treatment with sodium chloroacetate is done either by soaking and padding or by direct padding through chloroacetate solution followed by batching/drying. The dried samples are cured and washed. Otherwise, the cellulosic fabric can be soaked and padded through the mixture of sodium hydroxide and sodium chloroacetate, dried and cured.[2, 10, 34]

Chloroacetate solution is prepared by neutralizing the mono chloroacetic acid with a weak base like sodium carbonate, ammonium carbonate etc. The mono chloroacetic acid flakes are dissolved in deionized water. Solution concentrations up to 9.0 M have been

prepared and neutralized using the weak base. Carbon dioxide is evolved in the reaction as mono chloroacetic acid is neutralized. This solution is used to pad the cellullosic fabric followed by further treatment at various conditions. The hydroxyl groups on the cellulose chains are replaced by the stable ether linkages forming anionic cellulose as shown in Figure 2.11.

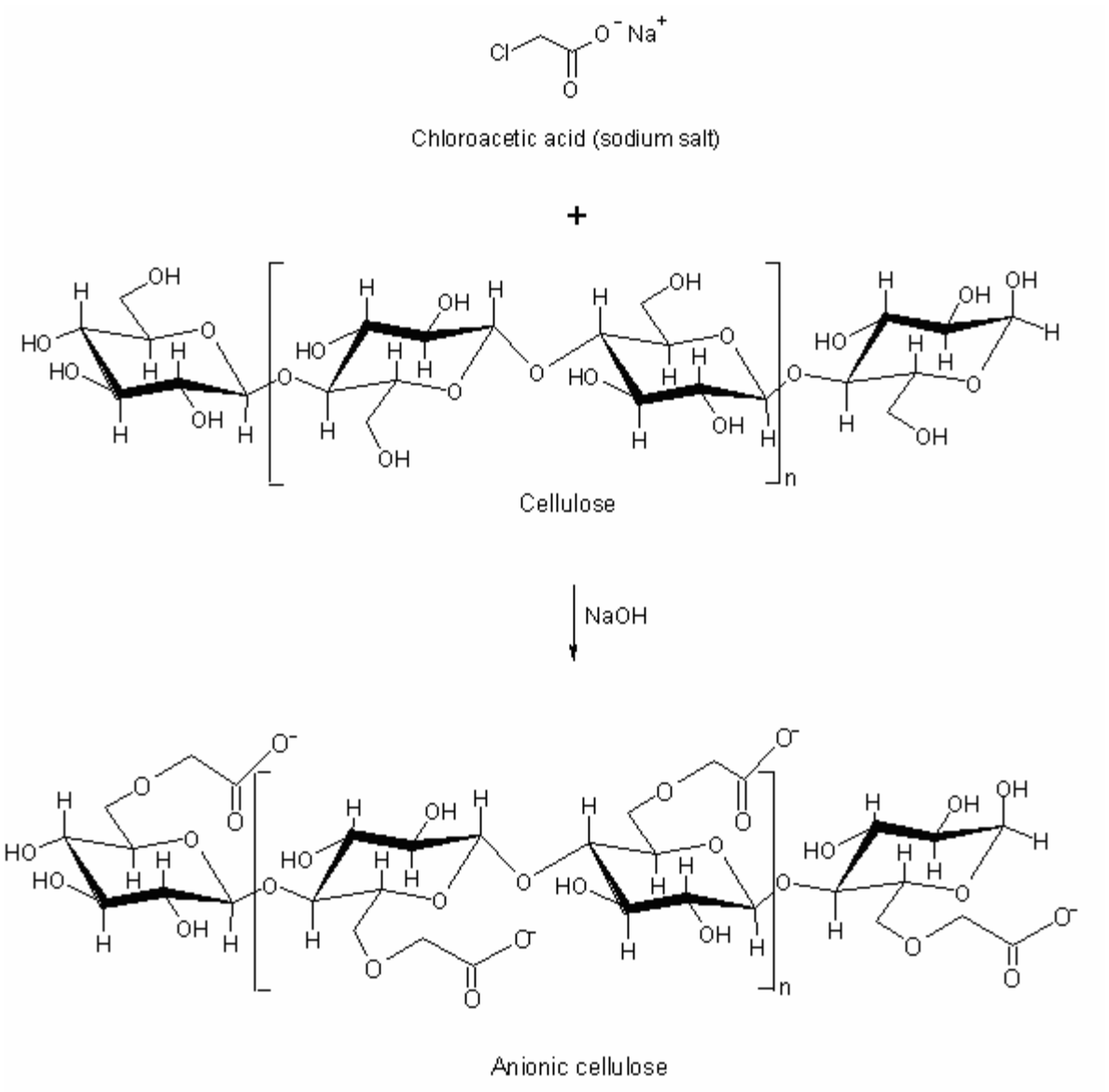


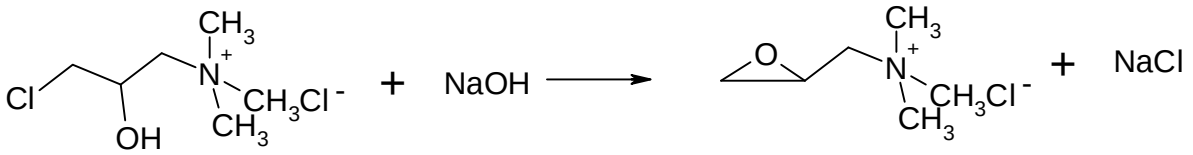
Figure 2.11 Carboxymethylation reaction of cotton cellulose[2]

2.7.3.2 Chemistry of cationization of cellulose

Cationization of cellulose is achieved using a cationic agent such as CHTAC. Reaction of cellulose with CHTAC depends on time, temperature and pH, and requires the addition of sodium hydroxide, which acts as a base catalyst. Several reactions occur simultaneously during the cationization of cellulose:

1. An epoxy intermediate (2,3-epoxypropyl trimethyl ammonium chloride) is formed from the chlorohydrin form of the reagent (equation 2.1)
2. The epoxy intermediate then reacts with cellulose chains (equation 2.2)
3. The epoxy intermediate undergoes hydrolysis to produce non-reactive 2,3- dihydroxy derivatives (equation 2.3)

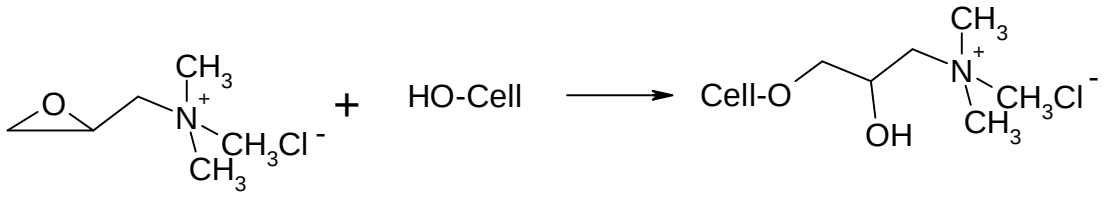
CHTAC and NaOH are mixed for the treatment. The NaOH: CHTAC mole ratio of 1.8 or slightly more is found the best for the reaction. Once these chemical are mixed, an epoxy intermediate is formed which starts hydrolyzing. The hydrolyzed product does not react with cellulose and hence the cellulosic fabric must be treated immediately after the mixture is made. The cationization reaction is shown in Figure 2.12



3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC)

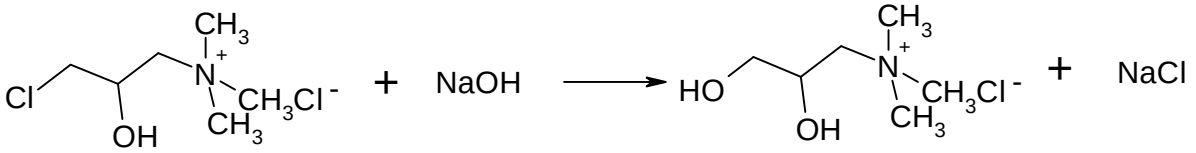
2,3-epoxypropyl trimethyl ammonium chloride

Equation 2.1



Cationic cellulose

Equation 2.2



Hydrolyzed CHTAC

Equation 2.3

Figure 2.12 Cationization of cotton cellulose with CHTAC[3]

2.7.3.3 Chemistry of ionic cross-linking

The anionic cellulosic fabric formed by carboxymethylation is soaked in cationized glycerin solution of varying concentrations. The negative charges on the cellulose form ionic bonds with the positive charges on the cationized glycerin forming ionic cross-links. Similarly, the cationized cellulosic fabric can be soaked in 1, 2, 3, 4- butane tetra carboxylic

acid (BTCA) solution to form ionic bonds between the positive charges on cotton cellulose and the negative charges on BTCA. The cross-linking is shown in Figure 2.13.

In the current research, we have adopted a different approach, which will be discussed in sections 3.3.4 and 4.5.

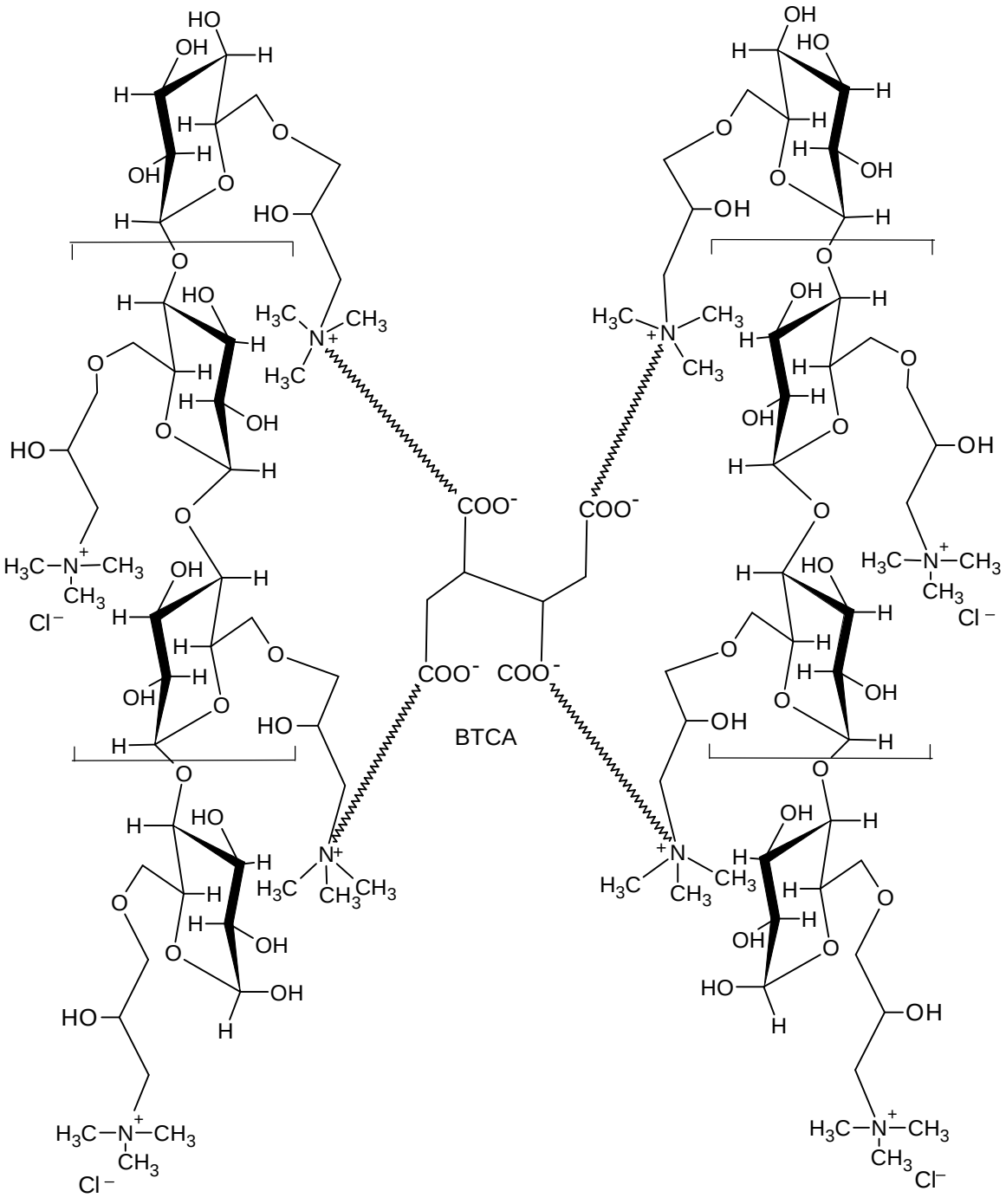


Figure 2.13 Ionic cross-linking with BTCA[2]

2.8 Research objective

For a long time, the textile industry has been looking for non-formaldehyde based finish for wrinkle resistant fabric, without reduction in strength due to the finish. The objective of this research was to develop non-formaldehyde based finishing route for the wrinkle resistant fabric with no involved losses in strength.

In the work reported here, fabric stabilization for wrinkle resistant fabrics was achieved by formation of ionic bonds between the cellulose chains opposed to the covalent bonds formed in the conventional DP finishes. The process involved production of zwitter ionic cellulose fabric by (1) treatment of cellulose with anionic material followed by reaction with cationic reactant, (2) treatment of cellulose with cationic material followed by treatment with anionic reactant and (3) treatment of cellulose with a mixture of oppositely charged ionic materials.

The treatments utilized existing equipment and used common industrial chemicals with no associated safety or environmental issues. There was no release of hazardous chemicals involved. The treatment with anionic material, mono chloroacetic acid in this case, produced partially carboxymethylated cellulose. This was termed carboxymethylation. Carboxymethylation was done previously by different routes.[2, 10] All the methods had inconsistent results that varied from person to person. This was thought to be due to several process parameters that were not evaluated precisely. Hence, in this research, process parameters for the best and most consistent carboxymethyl content were evaluated. This led to several single variable trials followed by a design of experiment to develop a functional relationship between the carboxymethyl (anionic) content and the process parameters. The pad-dry-pad-cure route of carboxymethylation was studied in detail. Analytical tools such as

confocal microscopy and scanning electron microscopy proved conclusive in observing the changes in cross-sectional geometry of the fiber and distribution of anionic sites. Treatment with cationic material, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) to produce cationic sites, was adopted from previous research.[47]

This work is based mainly on methods 1 and 2 with some preliminary studies for method 3. In method 1, cotton cellulose was partially carboxymethylated with salt of mono chloroacetic acid and then treated with CHTAC. In method 2, the sequence was reversed. Method 3 used a mixture of chloroacetate and CHTAC.

The treated fabrics were evaluated for WRA performance, tensile strength, elongation at break, stiffness and whiteness index and were compared to the DMDHEU treated samples.

3 Experimental procedures and designs

The materials, equipment, experimental procedures and designs used in this research are described in this section. Equipment are described and their manufacturers are mentioned, the fabric details are given and chemical specifications with the names of their commercial manufacturers are provided. The application procedures are described and the test procedures are listed with the appropriate references.

3.1 Materials and chemicals

The materials and chemicals used for this research are shown in Table 3.1 along with their descriptions and manufacturers. All of them are commercially available.

Table 3.1 Test materials and chemicals

Name or Group	**Description**	**Manufacturer**
Cotton Fabric	Bleached desized print cloth, style 400, 120g/m^2, 44"/45", 78×76, ISO 105/F02	Testfabrics, Inc.
Cationic agent	3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC), 69% solution	Dow Chemical
Base	Sodium hydroxide, 50% w/w aqueous solution	Fisher Scientific
Acid	Mono chloroacetic acid, 99%	Acros Organics

3.2 Equipment

A Corning stirrer/hot plate was used to make solutions by dissolving solid chemicals in water. Solution pH was measured accurately using a Fisher Scientific Accumet® Model 15 pH meter. The fabrics were padded in the pilot plant of the North Carolina State University,

College of Textiles using the Werner Mathis AG pad. The fabric speed and the pressure of the rolls could be controlled. The fabric samples of 14×19 inch were pinned on oven metal frames and dried and cured in a forced air oven manufactured by Werner Mathis AG.

3.3 Application procedures

In this section, the procedures for the application of chemicals and the details of the experimental methods and designs are provided.

3.3.1 Carboxymethylation

The process for the carboxymethylation of cellulose was developed in previous work.[2, 10, 34] There were three routes for the carboxymethylation treatment namely, pad-batch (PB), pad-dry-cure (PDC) and pad-dry-pad-cure (PDPC). Starting with the baseline procedure, using the previously established parameters and reaction conditions for the preparation of carboxymethyl cellulose (CMC), various variables involved in the treatments were optimized. This involved several single variable trials followed by trials in the Design of Experiments (DOE). The PDPC route was found to be the most efficient and was optimized in greater detail compared to the PB and the PDC routes.

3.3.1.1 Pad-batch route (PB)

The details of the baseline procedure and the single variable trials used to evaluate the effect of various process variables on the carboxymethylation reaction by PB route are mentioned below.

3.3.1.1.1 Baseline procedure

The procedure involved two steps. Step 1: Fabric was soaked in 20% w/w aqueous NaOH for 5 min, padded to approximately 100% wet pick up (wpu) and dried at 45°C under tension in the oven. Step 2: Mono chloroacetic acid was neutralized to pH 7.0 by sodium carbonate. The fabric from step 1 was padded with chloroacetate to 100% wpu and placed in a polyethylene bag. The air was removed from the bag before sealing. It is then held in the oven at 70°C for 1 hour. Then the fabric was removed, washed with cold water, neutralized with 2g/L acetic acid, washed with water and air-dried. This procedure was previously studied by Bilgen.[2]

3.3.1.1.2 Single variable trials

The effects of the substrate form, gaseous media and sodium hydroxide to sodium chloroacetate molar ratios on the carboxymethylation reaction were determined by single variable trials.

3.3.1.1.2.1 Effect of substrate form on carboxymethylation

The first set of experiments was run to determine the effect of substrate form on the reaction extent, which was evaluated by finding the carboxymethyl content. The different substrate forms used were cotton greige sliver, bleached yarn provided by R.L. Stowe Mills and knitted fabric made from the bleached yarn. The experiment was aimed to observe the behavior of these substrates towards the reaction. The concentration of sodium chloroacetate used was 2M.

3.3.1.1.2.2 Effect of gaseous media on carboxymethylation

A variation in carboxymethyl content was observed in the presence of air inside the bag. This was an important variable that was not previously controlled. Therefore, samples were prepared in carbon dioxide atmosphere and in air using the procedure mentioned in sec. 3.3.1.1.1. 1M sodium chloroacetate solution was used. One sample was placed in a polyethylene bag, air was removed by hand, the bag was sealed and placed in the oven for 1hour at 70°C. The other sample was placed in a vacuum oven. Air was removed using vacuum and carbon dioxide was purged. The temperature was raised to 70°C. The sample was batched for 1 hour. Both the samples were removed, washed with water twice, neutralized with 2g/L acetic acid, washed again with water and air-dried.

3.3.1.1.2.3 Effect of mole ratio of NaOH to sodium chloroacetate used on carboxymethylation

The effect of the mole ratio of NaOH used in the first step of treatment to the concentration of sodium chloroacetate used in the second step on the carboxymethyl content was evaluated by samples in Series 1. The mole ratios of NaOH to chloroacetate used were 6:1, 3:1 and 1:1. The procedure was same as mentioned in sec. 3.3.1.1.1.Table 3.2 below depicts the identifications of the samples

Table 3.2 Effect of mole ratio of NaOH to CAA on carboxyl content.

Sample name	NaOH/CAA mole ratio
1A	6:1
1B	3:1
1C	1:1
Untreated fabric (blank)	Water

3.3.1.2 Pad-dry-cure route (PDC)

In this section, the details of the baseline procedure and the single variable trials used to evaluate the effect of various process variables on the carboxymethylation reaction using PDC route are provided.

3.3.1.2.1 Baseline procedure

This is a one step method for the carboxymethylation of cellulose. In this method, mono chloroacetic acid was neutralized with sodium carbonate and 500ml of the neutralized solution was mixed with 500 ml aqueous solution of 20% NaOH. Samples were soaked for 60 sec, in this solution, padded to 100% wpu, dried at 35 ^{o}C for 15 min, cured at 115 ^{o}C for 10 min, washed with water, acidified with 2 g/l acetic acid solution, and finally washed with water and air dried. The treatment parameters were obtained from the previous work.[10]

3.3.1.2.2 Single variable trials

Single variable trials were run to study the effect on carboxymethyl content due to the free standing time of the mixed solution before samples were soaked into it, soaking time, drying, and prior neutralization of mono chloroacetic acid with a weak/strong base.

3.3.1.2.2.1 Effect of free standing time of the mixed solution before soaking samples on carboxymethylation

Series 2 evaluated the effect of free standing time of the mixed solution of 20% NaOH and 1M sodium chloroacetate before the samples were soaked into it. Table 3.3 shows the sample names and the associated delay time to soaking after the mixed solution was prepared. The samples were soaked for 1min. The rest of the procedure remains the same as in sec 3.3.1.2.1.

Table 3.3 Effect of delay time to soaking after mixed solution was prepared on carboxymethyl content

Sample name	Delay Time to soaking (min)
2A	0
2B	8
2C	15
2D	30
2E	60
2F	120
2G	240

3.3.1.2.2.2 Effect of soak time of samples in mixed solution on carboxymethylation

The effect on carboxymethyl content of the samples due to soaking time was evaluated by samples in Series 3. Mixed solutions had NaOH concentration of 20% and sodium chloroacetate of 1M. Samples were soaked for varying times of 0, 8, 15, 30, 60, 120 and 240 min. They were padded to 100% wpu, dried at 35℃ for 15 min, cured at 115℃ for 10min, washed with water twice neutralized with 2g/L acetic acid, washed with water and air dried. Table 3.4 gives the sample identifications.

Table 3.4 Effect of soaking time on carboxymethylation

Sample name	Soaking Time (min)
3A	0
3B	2
3C	4
3D	8
3E	16

3.3.1.2.2.3 Effect of soaking and intermediate drying on carboxymethylation

Following Series 3, Series 4 was designed to see if the soaking and intermediate drying steps have any effect on the reaction extent. The mixed solution had concentration of 20% NaOH and 1M sodium chloroacetate. Table 3.5 below shows the conditions for the treatment.

Table 3.5 Effect of soaking and intermediate drying steps on carboxymethylation

Sample name	Soak (10 min)	Dry (15 min, 35°C)
4A	No	Yes
4B	Yes	No
4C	Yes	Yes
4D	No	No

3.3.1.2.2.4 Effect of neutralization of mono chloroacetic acid with/without a weak base on carboxymethylation

Series 5 was designed to see if the same extent of reaction could be achieved without prior neutralization of mono chloroacetic acid with a weak base before mixing it with aqueous NaOH. The experiment focused on observing three important issues:

1. Whether neutralization reaction of mono chloroacetic acid with a strong base will result in the rise in temperature of the mixture,
2. Will that affect the reaction extent and
3. Compare reaction extent with/ without prior neutralization of acid.

Table 3.6 shows the sample identifications and conditions. The concentrations shown for NaOH and ammonium chloroacetate are the concentrations in the mixed solutions after the neutralization of the acid was complete. For samples 5A, 5C and 5E acid was neutralized by ammonium carbonate prior to mixing. In samples 5B, 5D, and 5F the acid was neutralized in situ by NaOH after mixing. For these samples, extra NaOH was added while mixing the

solutions to compensate for the neutralization reaction. In all the cases, NaOH solution was diluted before mixing and cooled to room temperature to nullify the temperature rise due to dilution of NaOH. The temperatures of the solutions were noted before and after mixing. The samples were padded to 100% wpu without soaking and cured at 115°C for 10min. They were then removed, washed with water twice, neutralized with 2g/l acetic acid, washed with water again and air-dried.

Table 3.6 Effect of prior neutralization of mono chloroacetic acid on carboxymethylation

Sample Name	NaOH concentration (%)	Ammonium chloroacetate concentration (M)	Temperature rise after mixing
5A	10	0.4	Allowed
5B	10	0.4	Allowed
5C	20	2	Allowed
5D	20	2	Allowed
5E	20	2	Allowed
5F	20	2	Not allowed (cooled by ice)

3.3.1.3 Pad-dry-pad-cure (PDPC)

The details of the baseline procedure, the single variable trials and the design of experiments used to evaluate the effect of various process variables on the carboxymethylation reaction using PDPC route are provided in this section.

3.3.1.3.1 Baseline procedure

This is a two-step method. In step 1, fabric samples were soaked in 20% NaOH for 10 min, padded to 100% wpu and dried at 45 °C for 12 min. The sample looked yellow and was completely dry. In step 2, mono chloroacetic acid was neutralized by the weak base sodium carbonate. The samples from step 1 were soaked in the aqueous sodium chloroacetate solution of the specified concentration for 5 min, padded to 100% WPU, cured at 85 °C for

30 min, washed with water, acidified with 2 g/L acetic acid, washed with water and dried in air.

This baseline procedure was modified based on the single variable trials, and the design of experiment was run to predict a model for carboxymethyl content.

3.3.1.3.2 Single variable trials

Single variable trials were run to evaluate the effect of neutralizing agent of mono chloroacetic acid, the soaking time in chloroacetate solution, concentrations of sodium hydroxide and chloroacetate and curing time on the carboxymethylation reaction.

3.3.1.3.2.1 Effect of neutralizing agent of mono chloroacetic acid on the carboxymethyl content

Series 6 evaluated the effect of neutralizing agent of mono chloroacetic acid on the carboxymethyl content. It also compared the use of strong base against the weak base for neutralization reaction. The neutralizing agents used were sodium carbonate, ammonium carbonate and ammonium hydroxide. Table 3.7 gives the specifications of the experiment. For all the samples, 2M mono chloroacetic acid was used. The samples were first padded with 20% NaOH and dried for 12 min at 45°C. Mono chloroacetic acid was neutralized by the respective neutralizing agent. The samples were then soaked for few seconds without stirring in the chloroacetate solution and padded to 100% wpu. They were then cured at 85 °C for 30 min in the oven. After curing, two water washes were given followed by neutralization with 2g/L acetic acid and water washes. The samples were then air-dried. Based on the observations (section 4.1.3.1), ammonium carbonate was selected as a neutralizing agent for all experiments henceforth unless specified.

Table 3.7 Effect of neutralizing agent on carboxymethyl content

Sample name	Neutralizing agent
6A	No neutralizing agent
6B	Sodium carbonate
6C	Ammonium Carbonate
6D	Ammonium hydroxide

3.3.1.3.2.2 Effect of soaking in ammonium chloroacetate solution on carboxymethylation

It was observed that the extent of carboxymethylation varies depending on soaking or non-soaking in the ammonium chloroacetate solution. To evaluate this effect, Series 7 was run. Sample 7A and 7B were soaked in 20% NaOH for 5 min, padded to 100% wpu, dried at 45°C for 12min. Then sample 7A was soaked in 2M chloroacetate (neutralized by ammonium carbonate) solution for 10 min and then padded to 100% wpu. Sample 7B was padded without soaking. Sample 7C and 7D were padded with 10% NaOH and dried at 45°C for 12min. A mixed solution of ammonium chloroacetate and NaOH with concentration of 2M and 10% respectively was prepared. Samples 7C was soaked in this solution for 10 min and then padded. Sample 7D was padded without soaking. Samples 7A, 7B, 7C and 7D were cured at 85°C for 30min. They were washed with water twice, neutralized with 2g/L acetic acid, water washed and air dried for 24 hours.

Table 3.8 Effect of soaking time on carboxymethyl content

Sample name	% of NaOH in step 1	% of NaOH in step 2 (mixed with ammonium chloroacetate)	Soaking time (min)
7A	20	0	10
7B	20	0	0
7C	10	10	10
7D	10	10	0

3.3.1.3.2.3 Effect of sodium hydroxide concentration used in step 1 on carboxymethyl content

Series 8 was run to estimate the effect of sodium hydroxide concentration used in step 1 on carboxymethyl content. Table 3.9 shows the details. The samples were soaked in NaOH for 5 min, padded to 100% wpu and dried at 45°C. They were then padded with 2M ammonium chloroacetate without soaking and cured at 85°C for 30 min. After curing two water washes were given followed by treatment with 2g/L acetic acid and water washes again. They were then air-dried.

Table 3.9 Effect of NaOH on carboxymethyl content

Sample name	NaOH concentration (%) in step 1
8A	0
8B	5
8C	10
8D	15
8E	20
8F	25

3.3.1.3.2.4 Effect of addition of NaOH in ammonium chloroacetate bath on carboxymethylation

Based on the results of Series 7 and Series 8, Series 9 was run to study if the addition of NaOH in the ammonium chloroacetate bath in step 2 would improve the carboxymethyl content and provide a provision for soaking the samples in chloroacetate. Instead of treating the samples with 20% NaOH in step 1, the concentration of sodium hydroxide was split into two concentrations. The first concentration was the step 1 treatment. The second concentration was added to the ammonium chloroacetate bath in step 2. Total concentration of NaOH to which a sample was subjected remained fixed at 20%. The samples were padded after soaking for 5 min in first concentration of NaOH, dried at 45°C for 12min, soaked in

bath of chloroacetate having second concentration of NaOH for 10min, padded to 100% wpu, cured at 85°C for 30 min, water washed twice, rinsed with 2g/L acetic acid, water washed again and then air dried. Sample details are given in Table 3.10

Table 3.10 Effect of addition of NaOH in step 2 bath on carboxymethyl content

Sample name	Concentration of NaOH in step 1(%)	Concentration of NaOH in step 2 added to ammonium chloroacetate bath (%)
9A	0	20
9B	5	15
9C	10	10
9D	15	5
9E	20	0

3.3.1.3.2.5 Effect of curing time on carboxymethyl content

The effect of curing time on carboxymethyl content was studied in Series 10. The samples were soaked for 5 min in 20% NaOH, padded to 100% wpu and dried at 45°C for 12min. They were then padded without soaking by 2M ammonium chloroacetate, cured at 85°C for specified time, washed twice with water, neutralized with 2g/L acetic acid, water washed and air dried. Table 3.11 shows the sample designation.

Table 3.11 Effect of curing time on carboxymethyl content

Sample name	Curing time (min)
10A	5
10B	10
10C	17
10D	25
10E	30

3.3.1.3.2.6 Effect of concentration of ammonium chloroacetate on carboxymethyl content

Series 11 was carried on to find the effect of concentration of ammonium chloroacetate on the carboxymethyl content. Table 3.12 shows the sample designations. Four samples were prepared for each concentration of ammonium chloroacetate. Samples in a

particular column were prepared on one same day. Different columns were run on different days. Samples were padded with 20% NaOH, dried at 45°C, padded with chloroacetate of given concentration to 100% wpu, cured at 85°C for 5 min, washed with water twice, rinsed with 2 g/L acetic acid, water washed again and air dried.

Table 3.12 Effect of ammonium chloroacetate concentration on carboxymethyl content

Day	**Day 1**	**Day 2**	**Day 3**	**Day 4**
Concentration of Ammonium chloroacetate (M)				
2.0	11A	11E	11I	11M
1.5	11B	11F	11J	11N
1.0	11C	11G	11K	11O
0.5	11D	11H	11L	11P

3.3.1.3.3 Comparison of PDC and PDPC

PDC and PDPC routes were found to be efficient compared to PB route. To select one out of the two, samples were prepared to compare them. Sample 12A was prepared by PDC route. The mixed solution had 20% NaOH and 2M ammonium chloroacetate concentration. The sample was padded without soaking to 100% wpu and cured at 115°C for 15 min in oven. Sample 12B was treated by PDPC route. It was padded to 100% wpu with 20% NaOH after soaking for 5 min, dried at 45°C for 12 min, padded without soaking to 100% wpu with 2M ammonium chloroacetate solution, cured at 85°C for 30 min in the oven. 12A and 12B are both washed with water twice after curing, neutralized with 2g/l acetic acid, water washed again and air-dried.

Table 3.13 Comparison of PDC and PDPC route

Sample name	Route used
12A	PDC
12B	PDPC

3.3.1.3.4 Design of experiment

Based on the observations of the single variable trials described in section 3.3.1.3.2, a design of experiment was set using SAS JMP software to evaluate the variables that determine the extent of carboxymethylation reaction. The design also aimed at providing a model for the carboxymethyl content based on the values for variables used for the treatment. The model is valid only in the range of variable values used in the design. The design is shown in Table 8.1 in the Appendix. Samples were padded with NaOH solution of specified concentration, dried at 45° C for 12 min, padded with ammonium chloroacetate to 100% wpu after soaking, cured at the respective temperature for the respective time. They were then washed with water twice, neutralized with 2g/L acetic acid, water washed again and air-dried.

3.3.2 Cationization of cotton cellulose

The procedure for cationization of cotton cellulose was adopted from previous work.[47] A mixed aqueous solution of CHTAC and NaOH in the molar ratio of 1:2.5 (CHTAC: NaOH) was used for cationizing cellulose. The CHTAC solution was measured and mixed with NaOH solution, and stirred for few seconds. The samples were soaked in this solution for 2 min and padded to 100% wpu. They were then dried at 35°C for 15 min, cured at 120°C for 15 min, washed with water twice, neutralized with 2g/l acetic acid, washed again with water and air dried. Series 14 was prepared to study the effect of the concentration

of CHTAC on the percent nitrogen content or mmol N/100g fabric. Four samples were prepared for each concentration of CHTAC. Samples in a particular row were prepared on one same day. Different rows were run on different days. The procedure used was the same as described above.

Table 3.14 Effect of concentration of CHTAC on the percent nitrogen content or mmol N/100g fabric

Concentration of CHTAC (M)	**0.36M**	**0.55**	**0.71**	**1.1**
Day				
Day 1	14A	14E	14I	14M
Day 2	14B	14F	14J	14N
Day 3	14C	14G	14K	14O
Day 4	14D	14H	14L	14P

3.3.3 Conventional DMDHEU treatment

Control reference samples were prepared for comparison by the conventional DP procedure with DMDHEU. The bath was prepared with 250 g/L of Freerez® 900 Reactant- 44% solids, 62.5 g/L of Freecat® 9 Accelerator- 30% solids, 1 g/L of Renex® 36- 60% solids and 686.5 ml of water. The samples were padded at 80-90% wpu after soaking for few seconds, dried at 105° C for 5 min and cured at 177° C for 2 min.

3.3.4 Ionic cross-linking

The procedures described in this section produced cellulosic fabric with Zwitter ionic cellulose chains, that is, the cellulose simultaneously had both anionic and cationic charges. These opposite charges may be present on the same or different cellulose chains.

3.3.4.1 Carboxymethylation of cellulose followed by cationization (Method 1)

Cellulosic fabric samples of size 14"× 18" were used for this treatment. Table 3.15 depicts the design that was run.

Table 3.15 Experimental design for carboxymethylation followed by cationization

Concentration of CHTAC (M)	**0.36M**	**0.55**	**0.71**	**1.1**	**COO^-**
Ammonium chloroacetate concentration (M)					
2.0	15A	15E	15I	15M	87.01
1.5	15B	15F	15J	15N	67.56
1.0	15C	15G	15K	15O	51.71
0.5	15D	15H	15L	15P	32.13

Treatment involved two steps. Step 1 was carboxymethylation. Samples were first carboxymethylated by the PDPC using four different concentrations of ammonium chloroacetate. They were first soaked in 20% NaOH for 5 min, padded to 100% wpu and dried at 45 ℃ for 12 min. The samples looked yellow and were dry completely. Chloroacetate aqueous solutions of concentrations 2M, 1.5M, 1.0M and 0.5M were prepared by using ammonium carbonate as neutralizing agent. The samples were padded with chloroacetate without soaking to 100% wpu, cured at 85 ℃ for 5 min, washed with water, acidified with 2 g/L acetic acid, washed with water and dried in air. They were then analyzed for carboxymethyl contents as described in section 3.4.1. The anionic contents (represented

as COO^-) for the samples expressed in mmol/100g were 87.04, 67.56, 51.71 and 32.13 respectively.

Above samples including the untreated fabric were then subjected to step 2: cationization with CHTAC, using mole ratio of NaOH to CHTAC of 2.5:1 in all the cases. Four different concentrations of CHTAC were used: 0.36M, 0.55M, 0.71M and 1.1M. For each CHTAC concentration, sodium hydroxide and CHTAC were taken in glass beakers in required amounts and diluted. Ice was used to ensure that their temperatures did not rise during dilution. The solutions were then mixed together and the volume was made up to the required mark by adding water and stirring for few minutes. The samples from step 1 were soaked into this solution for few seconds, padded to 100% wpu, dried at 35°C for 15 min, cured at 120°C for 15 min, washed with water twice, neutralized with 2g/l acetic acid, washed again with water and air dried.

3.3.4.2 Cationization of cellulose followed by carboxymethylation (Method 2)

Cellulosic fabric samples of size 14"× 18" were used for this treatment. Table 3.16 shows the Series 16 samples that were prepared.

Table 3.16 Experimental design for cationization followed by carboxymethylation

Concentration of CHTAC (M)	**0.36M**	**0.55**	**0.71**	**1.1**
Ammonium chloroacetate concentration (M)				
2.0	16A	16E	16I	16M
1.5	16B	16F	16J	16N
1.0	16C	16G	16K	16O
0.5	16D	16H	16L	16P
mmol N/100g	15	20.89	36.88	55.43

Treatment involved two steps. Step 1 is cationization with CHTAC. Four different concentrations of CHTAC were used: 0.36M, 0.55M, 0.71M and 1.1M. The molar ratio of NaOH to CHTAC of 2.5:1 was used in all the cases. For each CHTAC concentration, sodium hydroxide and CHTAC were taken in glass beakers in required amounts and diluted. Ice was used to ensure that their temperatures did not rise during dilution. The solutions were then mixed together and volume was made up to the required mark by adding water and stirring for few minutes. Samples were soaked into this solution for few seconds, padded to 100% wpu, dried at 35°C for 15 min, cured at 120°C for 15 min, washed with water twice, neutralized with 2g/l acetic acid, washed again with water and air dried. These samples were then analyzed for nitrogen content (section 3.4.3). The values in mmol N/100g were 15, 20.89, 36.88 and 55.43.

The above samples including the untreated fabric were then subjected to step 2: carboxymethylation with ammonium chloroacetate. Samples were carboxymethylated by the PDPC procedure. They were soaked in 20% NaOH for 5 min, padded to 100% wpu and dried at 45 °C for 12 min. They looked yellow and were dry completely. Mono chloroacetic acid of a particular concentration was neutralized by a weak base, ammonium carbonate. The samples from step 1 were padded with chloroacetate to 100% wpu without soaking, cured at 85 °C for 5 min, washed with water, acidified with 2 g/L acetic acid, washed with water and dried in air.

3.3.4.3 Method of mixture for ionic cross-linking (Method 3)

'Method of mixture' was also attempted to provide a Zwitter ionic cellulosic fabric for ionic cross-linking in one single step. Table 8.2 in the Appendix shows the details of the

samples that were prepared to find out the combination of the variables that would give the best wrinkle recovery performance.

Samples were soaked in 20% NaOH for 5 min, padded to 100% wpu and dried at 45 °C for 12 min. They looked yellow and were dry completely. Mono chloroacetic acid of a particular concentration was neutralized by a weak base, ammonium carbonate. CHTAC and NaOH were measured in required amounts and diluted. NaOH to CHTAC ratio was maintained at 2.5:1. Ammonium chloroacetate, diluted NaOH and diluted CHTAC were then mixed together. The temperature of the solution was kept at the ambient conditions by using ice during dilution of chemicals or during their mixing. The solution was made up to the required mark by adding water. Samples treated with NaOH were then padded through this mixture to 100% wpu without soaking, dried at 35°C for 15 min, and then cured at the specific temperature. They were washed with water, acidified with 2 g/L acetic acid, washed with water again and then dried in air.

3.4 Analysis methods

The test methods and analytical techniques used for the characterization of samples prepared in this work are described below with proper references.

3.4.1 Carboxymethyl content

The anionic content of the carboxymethylated samples was quantitatively determined by acid base titration and is reported in the units of mmol/100 g fabric. The method was adopted from previous work.[34]

Small pieces (2.5cm × 2.5cm) were cut from different parts of the treated sample. These pieces were further cut into small pieces (3mm × 3mm). They were then soaked in

0.5% hydrochloric acid overnight. The sample pieces were then filtered off, washed several times with deionized water until the washed water showed no presence of chloride by the silver nitrate drop test. The sample was then dried at 105°C for 3 hours. It was then weighed accurately to 0.25 g and soaked overnight at room temperature in 25 ml of 0.05N NaOH. The blank was kept without any fabric sample in it. The next day, the blank was first titrated with 0.05N aqueous HCl using phenolphthalein indicator. At the endpoint the volume of HCl spent was recorded as V_{blank}. The procedure was repeated for the soaked sample and reading was noted as V_{sample}. The carboxymethyl content was determined using the equation:

$$mmol\ of\ carboxymethyl\ content/100g = 100 \times (V_{blank} - V_{Sample}) \times N_{HCl} \div 0.25$$

Where, N_{HCl} = 0.05N, the normality of the titrant HCl solution.

An example of the sample data (Table 3.17) obtained and sample calculations performed is shown below:

Table 3.17 Sample data for determination of carboxymethyl content

Sample	**Sample Weight (g)**	**V_{blank} (ml)**	**V_{sample} (ml)**	**Carboxymethyl content (mmol/100g)**
Blank	-	19.0	-	-
A	0.250	-	16.0	60

Sample calculation:

$$mmol\ of\ carboxymethyl\ content/100g = 100 \times (19.0 - 16.0) \times 0.05 \div 0.25 = 60$$

In the result and discussion section (section 4.0), samples characterized for the carboxymethyl contents are mentioned by their respective designations and corresponding carboxymethyl contents (as seen in column 5 of Table 3.17) are provided.

3.4.2 Confocal microscopy

Confocal microscopy is a non-destructive technique for examination of the cross-sections and surfaces of the fibers. It uses a fluorescent cationic dye, which absorbs energy at one wavelength and emits it at a longer wavelength producing fluorescence in the visible region. It was used in this research to find qualitatively whether the carboxymethylation reaction occurs all across the fiber diameter or only on its surface. Samples from PB, PDC and PDPC methods were evaluated using this technique. The micrographs also showed the change in fiber cross-section geometry compared to the untreated controls. The PB and PDPC samples were made using 20% NaOH and 2M ammonium chloroacetate, whereas PDC sample was made with the mixture having 10% NaOH and 1M ammonium chloroacetate. The sample preparation and settings used for taking micrographs are described below.

A buffer was prepared by adjusting the pH of 0.2M NH_4Cl to 9.3 using ammonia. This solution was used to prepare 0.1% solution of a fluorescent basic dye, Sevron® Brill Red 4G 200%. The samples were stained with this dye in beakers using 40:1 liquor-to-goods ratio and 50°C temperature for 16 hours with continuous agitation in a mechanical shaker at 150 strokes/min. They were then given a initial rinse in the buffer solution to remove the excess surface dye layer, given two 20-min rinses in buffer solution with liquor: goods ratio of 150:1 at room temperature with vigorous shaking (150 strokes/min) and then dried in air.[48] The dried samples were then scanned using the following settings.

Laser: Argon laser (Blue; 488 and 514 nm)

Microscope filter set: FITC LP (Block I3) Excitation 470/40 Dichroic 510, Emission 515LP

Longitudinal and radial cross-sections were taken. Three-dimensional pictures were also created from the longitudinal sections to look at the fiber geometry.

3.4.3 Nitrogen Content

Nitrogen content analysis for the samples was done using the Perkin- Elmer PE 2400 CHN Elemental Analyzer in the Soil Science Department. The machine was calibrated using Soybean leaves. Samples were analyzed after the confirmation of the error free functioning of the machine using internal standards of NBS 1572- citrus leaves and NBS 1564-Wheat flour.

3.4.4 Scanning electron microscopy

Scanning electron microscopy was performed on untreated, sodium hydroxide treated, carboxymethylated only, cationized only, Series 15 and Series 16 samples. A Hitachi S3200N SEM was used. Micrographs were taken in the vacuum mode (charge reduction mode) without gold sputtering and in high vacuum mode with gold sputtering, at 20kV and 4000X magnification. The images in the high vacuum mode were from secondary electrons, whereas those from vacuum mode were from back scattered electrons. Micrographs were used to study the changes in the fiber cross-sectional geometry. They served as an aid to the results obtained by confocal microscopy.

3.4.5 Wet and dry wrinkle recovery angles

The WRA were measured as per the AATCC Standard Test Method 66-1998 option 2 Wrinkle Recovery of Woven Fabrics: Recovery Angle Method[49]. The angles recorded were the added totals of respective warp and weft averages.

3.4.6 Basis weight and bending rigidity

Basis weights of the treated samples were determined for the ASTM D 1388-96 Standard Test Method for Stiffness of Fabrics.[50] The test requires the basis weight to determine the bending rigidity. Four specimens of 1 inch by 8 inch were weighed and basis weight of the sample was calculated. Two samples in the warp direction and two in the weft direction were used for this purpose.

ASTM D 1388-96 Standard Test was used to determine the bending rigidity. Option A: Cantilever Bending Test was used. Drape- Flex stiffness Tester from Fabric Development Tests was used. Two specimens were tested for each treated fabric in the warp direction and the average bending rigidity was recorded.

3.4.7 Tensile strength

Tensile strength of the samples was determined by the ASTM Test Method D5035.[51] A Q-Test 1/5 tensile tester was used. Two specimens for each treated fabric were tested in the warp direction and the average breaking load (Lb) was recorded.

3.4.8 Whiteness index

The whiteness index of the samples was determined by AATCC test method 110-2000[52] using Spectraflush SF600X a double beam spectrophotometer, manufactured by DataColor. CIE standard illuminant D_{65} and 1964 10° observer were used. Four measurements were made for each sample and the average was calculated.

4 Results and discussion

In this section the results for the experiments described in section 3 are presented in several experimental series. Samples in Series 1 to Series 11 and Series 13 were prepared to evaluate the effect of various process parameters of carboxymethylation treatment on carboxymethyl content. The objective was to reduce the inconsistencies in the results of carboxymethylation treatment, which were seen in previous research, by determining the key parameters that affect the carboxymethyl content.

Series 12 compared PDC route to PDPC route, whereas Series 14 was run to study the effect of CHTAC concentration on nitrogen content of the samples. Series 15 to Series 17 evaluated the ionic cross-linking of the treated cellulosic fabric for wrinkle recovery performance. The approach used in these series was different than the previous studies and was designed to solve the problem of poor durability of the finish.[10] Series 1 to series 13 and Series 15 were analyzed for carboxymethyl contents, whereas Series 14 to Series 17 were analyzed for percent nitrogen contents.

The results of the physical properties such as stiffness, tensile strength, elongation and whiteness index for untreated samples, DMDHEU treated samples, samples in Series 15 Series 16, and Carboxymethylated/cationized only samples are also discussed. WRA for Series 15 to Series 17 are presented. The evaluation of the treatments using confocal microscopy and scanning electron microscopy is explained using figures. Table 4.1 lists all the series and the corresponding purpose/effect studied.

Table 4.1 Series numbers and the corresponding purpose/effect studied

Pad-batch (PB) route for carboxymethylation	
Series 1	Effect of mole ratio of sodium hydroxide to sodium chloroacetate on carboxymethyl content
Pad-dry-cure (PDC) route for carboxymethylation	
Series 2	Effect of delay time to soaking after the mixed solution was prepared on the carboxymethyl content
Series 3	Effect of soaking time on carboxymethylation
Series 4	Effect of soaking and intermediate drying steps on carboxymethylation
Series 5	Effect of prior neutralization of mono chloroacetic acid on carboxymethylation
Pad-dry-pad-cure (PDPC) route for carboxymethylation	
Series 6	Effect of neutralizing agent on carboxymethylation
Series 7	Effect of soaking time in ammonium chloroacetate bath on carboxymethylation
Series 8	Effect of sodium hydroxide concentration used in step 1 on carboxymethylation
Series 9	Effect of addition of sodium hydroxide in ammonium chloroacetate bath in step 2 on carboxymethylation
Series 10	Effect of curing time on carboxymethylation
Series 11	Effect of ammonium chloroacetate concentration on carboxymethylation
Series 12	Comparison of PDC and PDPC route
Series 13	Design of experiment to determine the functional relationship between carboxymethyl content and various process parameters
Cationization of cotton cellulose with CHTAC	
Series 14	Effect of concentration of CHTAC on percent nitrogen content or mmol N/100g fabric
Ionic cross-linking	
Series 15	Experimental design for ionic cross-linking by cationization following carboxymethylation
Series 16	Experimental design for ionic cross-linking by carboxymethylation following cationization
Series 17	Experimental design for ionic cross-linking by ‘Method of mixture’

4.1 Carboxymethyl content

Series 1 to Series 13 studied the process parameters involved in different routes of carboxymethylation treatment. The PDPC route was studied in detail starting with single variable trials (Series 6 to Series 11) and following them with a design of experiment (Series

13). The samples in Series 1 to Series 13 were analyzed for the anionic content using the procedure described in section 3.4.1. The data was obtained as shown in column 1 to column 4 in Table 3.17. Values in column 5 were determined using the calculation steps shown in section 3.4.1. The data tables for carboxymethyl content presented in this section (section 4.1) have columns that resemble column 1 and column 5 of Table 3.17. The data as shown in columns 2 to 4 in Table 3.17 is not presented.

4.1.1 Pad-batch route

The results and discussion for the single variable trials performed to study the effect of various process parameters on carboxymethyl content described in section 3.3.1.1 are provided under appropriate headers in this section.

4.1.1.1 Effect of substrate form on carboxymethylation

Samples prepared to determine the effect of substrate form on the carboxymethylation reaction extent were analyzed for carboxymethyl content. It was observed that although the sliver had a much more open structure than the yarn and knitted fabric, it reacted to a lesser extent (Table 4.2). This may be due to the difficulty in wetting the greige fibers completely.

Table 4.2 Effect of substrate form on carboxymethylation

Substrate	**Carboxymethyl content (mmol/100g)**
Cotton greige sliver	27.5
Bleached Yarn	36.1
Knitted Fabric	35.2

4.1.1.2 Effect of gaseous media on carboxymethylation

The results for experiments performed to determine the effect of various gaseous media on the reaction extent are shown in Table 4.3.

Table 4.3 Effect of gaseous atmospheres on carboxymethylation

Atmosphere	Carboxymethyl content (mmol/100g)
Air	29.64
Carbon dioxide	19.64

It was found that the extent of reaction decreased almost by 33% in carbon dioxide atmosphere. This is thought to be due to neutralization of sodium hydroxide by the gas during the batching process resulting in insufficient alkali for the carboxymethylation reaction. This experiment established the fact that in the PB route (perhaps in other routes as well) the presence of alkali is an important parameter for achieving higher carboxymethyl content.

4.1.1.3 Effect of mole ratio of NaOH to sodium chloroacetate used on carboxymethylation

The effect of mole ratio of NaOH to sodium chloroacetate used on the carboxymethyl content (anionic content) was demonstrated by samples in Series 1. Table 8.3 in the Appendix and Figure 4.1 depict the results. It can be seen that as the mole ratio increased the anionic content increased suggesting that presence of NaOH in optimum amounts is necessary to make the reaction efficient.

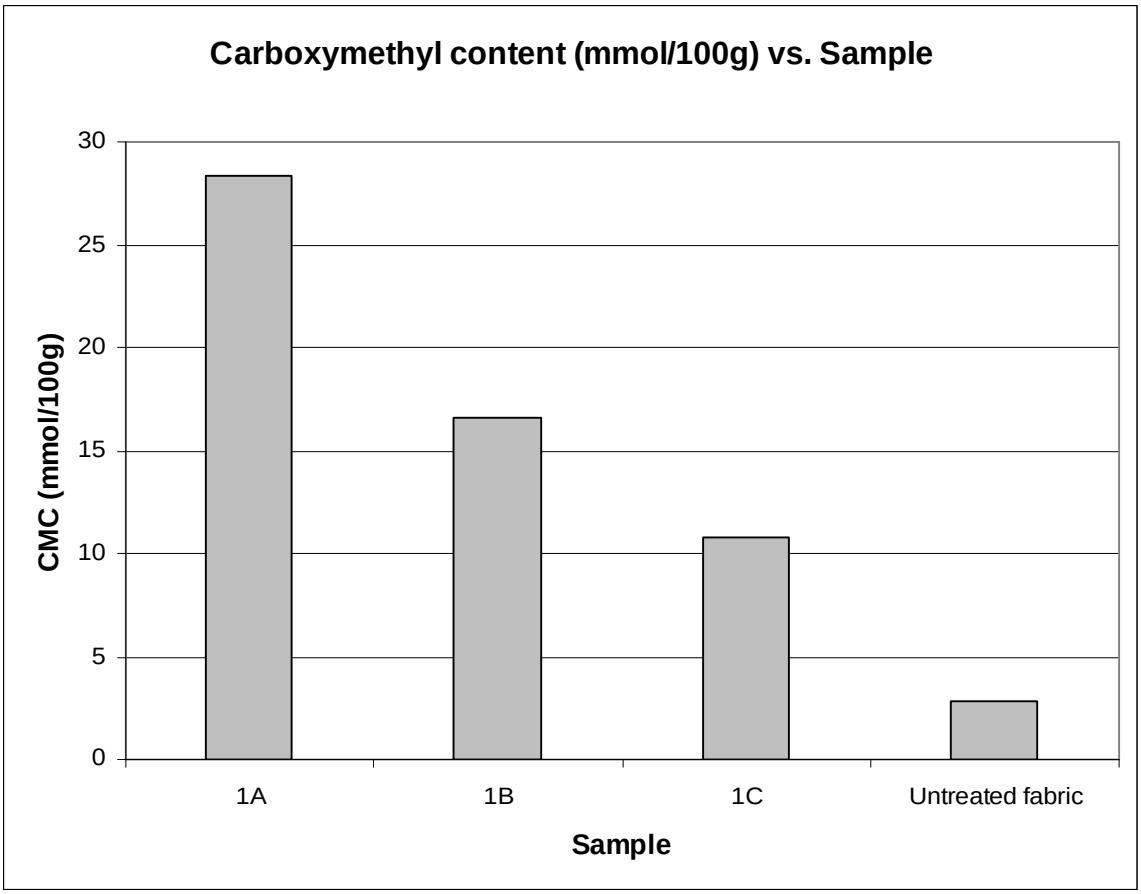


Figure 4.1 Effect of mole ratio of NaOH to ammonium chloroacetate on carboxymethyl content. Sample name-NaOH(M): chloroacetate(M) are 1A-6:1, 1B-3:1 and 1C- 1:1.

4.1.2 Pad-dry-cure route

The results and discussion for the single variable trials for studying the effect of various process parameters on carboxymethyl content described in section 3.3.1.2 are provided in this section.

4.1.2.1 Effect of free standing time of the mixed solution before soaking samples on carboxymethylation

Series 2 studied the effect of free standing time of the mixed solution of NaOH and sodium chloroacetate on the carboxymethyl content.

Table 8.4 in the Appendix shows the results. Figure 4.2 is a plot of carboxymethyl content vs. the delay time to soaking. As the delay time to soaking was increased the anionic content of the samples decreased. This implied that the bath was unstable. This may be due to the hydrolysis of C-Cl bond in sodium chloroacetate in the presence of a strong alkali, NaOH.

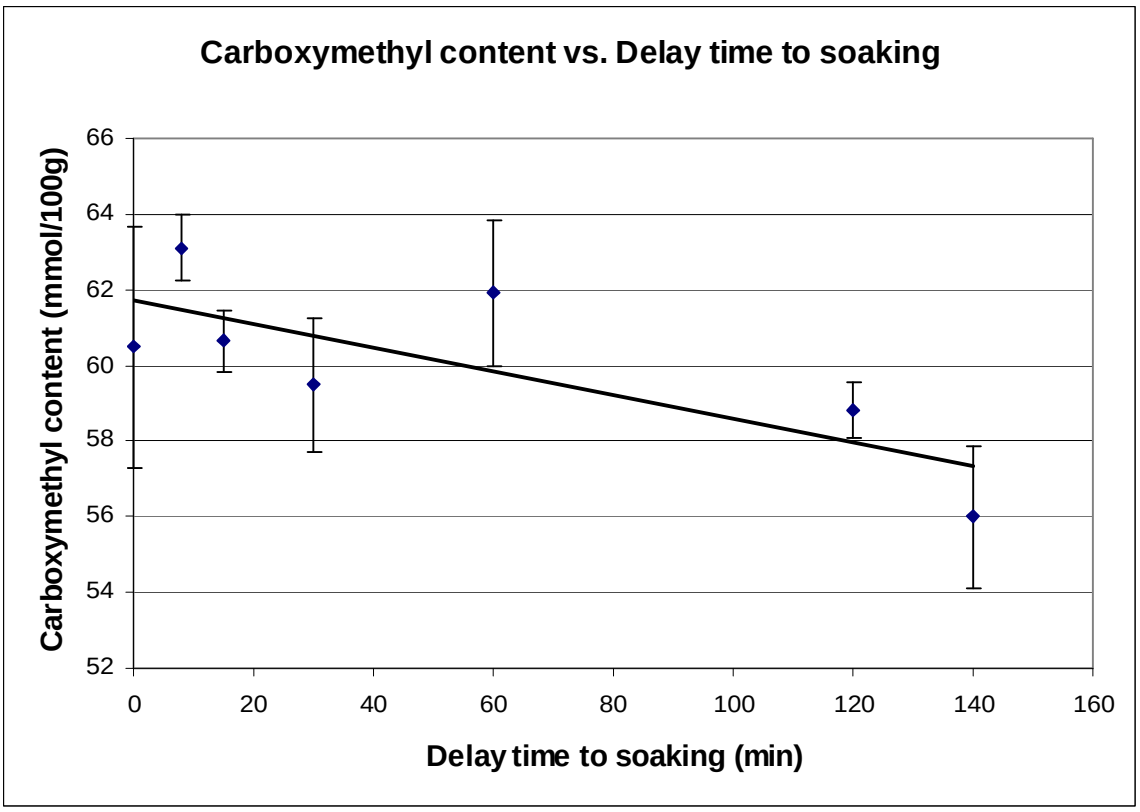


Figure 4.2 Effect of delay time to soaking on carboxymethyl content

4.1.2.2 Effect of soak time of samples in mixed solution on carboxymethylation

The effect of soaking time in the mixed solution on the anionic content of the fabric (Table 8.5 in the Appendix) was studied by Series 3. In the time limits employed, no significant difference in carboxymethyl content was seen.

4.1.2.3 Effect of soaking and intermediate drying on carboxymethylation

Series 4 was run to determine if soaking in the mixed solution and intermediate drying after padding had any effect on carboxymethyl content. Table 4.4 shows the results. From the table it can be seen that sample 4D which was not soaked in the mixed solution and was not dried intermediately had the best results. Thus, soaking in the mixed solution and then intermediate drying after padding was not beneficial, and these steps could be eliminated.

Table 4.4 Effect of soaking and intermediate drying on carboxymethyl content

Sample name	Soak (10 min)	Dry (15 min, 35°C)	Carboxymethyl content (mmol/100g)
4A	No	Yes	62.50
4B	Yes	No	68.81
4C	Yes	Yes	61.31
4D	No	No	70.1

4.1.2.4 Effect of neutralization of mono chloroacetic acid with/without a weak base on carboxymethylation

Series 5 studied the effect of prior neutralization of mono chloroacetic acid before mixing it with NaOH on carboxymethyl content. The main objective of the experiment was to determine if the prior neutralization step of mono chloroacetic acid with a weak base could be replaced by its in situ neutralization by sodium hydroxide in the mixture. The results are shown in Table 4.5. Three main aspects were studied:

1) Whether neutralization reaction with a strong base will result in rise in temperature
2) Will that affect the reaction extent and
3) Compare reaction extent with/without prior neutralization of acid

Sample 5A and 5B studied if the neutralization reaction was the cause for rise in temperature. The effect of temperature rise due to dilution of NaOH was eliminated largely

by using low concentration of NaOH and its prior dilution before mixing using ice to maintain the temperature near ambient conditions. The temperature did not rise for sample 5A, but 5B showed an increase of about 6°C upon mixing. Thus, this rise in temperature was due to neutralization reaction.

Furthermore, to confirm this, the experiment was repeated for samples 5C and 5D using increased concentrations of NaOH and ammonium chloroacetate. Sample 5C that had prior-neutralized mono chloroacetic acid showed no temperature change on mixing. Sample 5D having un-neutralized acid showed a temperature rise of about 17°C. Thus, the rise in temperature increased with the concentration of both the chemicals. This was due to more neutralization reaction taking place between NaOH and the acid. This observation confirmed that neutralization reaction with a strong base was the cause for temperature rise of the mixture.

To determine if the temperature rise affected the carboxymethylation reaction, samples 5C and 5D were analyzed for carboxymethyl content. Sample 5C showed higher carboxymethyl content than 5D, which implied that the temperature rise due to the neutralization reaction is facilitating some other undesired side reaction that probably hydrolyzes C-Cl bond in mono chloroacetic acid and thereby reduces the desired reaction. This side reaction could be between the strong base (NaOH) and C-Cl bond of the acid. The observation also implied that reaction is efficient when neutralization of the acid is carried before mixing that would prevent temperature rise. Thus, temperature rise due to neutralization reaction and the use of strong base were thought to be responsible for reduced reaction with cellulose.

In order to determine the contributions of temperature rise and use of strong base in reducing the carboxymethylation reaction, samples 5E and 5F were run with the same concentration as 5C and 5D with the only difference that during mixing the temperature was not allowed to rise for 5F due to neutralization reaction, which eventually reduced the effect on carboxymethylation due to rise in temperature. Temperature for 5E did not show any significant rise on mixing. Carboxymethyl content of 5F was marginally more than 5D, but less than 5C or 5E. . The side reaction was slightly reduced, but not completely eliminated for 5F suggesting that the unwanted side reaction was mainly due to the use of strong base for neutralization and partly due to rise in temperature. Thus, prior neutralization of mono chloroacetic acid with a weaker base than the stronger one would produce much higher carboxymethyl content.

Table 4.5 Effect of prior neutralization of mono chloroacetic acid on carboxymethylation

Sample Name	**NaOH concentration (%)**	**Ammonium chloroacetate concentration (M)**	**Temperature rise after mixing**	**Temperature rise before mixing (°C)/ after mixing (°C)**	**Carboxyme-thyl content (mmol/100g)**
5A	10	0.4	Allowed	28/28	-
5B	10	0.4	Allowed	28/34	-
5C	20	2	Allowed	28/28	85.09
5D	20	2	Allowed	28/45	55.04
5E	20	2	Allowed	28/28	84.39
5F	20	2	Not allowed (cooled by ice)	28/28	61.92

4.1.3 Pad-dry-pad-cure route

The results and discussion for the single variable trials and the design of experiment performed for determining the effects of various process parameters on carboxymethyl content described in section 3.3.1.3 are provided in this section. The results for the comparison between PDC and PDPC are also discussed.

4.1.3.1 Effect of neutralizing agent of mono chloroacetic acid on carboxymethyl content

The effect of different neutralizing agents of mono chloroacetic acid on carboxymethyl content (Table 4.6) was studied by Series 6. Use of sodium carbonate gave the best carboxymethyl content followed by ammonium carbonate. Use of stronger bases like sodium hydroxide and ammonium hydroxide was not effective. This is thought to be due to hydrolysis reaction of the C-Cl bond of mono chloroacetic acid by a strong base as was described previously in section 4.1.2.4.

Table 4.6 Effect of neutralizing agent on carboxymethyl content

Sample name	Neutralizing agent	Carboxymethyl content (mmol/100g)
6A	No neutralizing agent	9.5
6B	Sodium carbonate	117
6C	Ammonium Carbonate	95
6D	Ammonium hydroxide	11.6

In all the experiments following these results, ammonium carbonate was selected as a neutralizing agent due to the ease of ammonia release (from the cationic NH_4^+ ions) during the curing process facilitating ionic cross-linking in later stages of treatment for improved WRA performance. This was expected to increase the dry WRA in particular due to the formation of ionic bonds in dry state.

4.1.3.2 Effect of soaking in ammonium chloroacetate solution on carboxymethylation

Series 7 evaluated if the carboxymethylation varied with soaking/no soaking in ammonium chloroacetate solution. The results are shown in Table 4.7.

Table 4.7 Effect of soaking time on carboxymethyl content

Sample name	% of NaOH in step 1	% of NaOH in step 2 (mixed with ammonium chloroacetate)	Soaking time (min)	Carboxymethyl content (mmol/100gm)
7A	20	0	10	4.81
7B	20	0	0	98.41
7C	10	10	10	60.12
7D	10	10	0	81.82

Comparison of 7A with 7B showed that soaking of NaOH treated sample in chloroacetate gave poor carboxymethylation. This may be due to the washing off of NaOH during soaking leading to its unavailability for the reaction in the curing step. When 7A was compared with 7C, the carboxymethyl content was higher for 7C than 7A implying that the presence of NaOH in step 2 along with chloroacetate reduced the loss of NaOH from NaOH padded samples during soaking and hence facilitated more reaction later on. This reduction in wash off was not good enough to get the comparable results as sample 7B.

Comparing sample 7B with sample 7D we could say that all of NaOH when used in Step 1 would give the best reaction results. The splitting of NaOH concentration in two steps does not give comparable results as 7B. This may be attributed to more opening of cellulose when it was treated with all of NaOH concentration (20%) in step 1, and formation of soda-cellulose required for the carboxymethylation reaction. A more detailed experiment was performed with Series 9 to confirm if splitting of NaOH in two steps would work efficiently.

4.1.3.3 Effect of sodium hydroxide concentration used in step 1 on carboxymethyl content

The effect of NaOH concentration on anionic content was studied by Series 8. Table 8.6 in the Appendix and Figure 4.3 depict the results. Ammonium chloroacetate (2M) solution was used in step 2.

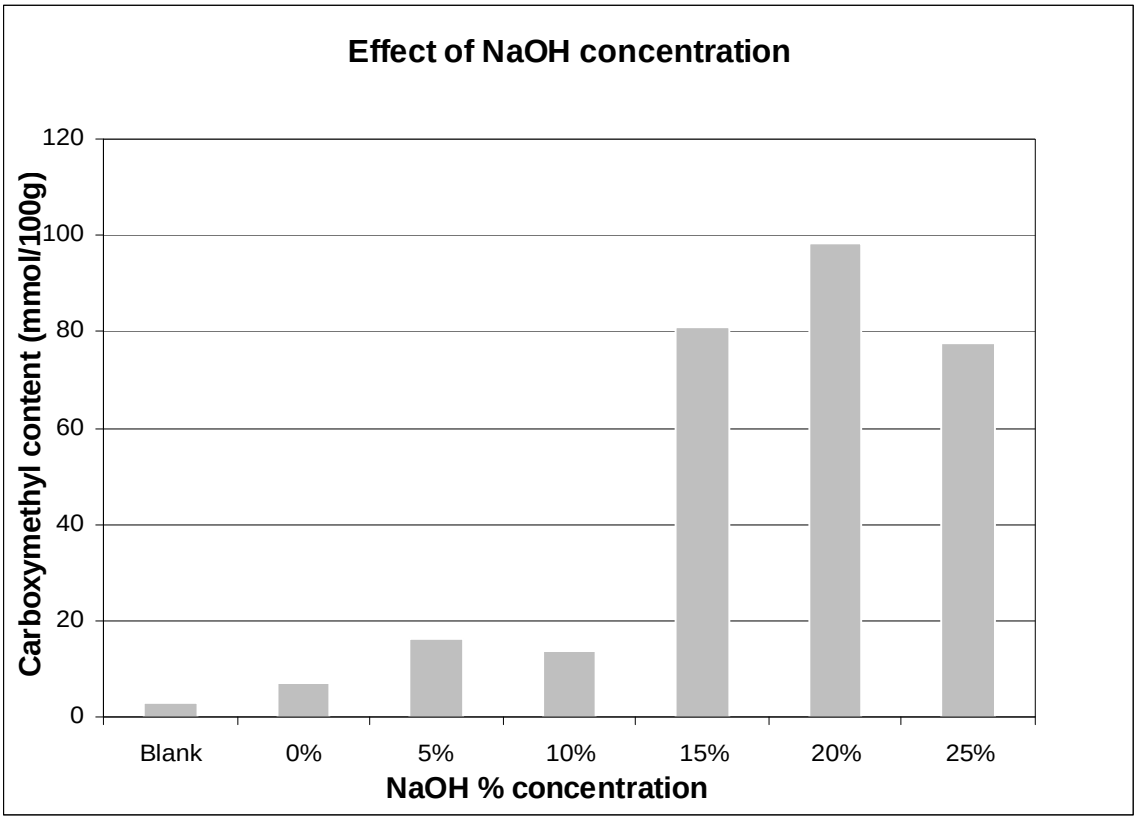


Figure 4.3 Effect of NaOH concentration on carboxymethyl content

No significant increases in the carboxymethyl contents were seen up to 10% concentration of NaOH. It increased significantly for concentrations above 15% and decreased at concentration of 25% after reaching a peak at 20%. Thus, for the best carboxymethyl content, the fabric should be treated with NaOH concentration of 15% - 25%.

4.1.3.4 Effect of addition of NaOH in ammonium chloroacetate bath on carboxymethylation

Series 9 expanded the study in Series 7, by investigating the effect of splitting the 20% NaOH concentration in two steps of treatment, thus providing a provision for soaking in the ammonium chloroacetate solution. This was important from the commercial point of view for soaking would be inevitable in the case of machine failure in continuous fabric processing.

The results for Series 9 samples are shown in Table 8.7 in the Appendix and Figure 4.4. With the splitting of NaOH concentration in two steps, the results comparable to sample 7B (also shown in Table 8.7 for comparison) were not observed. The addition of NaOH in the chloroacetate bath reduced the NaOH wash off during soaking in step 2. This reduction was still not enough to get the anionic content as high as seen for sample 7B. Thus, the efficient path would be to use all of NaOH in step 1 and no soaking in ammonium chloroacetate bath.

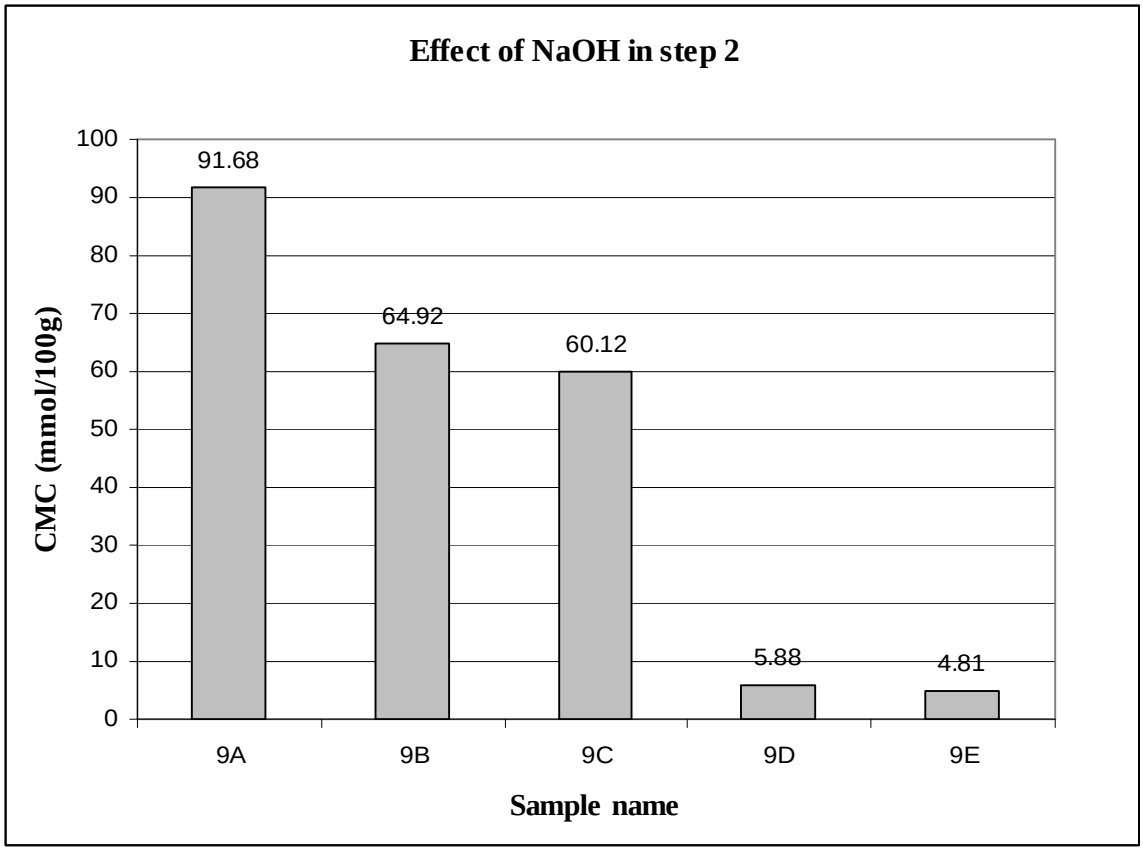


Figure 4.4 Effect of addition of NaOH with ammonium chloroacetate in step 2 on carboxymethyl content. Sample name- NaOH in step 1 (%): NaOH in step 2 (%) are 9A- 0:20, 9B- 5:15, 9C-10:10, 9D- 15:5 and 9E- 20:0

4.1.3.5 Effect of curing time on carboxymethyl content

Series 10 evaluated the effect of curing time. Table 8.8 and Figure 4.5 show the results. The carboxymethyl content increased with the increase in curing time. The increase was steep from 5-10 min., then it slowed down.

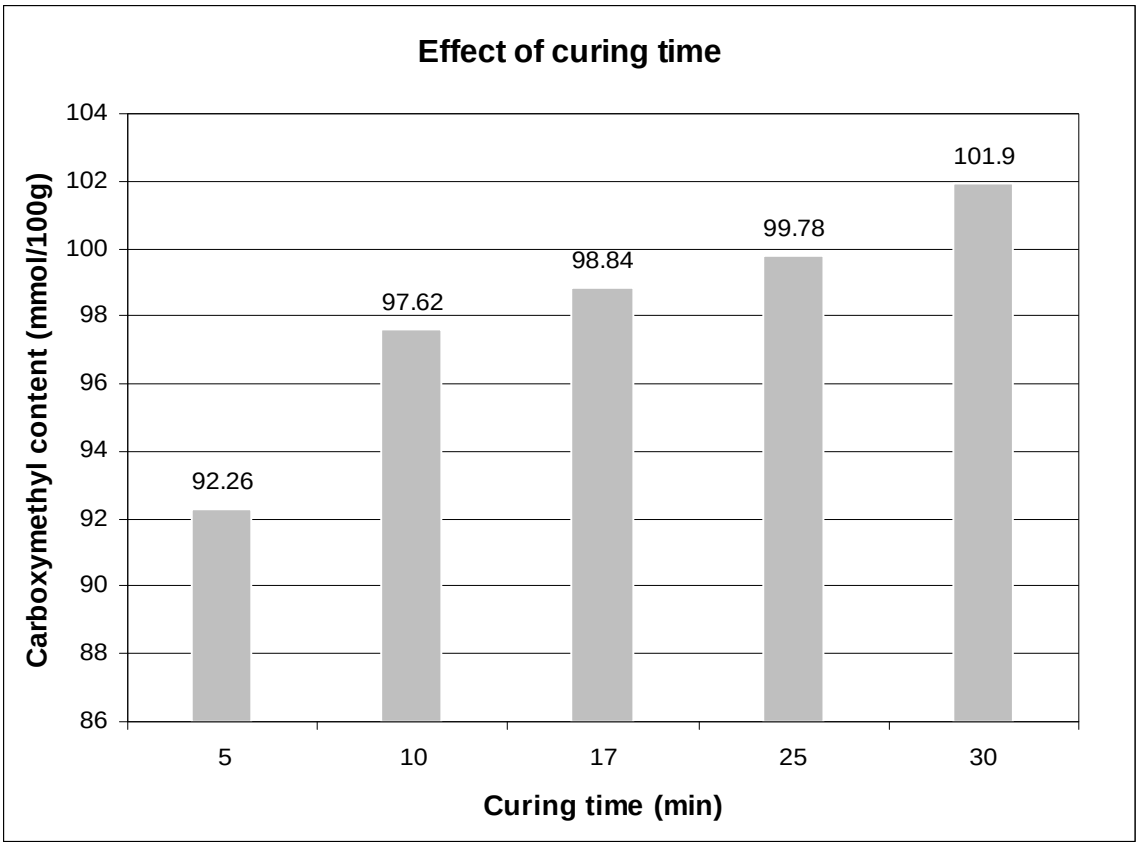


Figure 4.5 Effect of curing time on carboxymethyl content

4.1.3.6 Effect of concentration of ammonium chloroacetate on carboxymethyl content

The change in carboxymethyl content with the concentration of ammonium chloroacetate (Table 8.9 in the Appendix and Figure 4.6) was evaluated by Series 11. As the concentration of chloroacetate increased the carboxymethyl content increased linearly. The coefficient of determination (R^2) of 0.9983 was found. The increase in carboxymethyl content with chloroacetate concentration was due to the increased availability of reactive species near the cellulose molecules for reaction.

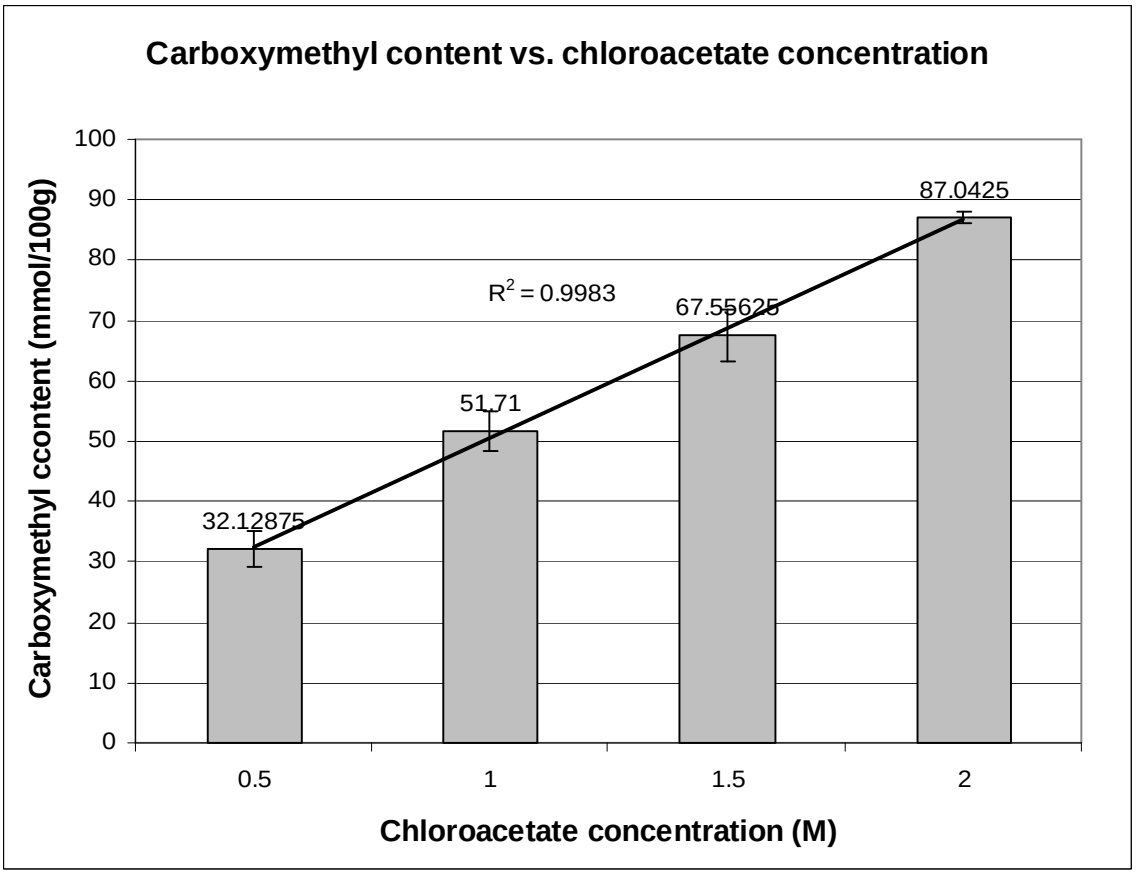


Figure 4.6 Effect of ammonium chloroacetate concentration on carboxymethyl content

4.1.3.7 Comparison of PDC and PDPC

Comparison of the PDC and PDPC routes (Series 12) served to choose one route over the other. The results are shown in Table 4.8. PDPC gave higher carboxymethyl content compared to PDC and hence was chosen for further experiments.

Table 4.8 Comparison of PDC and PDPC route

Sample name	Route used	Carboxymethyl content (mmol/100g)
12A	PDC	85.64
12B	PDPC	102.95

4.1.3.8 Design of experiment

Based on the results of Series 6 to Series 11, a design of experiment was made to evaluate the parameters that determine the extent of carboxymethylation. Series 13 results for this purpose are shown in Table 8.1. This data was fit to a model. The results for initial analysis are shown in Figure 8.1 in the Appendix. Soaking time was an insignificant parameter for the carboxymethyl content. This may be because of the correlation between the soak time and the washing off of the NaOH from the fabric. With soaking NaOH padded on the fabric would wash off. Curing time was also near the insignificant P-value. NaOH concentration, ammonium chloroacetate concentration and curing temperature were the most significant parameters. Knowing this, the data was fit only to the significant parameters. Concentration of NaOH was squared and added to the parameter list. This analysis is shown in Figure 8.2 in the Appendix. NaOH and chloroacetate concentrations, curing temperature, square of NaOH concentration were significant. Curing time was on the edge of insignificance with the P- value (the significance probability) of 0.0787. Hence it was also included in the model. Using these factors and a linear function, a model was generated. A line fit to a graph of the actual vs. predicted values had the R^2 value of 0.80. The parameter estimate was used to get a functional relationship between carboxymethyl content and the independent parameters: concentration of NaOH, concentration of ammonium chloroacetate, curing temperature and time. The equation generated could be used to predict the carboxymethyl content once the parameter values are known.

$$C_{CMC} = 191.49C_1 + 23.28C_2 + 19.47C_3 + 10.97C_4 - 4.63C_1^2 + 272.26$$

Where, C_{CMC}= Carboxymethyl content (mmol/100g), C_1= Concentration of NaOH (M), C_2= Concentration of ammonium chloroacetate (M), C_3= Curing temperature (°C) and C_4= Curing time (min).

4.2 Confocal microscopy

PB, PDC and PDPC samples were qualitatively analyzed by confocal microscopy to detect if the carboxymethylation reaction occurs all across the fiber diameter. The micrographs obtained also showed the geometric change in the fiber cross-sections due to treatments.

Figure 4.7 shows the micrograph for the untreated sample. The fiber cross-section was kidney shaped. The fiber was unevenly dyed across the cross-section, though it did not show any surface dyeing. This dyeing was due to the residual carboxymethyl content naturally present in cellulose fibers.

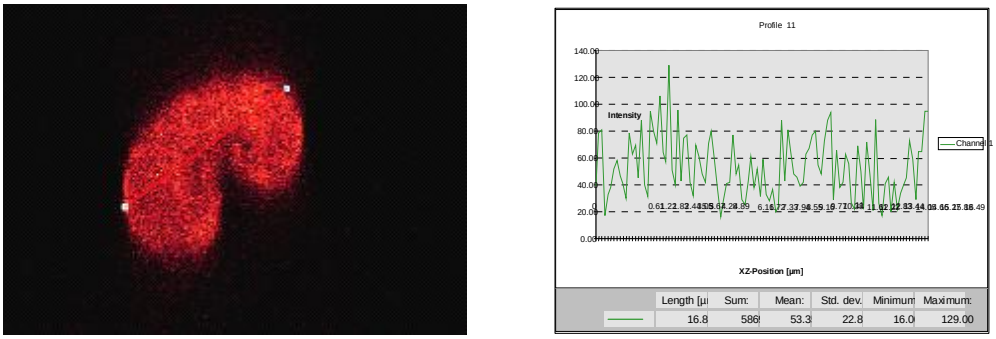
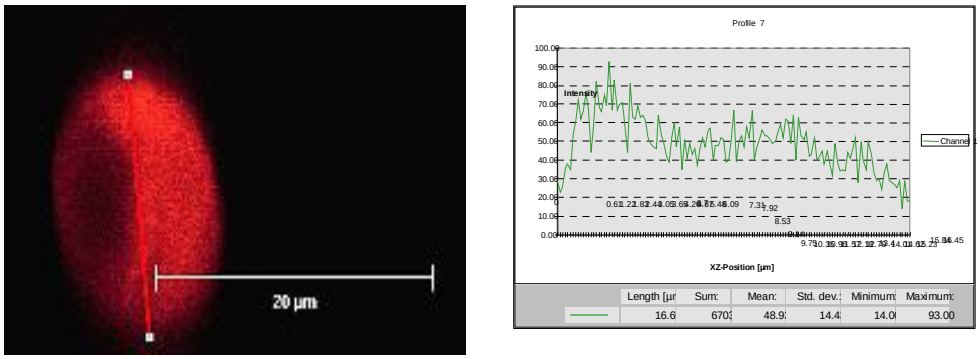


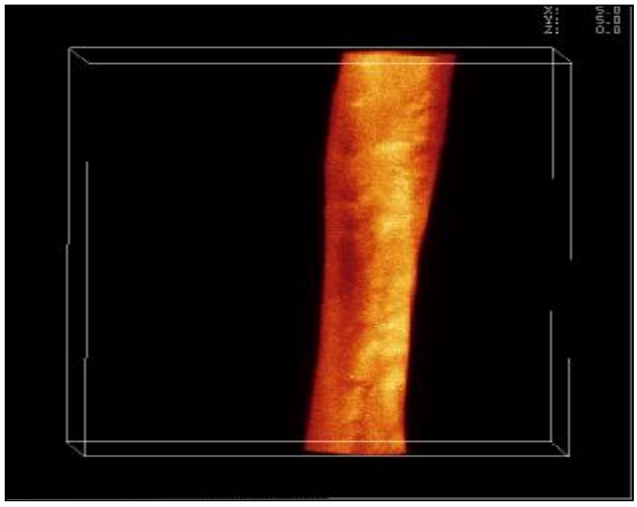
Figure 4.7 Cross-sectional confocal micrograph of the dyed untreated control

Figure 4.8 (a) shows the cross-sectional image for the PB treated sample. The fiber had oval shaped cross-section. The change in geometry must have occurred during the fabric treatment with NaOH in the first step of PB route. Treatment with NaOH at the 20% concentration leads to fiber swelling resulting in loss of convolutions natural to cotton fibers. This is observed for mercerized fibers where concentrations of NaOH used are similar to the

concentration used in our treatment, that is, 20%. Also, the fiber looked more evenly dyed compared to the untreated control implying that the reaction had occurred inside the fiber. Figure 4.8 (b) shows three-dimensional image of the fiber. The fiber looks oval in shape, which matched with the cross-sectional view.



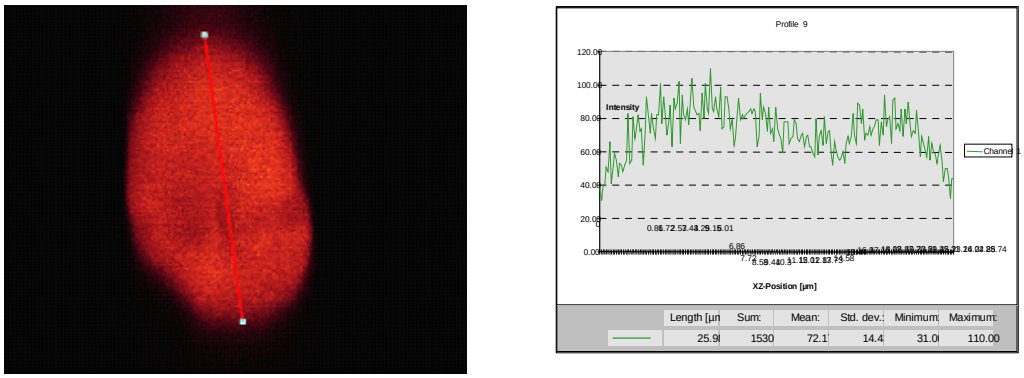
(a) Cross-section of the fiber



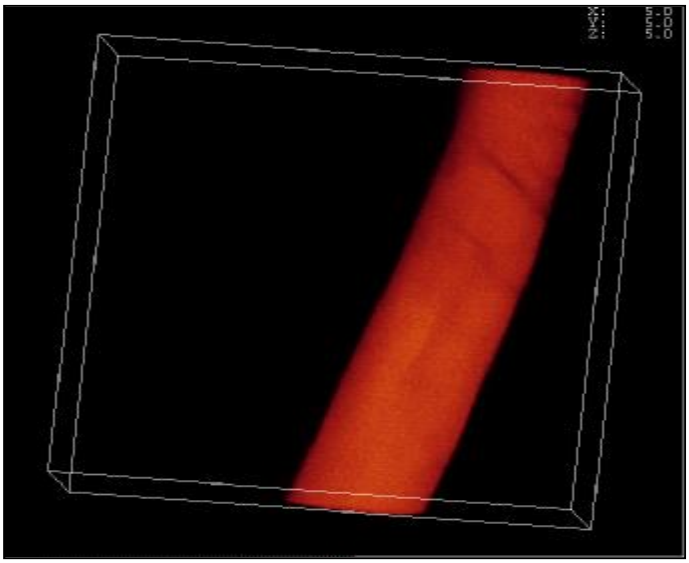
(b) 3- dimensional image of the fiber

Figure 4.8 Confocal micrographs for the PB treated sample

Figure 4.9 (a) shows the fiber cross-section for the PDPC samples. The cross-section is oval in shape and evenly dyed compared to the untreated sample implying that the carboxymethylation reaction occurred all across the fiber diameter. The three dimensional image (Figure 4.9 (b)) of the fiber did not show any convolutions in the fiber. The reasons for the oval shape is as mentioned for the PB treated sample.



(a) Cross-section of the fiber

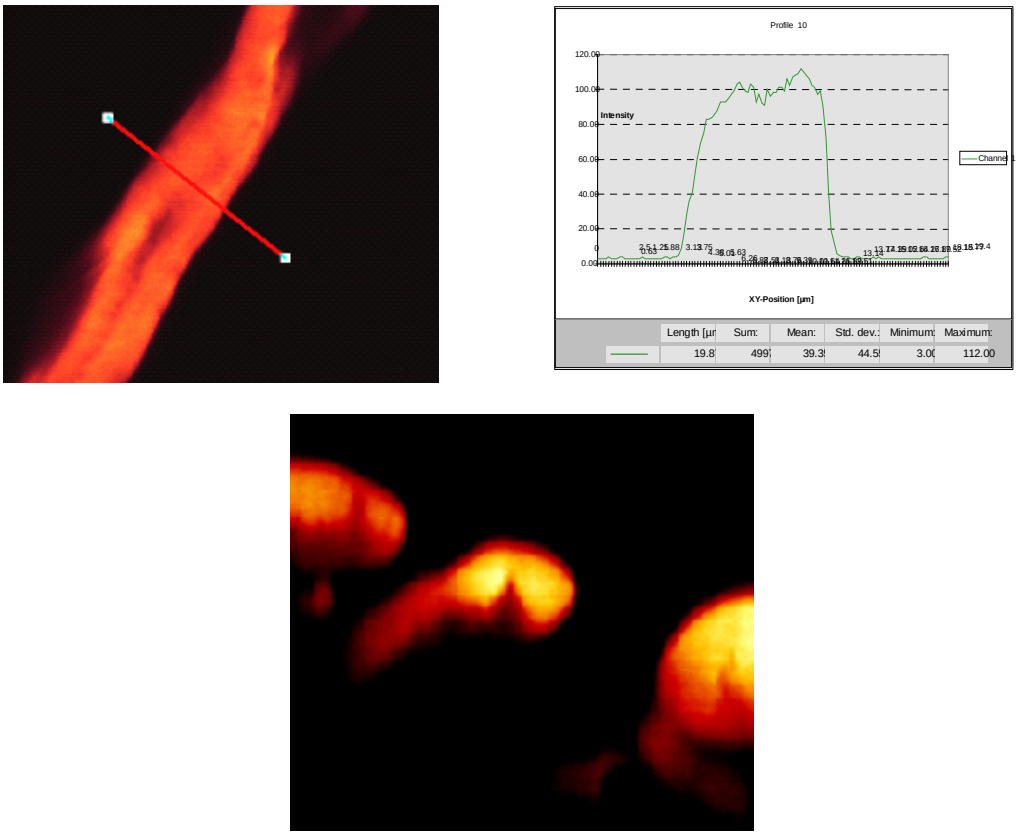


(b) 3-dimensional image of the fiber

Figure 4.9 Confocal micrographs for PDPC treated sample

Figure 4.10 (a) shows the fiber cross-section for the PDC treated sample. The cross-section was kidney shaped, though lesser than the untreated sample. For this sample, 500ml of 2M ammonium chloroacetate and 500 ml of 20% NaOH were mixed giving NaOH concentration of 10%. This concentration was not enough to swell the fibers to introduce the morphological changes. The 3-dimensional image (Figure 4.10 (b)) confirms the retention of

convolutions by the fibers. The fiber cross-section is more evenly dyed than the untreated control implying that the treatment occurred in the fiber interior.



(a) Cross-section of the fiber

(b) 3-dimensional image of the fiber

Figure 4.10 Confocal micrographs for the PDC treated sample

4.3 Nitrogen content

The untreated cellulosic fabric had nitrogen content of about 0.02% due to the naturally occurring impurities such as proteins, minerals, pectin and waxes.[7] Carboxymethylation treatment did not significantly change the nitrogen content of the fabric. The treatment of samples with CHTAC changed their %N contents.

Nitrogen content analysis was done for Series 14, 15, 16 and 17. For all the samples, the nitrogen content was determined after the complete treatment. The machine provided nitrogen contents as percent values from which mmol N/100g of fabric were calculated. For example, 0.10 % nitrogen content can be expressed in mmol N/100 g as shown below:

$$mmol\ N/100g = \%N \times 1000/14 = 0.1 \times 1000/14 = 7.14$$

Series 14 showed that as the concentration of CHTAC increased the %N or mmol N/100g of treated fabric increased. This was due to the increase in the availability of reactive species near the cellulose molecules with the concentration of CHTAC. A linear fit with the coefficient of determination (R^2) of 0.97 was obtained. The data is shown in Table 8.10 in the Appendix and Figure 4.11.

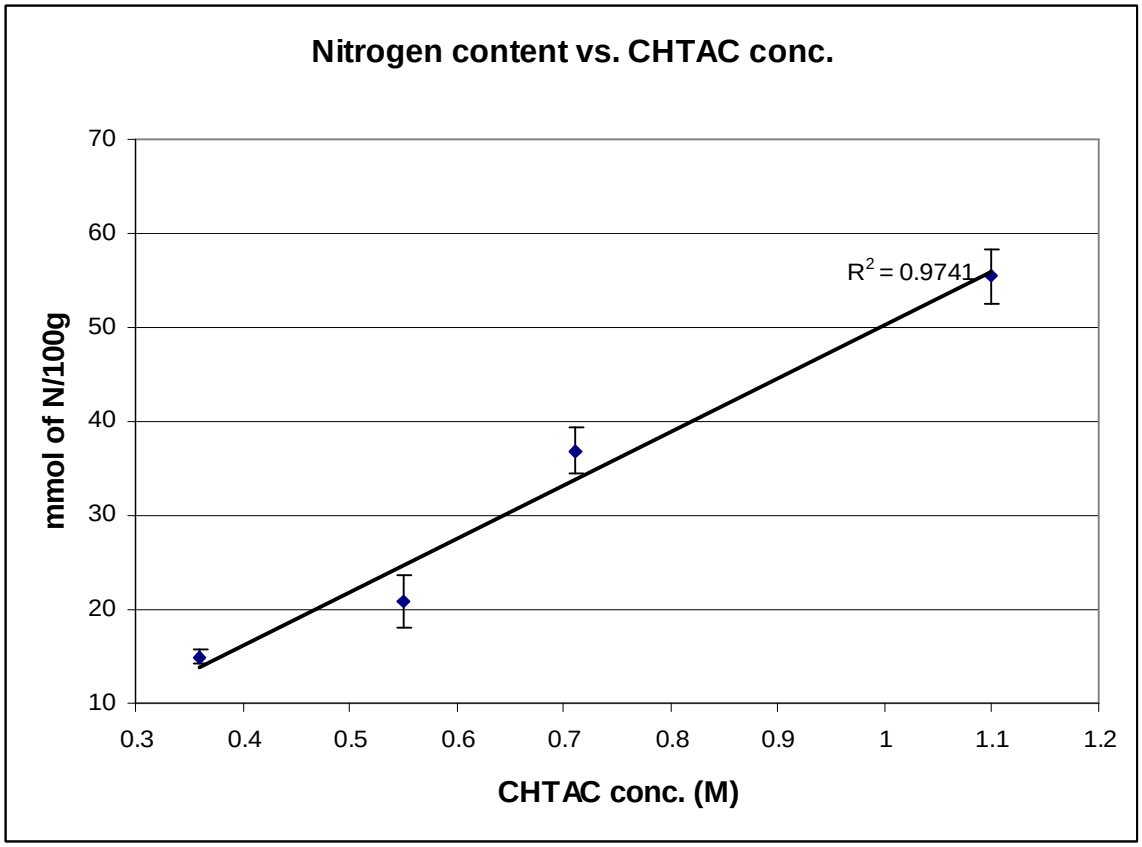


Figure 4.11 Effect of concentration of CHTAC on mmol N/100g fabric

The carboxymethylated samples of Series 15 were treated with CHTAC and then analyzed for nitrogen content (Table 8.11 in the Appendix). For a specific CHTAC concentration, the nitrogen content did not show any significant variation as the carboxymethyl content of the fabric increased. Hence, the average value of the nitrogen content was calculated for every concentration of CHTAC and used in further analysis. However, when the nitrogen contents of the samples were plotted against the CHTAC concentration (Figure 4.12), a coefficient of determination (R^2) of 0.76 was obtained with a linear fit. The nitrogen content increased as the concentration of CHTAC increased.

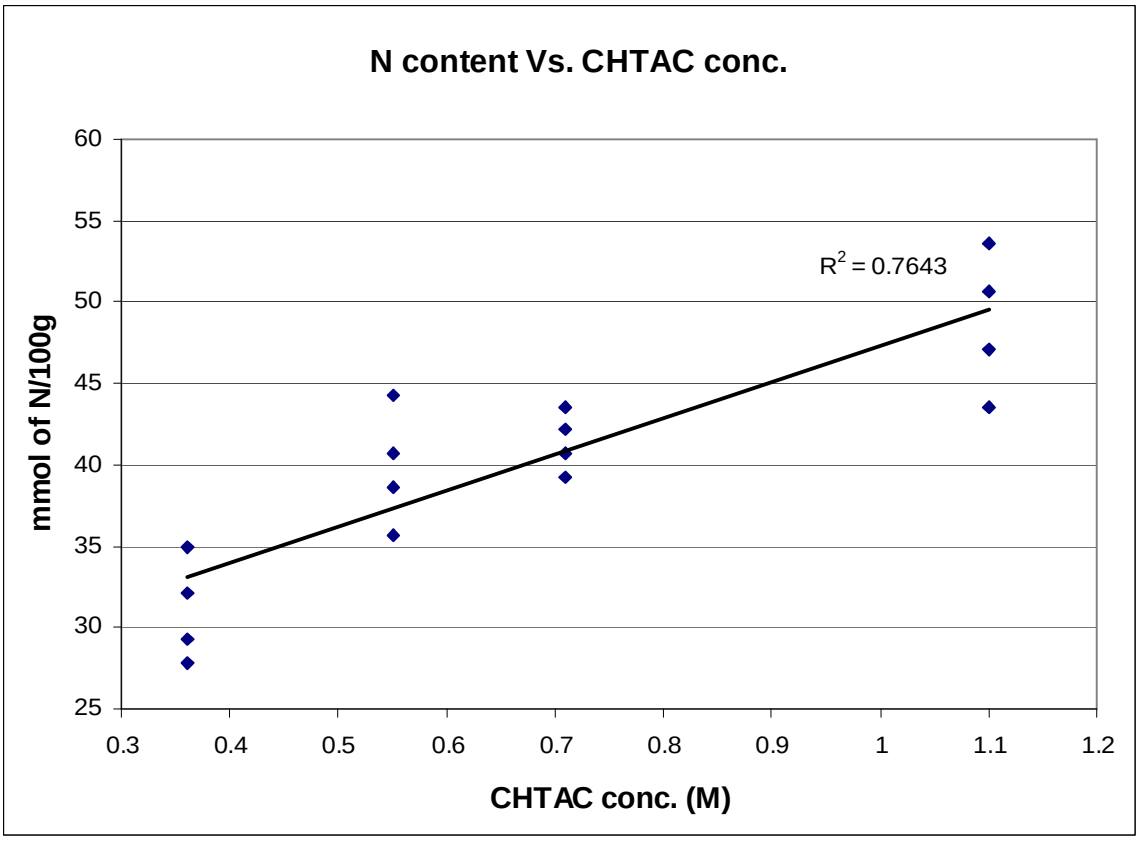


Figure 4.12 Correlation between N content and CHTAC concentration for carboxymethylated samples

The nitrogen content was also found for Series 17, which is shown in Table 8.2 in the Appendix.

4.4 Scanning electron microscopy

Scanning electron microscopy was used to determine the changes in cross-sectional geometry of the fibers at each step of treatment for ionic cross-linking. Micrographs were taken for untreated, sodium hydroxide treated, carboxymethylated/cationized only, and Series 15 and Series 16 samples. Table 4.9 lists the micrographs that were taken.

Table 4.9 List of scanning electron micrographs

Figure label	**Sample description**	**Mode of operation**
Figure 4.13 (a)	Untreated control	Vacuum mode
Figure 4.13 (b)	Sodium hydroxide (20%) treated	Vacuum mode
Figure 4.13 (c)	15E	Vacuum mode
Figure 4.13 (d)	Carboxymethylated only (anionic content same as 15E)	Vacuum mode
Figure 4.13 (e)	16P	Vacuum mode
Figure 4.13 (f)	Cationized only (cationic content same as 16P)	Vacuum mode
Figure 4.13 (g)	Carboxymethylated only (anionic content same as 15E)	High vacuum mode
Figure 4.13 (h)	Carboxymethylated only (anionic content same as 15E, gold sputtered)	Vacuum mode

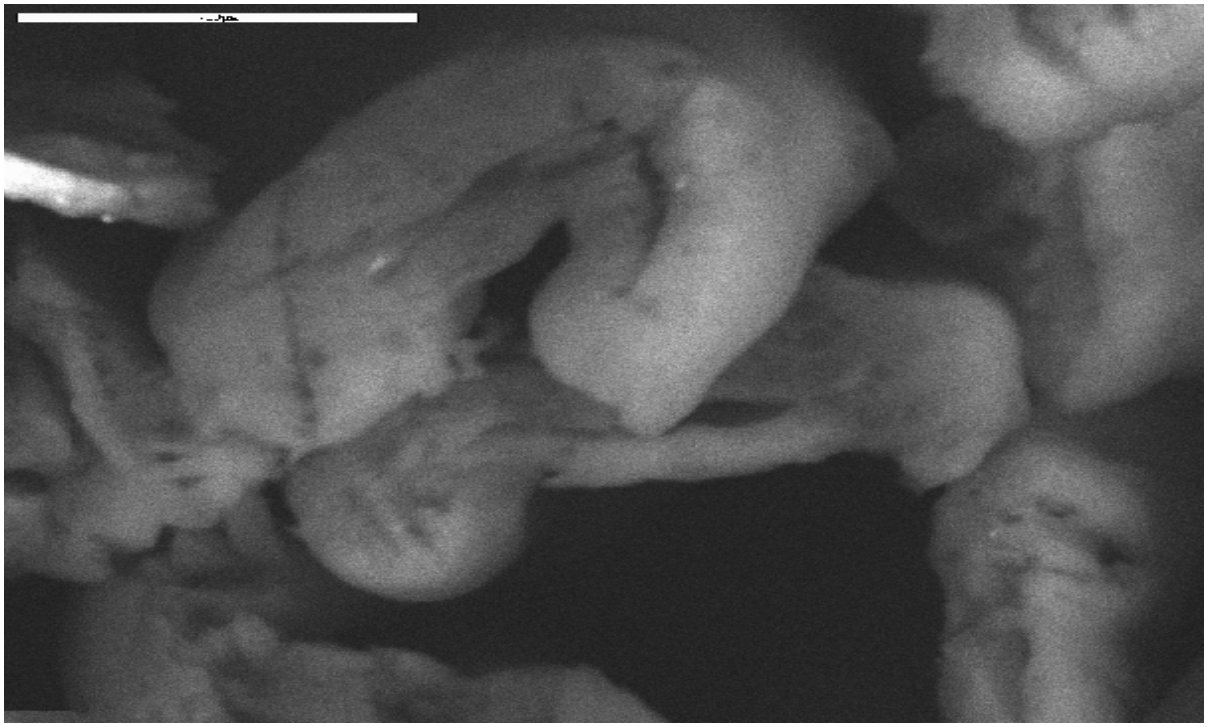
Figure 4.13 (a) shows the cross-section of the untreated fiber. The cross-section is kidney shaped. Comparing (a) and (b), it can be seen that the cross-section is oval in shape in (b), which was due to the action of sodium hydroxide on cellulose which led to swelling. When (b) and (d) were compared, no difference in cross-section was observed implying that reaction step with ammonium chloroacetate made no significant changes to the cross-sectional geometry. Similarly, (b) and (c) showed no difference, which suggested that cationization step had no contribution to the change in geometry. Thus, treatment with

sodium hydroxide was mainly responsible for the observed change in fiber cross-sectional geometry.

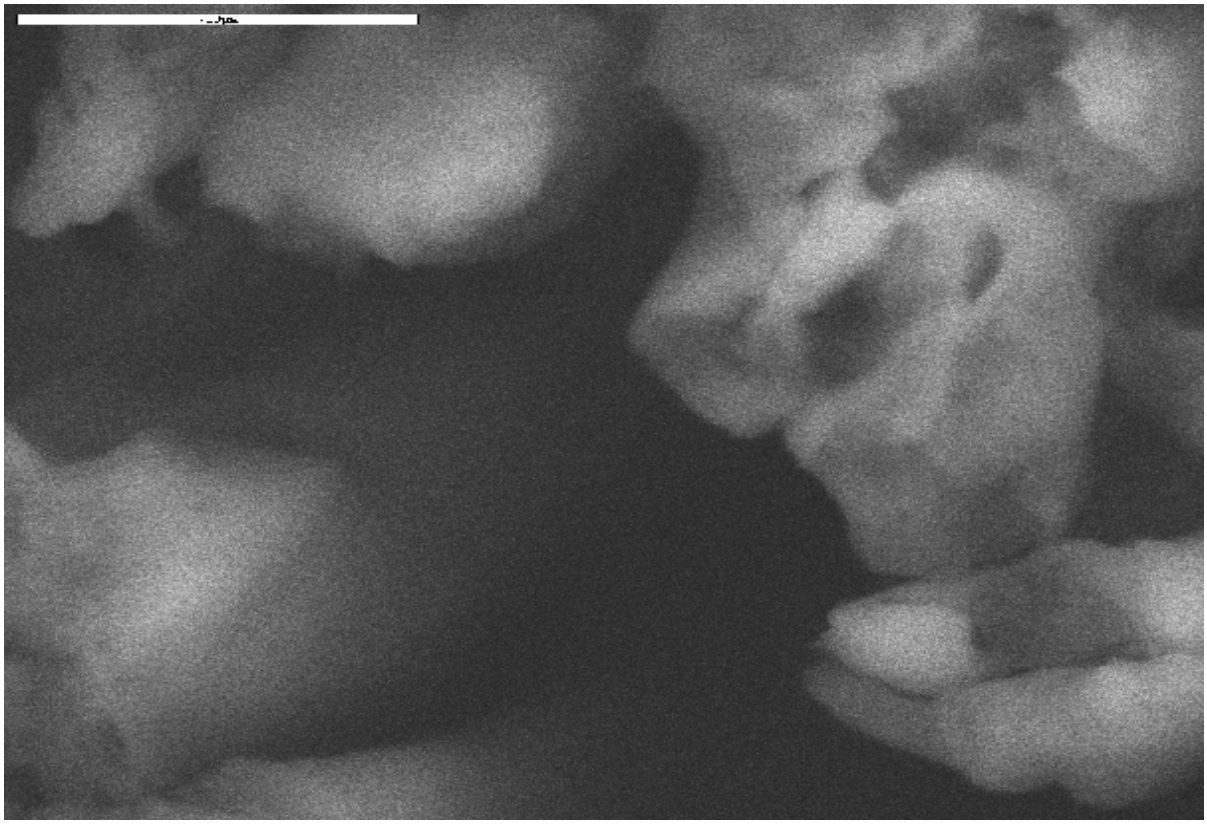
Figure 4.13 (f) showed kidney shaped fiber cross-section as the untreated control which further confirmed that cationization step made no significant change in the fiber cross-sectional geometry. Comparing (e) with (f), a change in geometry was seen with (e) being oval shaped. This was due to the action of sodium hydroxide treatment in the carboxymethylation process.

Figure 4.13 (a), (b), (c), (d), (e) and (f) showed dark spots in the cross-sections, which appeared as the electron beam incidence time was increased. The appearance of spots was thought to be due to fiber damage caused by the direct interaction of the beam with the fibers. This was studied by comparing (d) and (h). The dark spots did not appear in gold sputtered sample (h). Also, (g) showed no appearance of dark spots as the electron beam was incident for longer times.

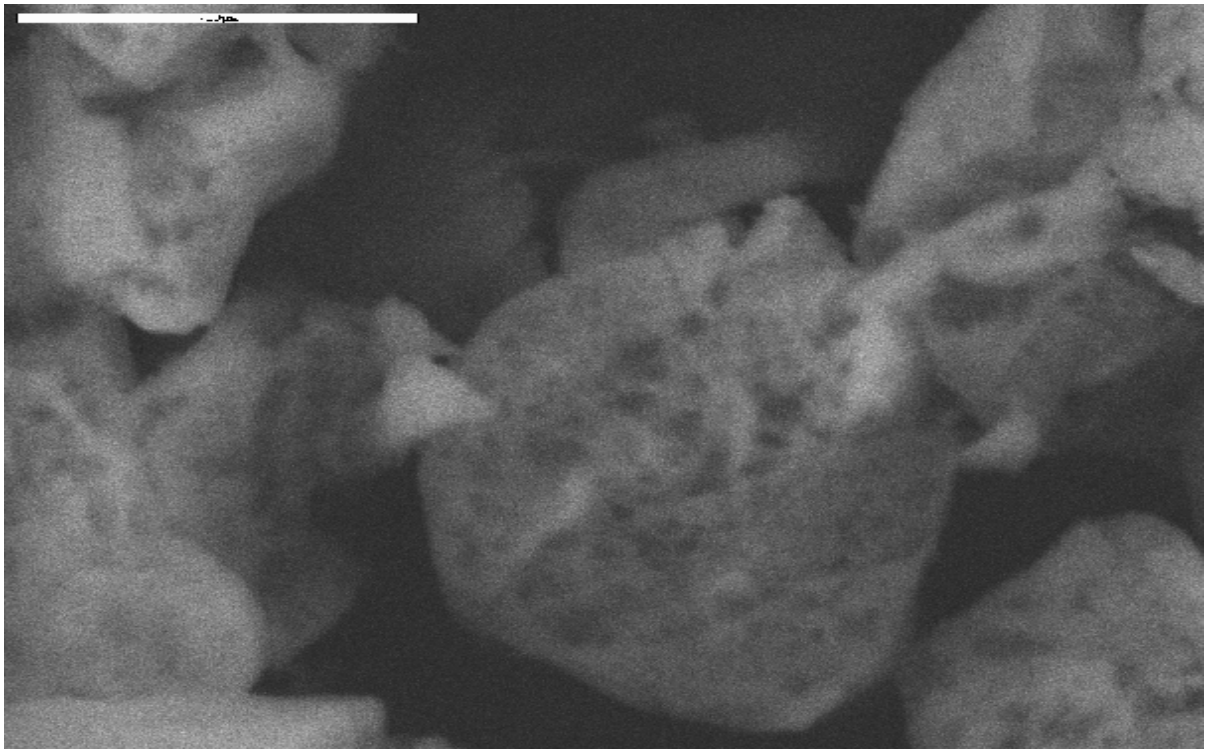
Figure 4.13 SEM micrographs for fiber cross-sections at 20kV and 4000X magnification



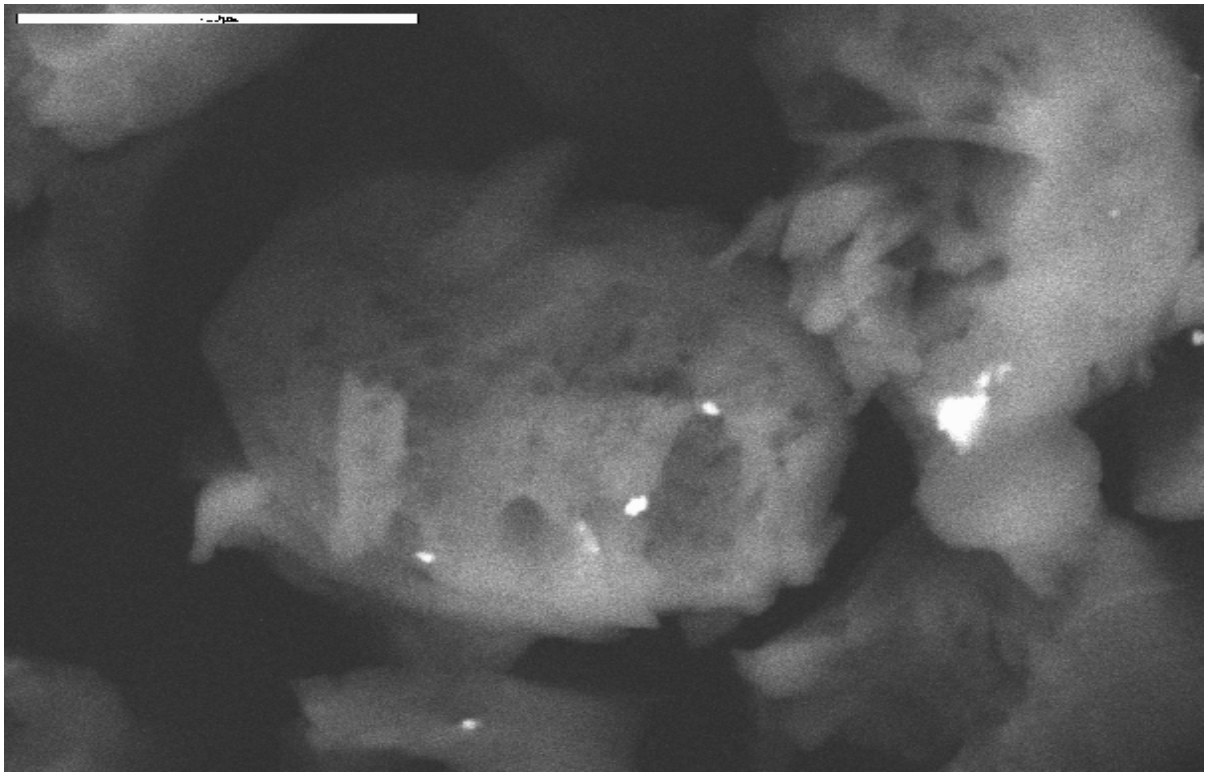
(a) Untreated control



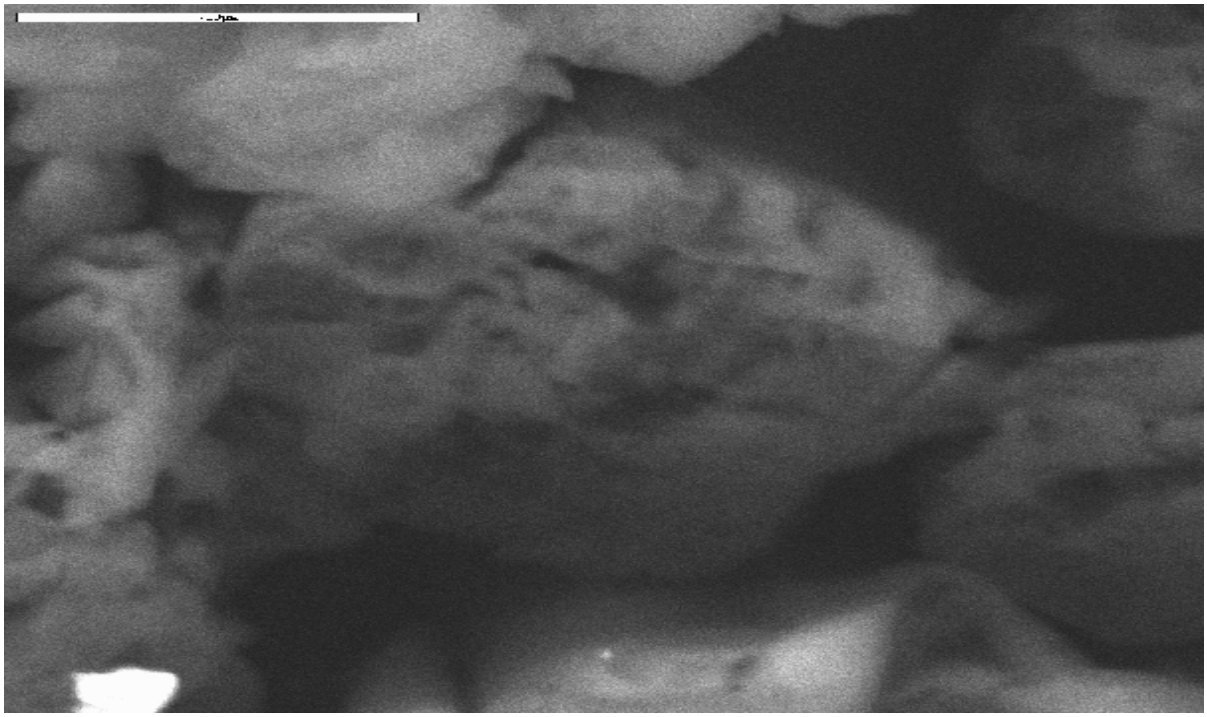
(b) Sodium hydroxide treated



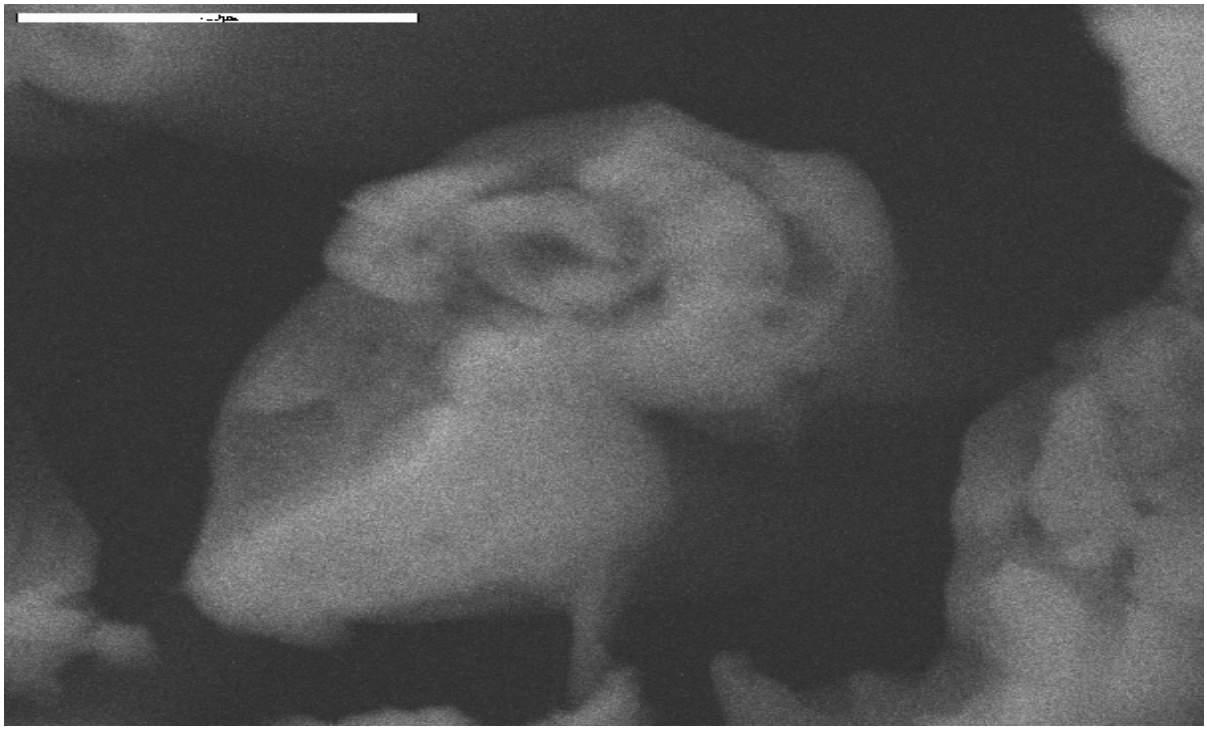
(c) 15E



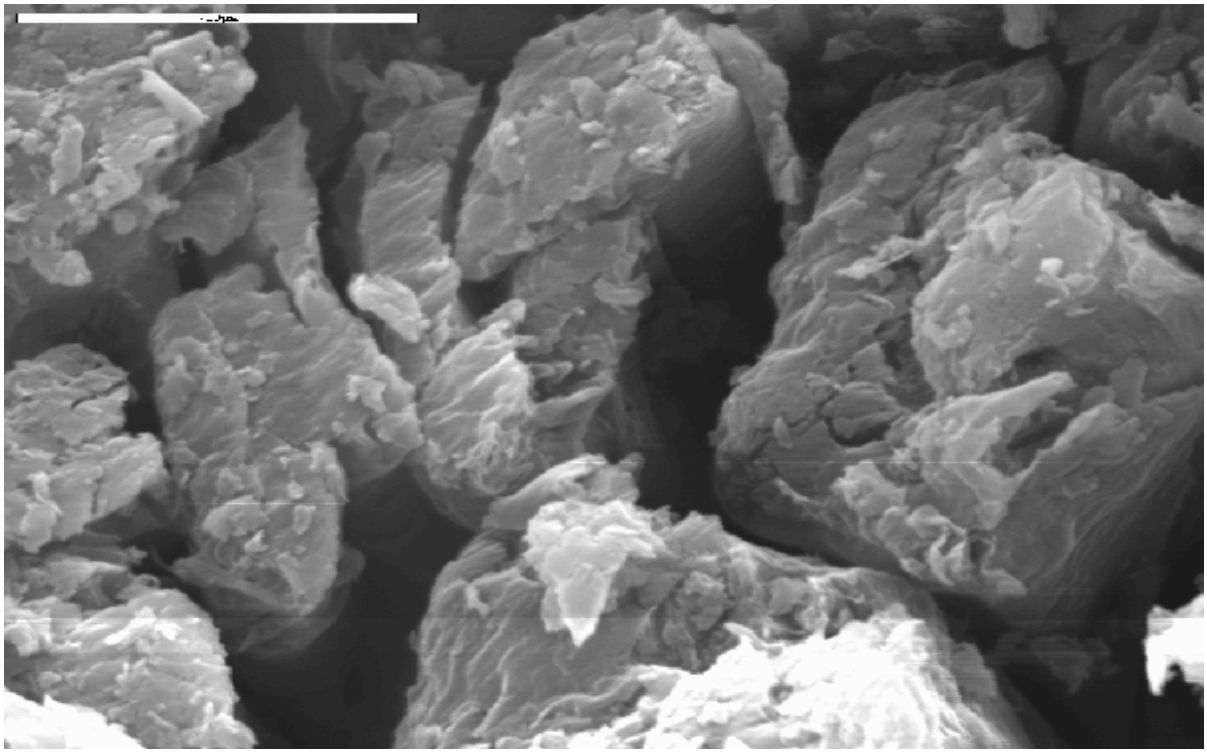
(d) Carboxymethylated sample with the same anionic content as 15E



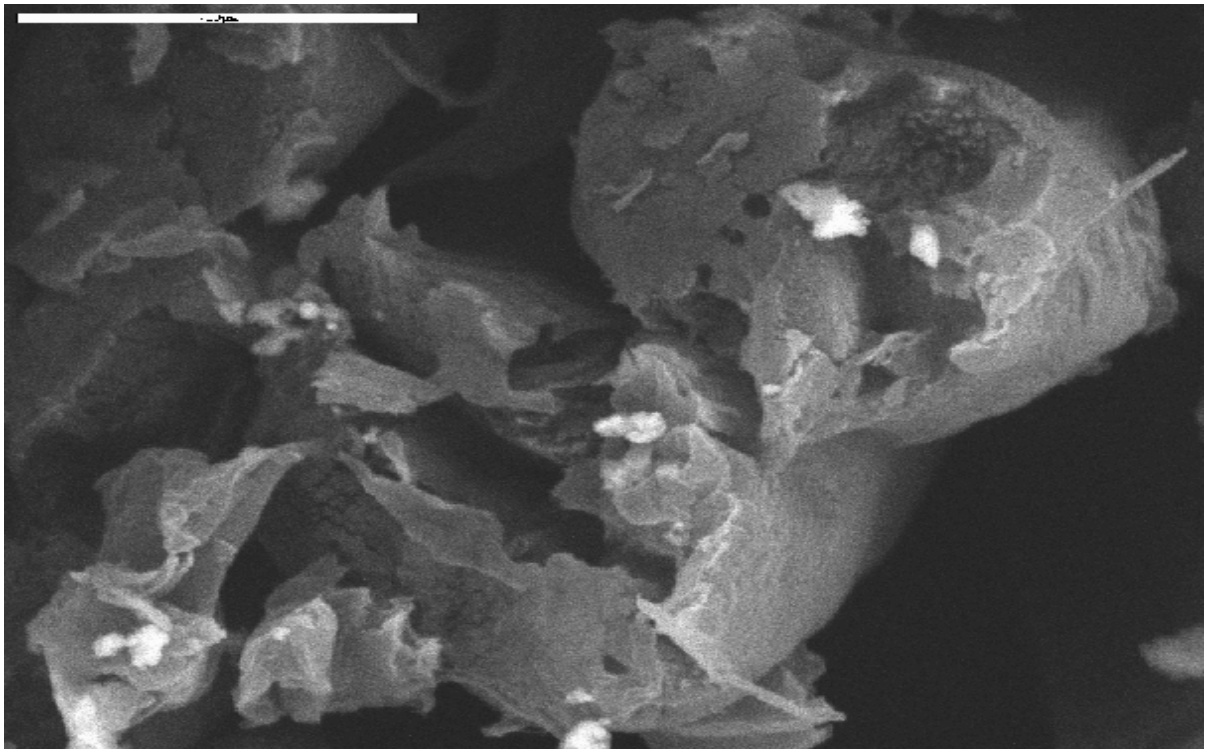
(e) 16P



(f) Cationized sample with same cationic content as 16P



(g) Carboxymethylated only (Gold sputtered, High vacuum mode)



(h) Carboxymethylated only (Gold sputtered, vacuum mode)

4.5 Wet and dry wrinkle recovery angles (WRA)

Wet and dry WRA were determined for untreated and DMDHEU treated samples; carboxymethylated/cationized only samples; and samples in Series 15, 16 and 17. As an example, sample data obtained from the test for wet WRA is shown in Table 4.10. Similar data was obtained for dry WRA. Three specimens in each direction, warp and weft, were tested for every sample and angles were noted. Average values were calculated for each direction. These values were then added and reported as shown in row 5 of Table 4.10. In this work, the values for WRA that were obtained by the sum of average values in warp and weft directions rounded to the nearest number (as shown in row 5 of Table 4.10) are presented.

Table 4.10 Sample data for wet WRA (degrees)

	Warp direction			**Weft direction**		
Sample	**Angle 1**	**Angle 2**	**Angle 3**	**Angle 4**	**Angle 5**	**Angle 6**
X	112	114	118	120	115	119
Average	(112+114+118)/3 = 114.66 = 115			(120+115+119)/3 = 118		
Sum	115 + 118 = 233					

4.5.1 Wrinkle recovery angles of DMDHEU treated fabrics

Crease angle recovery test was performed on DMDHEU treated fabrics for comparison with the WRA of the ionic cross-linked fabrics. The wet/dry crease recovery angles were 252/275 degrees respectively, which were taken as the target values.

4.5.2 Wrinkle recovery angles for cellulose having cationic and anionic charges simultaneously (Series 15, Series 16 and Series 17)

Treatment of cotton cellulosic fabric with ammonium chloroacetate in the presence of sodium hydroxide gives anionic cellulose as shown in Figure 4.14. Cationization with CHTAC gives cationic cellulose as shown in Figure 4.15. When these treatments were given one after another, or simultaneously in a mixture we get both anionic and cationic charges on

the fibers. These charged groups show durability to washing as they are covalently bound to the cellulose chains. The anionic carboxymethyl groups and the cationic quaternized groups may be present on the same cellulose chains or different. If they are present on the same chains we may have Zwitter ionic cellulose chains. If these ionic groups are present adjacent to each other on two different cellulose chains, they may form ionic cross-links as shown in Figure 4.16. When this is achieved, an improvement in the wrinkle recovery performance of the fabric may be observed. The wrinkle recovery performance depends on degree of cross-linking, location of the cross-links, distribution of ionic groups across the cross-section of the fibers, the ratio of inter and intra chain cross-links and the fabric state during measurement of the WRA.[3] We suspect that the change in the crystalline and morphological structures of the fibers in one step of treatment may affect the subsequent distribution of ionic groups across the fiber cross-section, which in turn may affect the ionic cross-linking and hence the WRA performance.

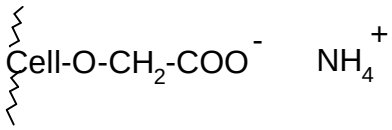


Figure 4.14 Anionic cellulose chains

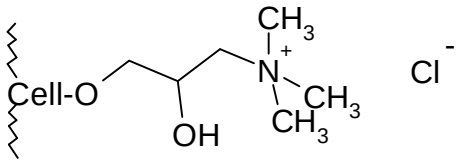


Figure 4.15 Cationic cellulose chains

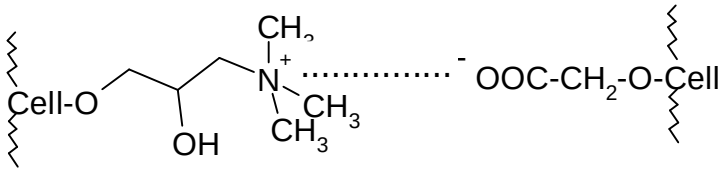


Figure 4.16 Ionic cross-linked cellulose chains

4.5.2.1 Wrinkle recovery angles for samples obtained by CHTAC treatment of anionic cellulose (Series 15)

The wet and dry WRA of the untreated, carboxymethylated, cationized and cross-linked samples are shown in Table 8.12 and Table 8.13 in the Appendix respectively. The relationship between nitrogen content of the fabric, carboxymethyl content (symbolized as COO-) of the fabric and wet/dry WRA are shown in Figure 4.17 and Figure 4.18 respectively. Improvements in wet angles were seen for all the samples with the average values ranging between 178 degrees to 214 degrees, that is, a rise of 18 to 54 degrees over untreated control were obtained.

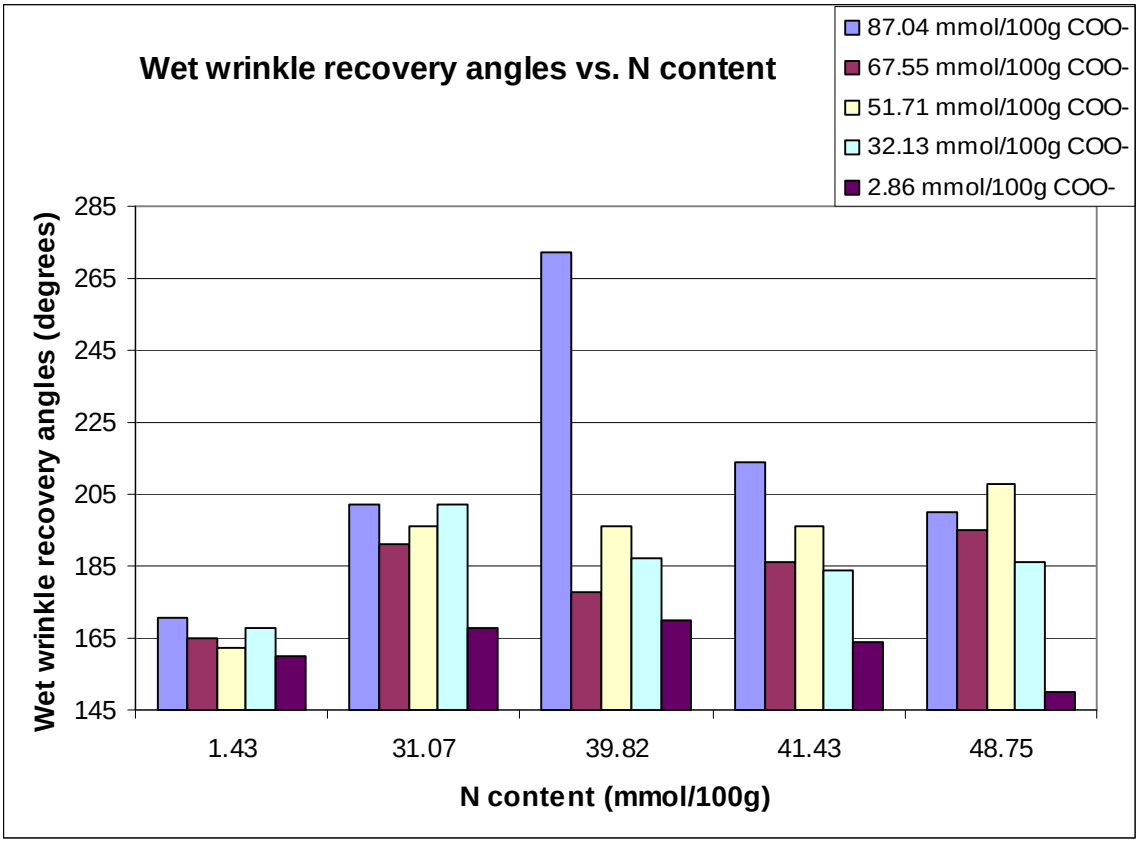


Figure 4.17 Effect of nitrogen and carboxyl contents on wet WRA of Series 15 samples

As can be seen from Table 8.12, the carboxymethylation treatment only or the cationization treatment only did not change the wet WRA significantly compared to the

untreated controls. From Figure 4.17, it can be observed that the wet crease angles improved in all the samples that were cationized following carboxymethylation. We believe that this improvement was due to ionic cross-linking.

For the treated samples, the improvements were not very significant for low carboxymethyl content fabrics. The fabric with highest carboxymethyl content (87.04 mmol/100g) showed the maximum improvement in WRA performance. We suspect that these samples had enough number of anionic groups in the vicinity of quaternized groups to form ionic bonds for noticeable wrinkle recovery performance.

In the samples with 87.04 mmol/100g of carboxymethyl contents, the wet WRA improved initially as the nitrogen content of the samples increased, then reached a maximum value and then decreased. The nitrogen content of the samples is proportional to their cationic content. We suspect that at low nitrogen contents, there were not enough of cationic groups to form ionic cross-links. At very high nitrogen contents the repulsive forces between the quaternized groups dominated disallowing the formation of stable ionic bonds. Hence, the WRA performance decreased at higher nitrogen contents. At the intermediate nitrogen contents the number, density and locations of quaternized groups were just optimum to form ionic bonds and improve the WRA performance.

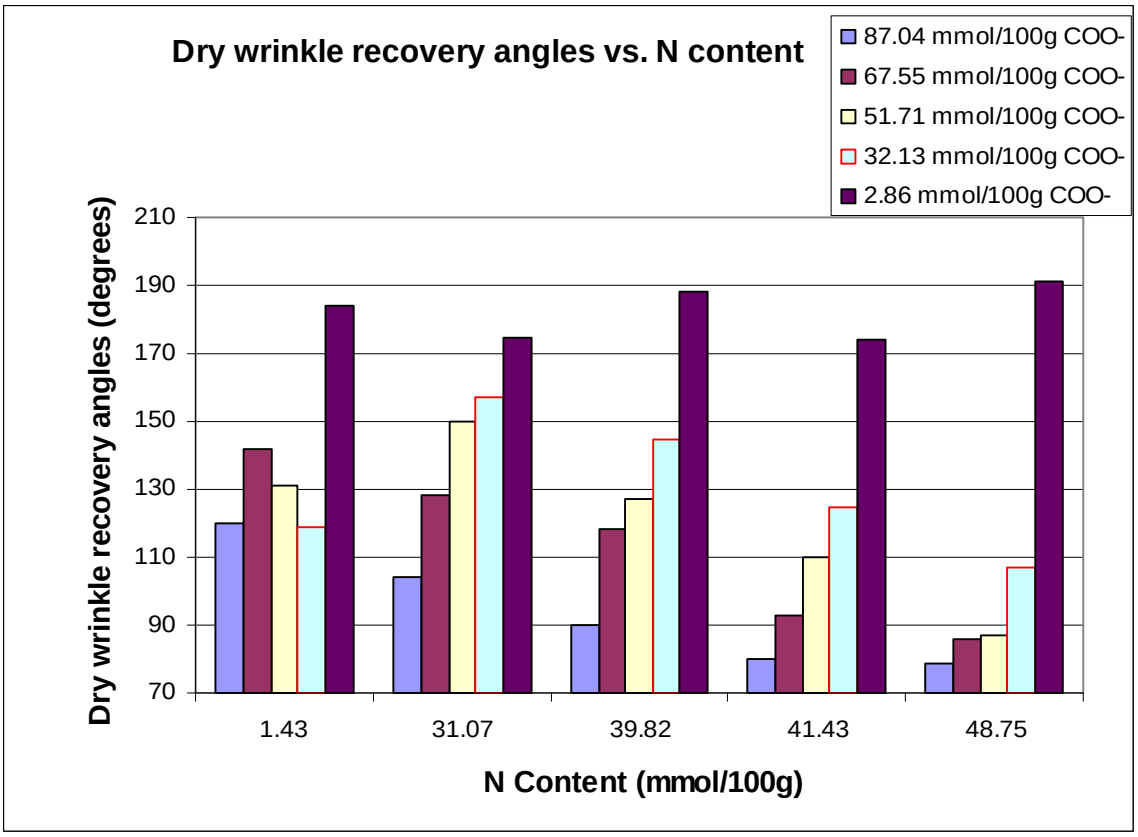


Figure 4.18 Effect of nitrogen and carboxyl contents on wet WRA of Series 15 samples

Figure 4.18 shows the dry WRA of Series 15 samples. From Table 8.13 we see that the carboxymethylation treatment reduced the dry WRA. Samples that were cationized only showed either no change or slight improvement in the dry WRA. This may be due to ionic cross-linking between the quaternized groups and the residual carboxymethyl content natural to cotton. The samples that were both carboxymethylated and cationized showed lower dry WRA than the carboxymethylated only or cationized only samples.

The improvement in the wet WRA may be explained as follows. The fabric is swollen in the wet state. The anionic and cationic chains have more mobility to move around. They can find each other more easily and form ionic bonds. This mobility is not available in the dry state of the fabric. The decrease in the dry WRA may be explained on the basis of fabric stiffness. As we would discuss later, the steps of carboxymethylation and cationization make

the samples stiff. This stiffness may be responsible for the lower WRA performance. It is also suspected that under stress new ionic bonds are formed at the creases and the old ones are broken holding the fabric in its creased state after the stresses are released. This may be the reason for the lower dry WRA than the untreated and carboxymethylated/cationized only samples. This is a hypothesis and needs further investigation.

To explain the above observations in more detail, we need to study quantitatively the distribution of the ionic charges on the fiber surface and in cross-section, their density and locations. The carboxymethylation step, which opens the fiber and creates reacted regions, may be primarily responsible for the subsequent distribution of cationic groups in the fibers. As the concentration of ammonium chloroacetate varies, the reaction extents of the fibers would vary. Thus, each fiber treated with a different concentration of chloroacetate would offer a different resistance for the cationic agents to penetrate and react. This would lead to a variation in the distribution of the cationic charges from the inside to the outside of the fibers. Although we have qualitatively studied the distribution of anionic charges by confocal microscopy, we are yet to study quantitatively the distribution of anionic and cationic charges across the fiber cross-section. This information would help further to explain the WRA behavior of the fabrics.

4.5.2.2 Wrinkle recovery angles for samples obtained by carboxymethylation of cationic cellulose (Series 16)

The wet and dry WRA of the untreated, carboxymethylated, cationized and cross-linked samples are shown in Table 8.14 and Table 8.15 in the Appendix respectively. The relationships between nitrogen content of the fabric, ammonium chloroacetate concentration

and wet/dry WRA are shown in Figure 4.19 and Figure 4.20 respectively. Improvements in average wet angles up to 49 degrees over the untreated samples were seen.

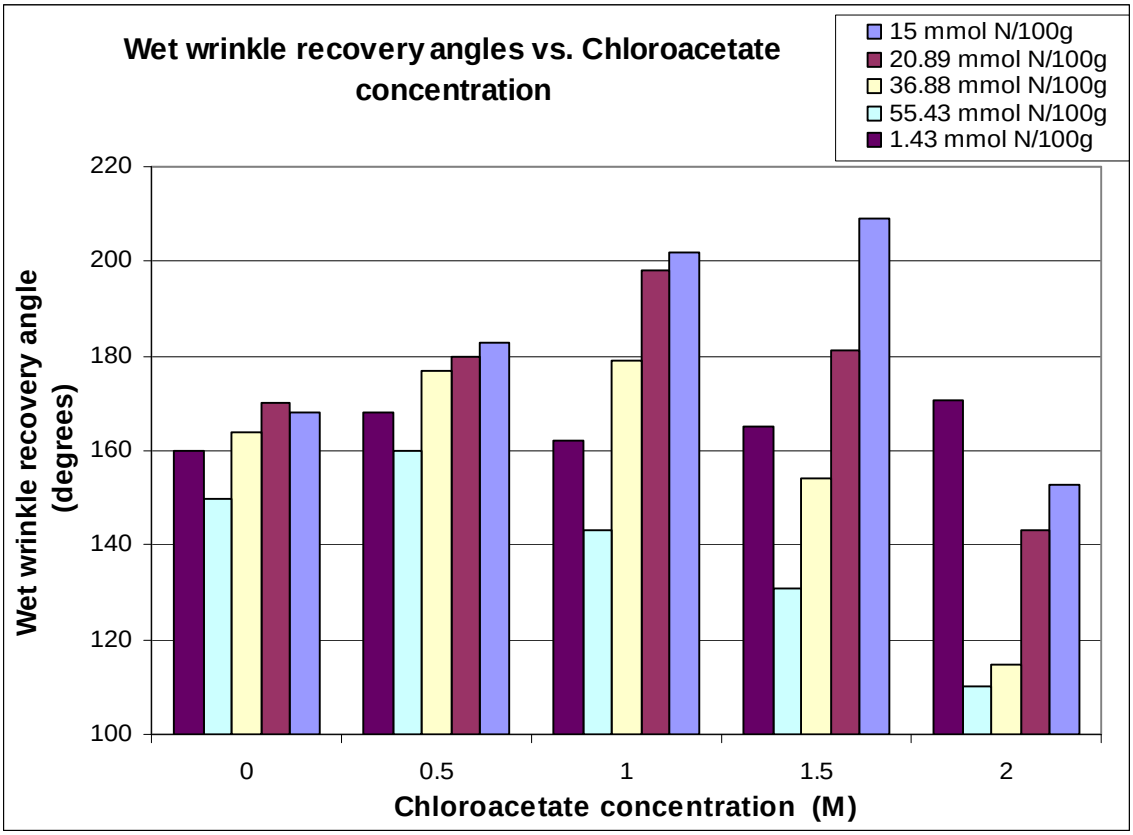


Figure 4.19 Effect of nitrogen and ammonium chloroacetate concentration on wet WRA of Series 16 samples

As can be seen from Table 8.14, the carboxymethylation treatment only or the cationization treatment only did not change the wet WRA significantly compared to the untreated ones. From Figure 4.19, we see that the wet crease angles improved in all the samples that were cationized first followed by carboxymethylation except when very high nitrogen contents were present. We believe that this improvement was due to the ionic cross-linking. The wet WRA performance decreased with the increase in nitrogen content. This may be due to the repulsions occurring between the cationic groups as their number/area increased.

In this treatment procedure, cationization was done before the carboxymethylation steps. So, during cationization the fibers were not open and swollen as in Series 15 samples. This might have affected the penetration of cationic agent in the fiber. Also, during the pad-dry cure procedure used in the treatment, the reactants would migrate to the surface giving high reaction there. Thus, we suspect that the distribution of cationic groups may be uneven across the fiber cross-section. Further investigation is needed. Also, the cationic groups might influence the distribution of anionic groups across the fiber cross-section. The resulting distribution of charged groups would affect the ionic cross-linking and thereby the WRA performance.

The improvements were not very significant for lower concentrations of ammonium chloroacetate. The wet angles showed significant improvements at moderate chloroacetate concentration. This moderate concentration would give optimum number of anionic charges to the fiber to form ionic cross-links without any repulsion amongst themselves. The improvement in wet recovery angles were marginally lower than that seen in Series 15 samples.

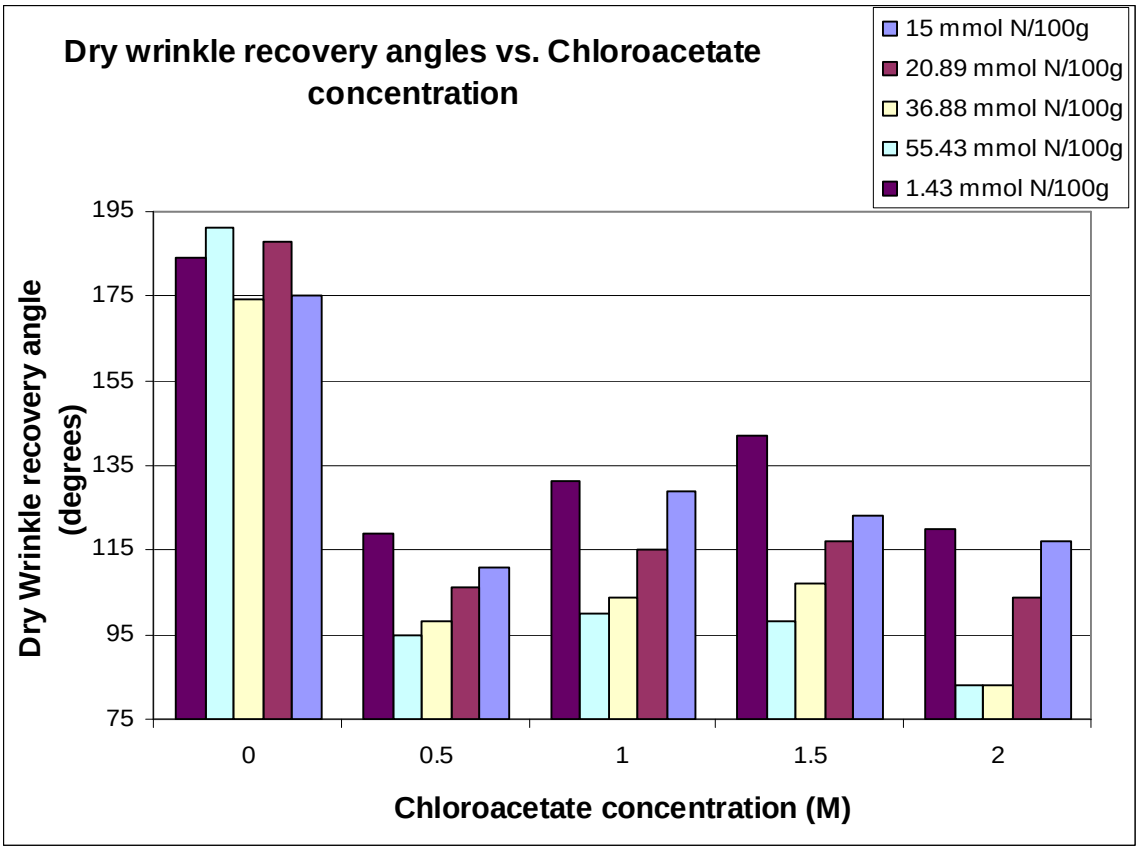


Figure 4.20 Effect of nitrogen and ammonium chloroacetate concentration on dry WRA of Series 16 samples

Figure 4.20 shows the dry WRA of the Series 16 samples. From Table 8.15 we see that the carboxymethylation treatments reduce the dry WRA. Samples that were cationized only showed either no change or slight improvement in the dry WRA. We assign this to the ionic cross-linking between the quaternized groups and the residual carboxymethyl content natural to cotton. The samples that were both cationized and carboxymethylated showed lower dry WRA than the only cationized or only carboxymethylated samples.

The improvement in the wet and dry WRA may be explained in the same way as was discussed in section 4.5.2.1.

4.5.2.3 Wrinkle recovery angles for samples obtained by 'Method of mixture'

The wet and dry WRA for the samples obtained by the 'Method of mixture' are shown in Table 8.2 in the Appendix. All the combinations of parameters showed that the wet WRA were more than the untreated control except one combination. The dry WRA were less in all cases except one compared to the untreated control. The control had wet/dry angles of 160/184 degrees. The increase in the wet angles was comparable to Series 15 and Series 16 samples. The improvement ranged between 18 to 53 degrees over the controls. The model was fit to the design. It was not a significant model and did not show any significant factors (Figure 8.3). A better design is required in future to optimize the treatment. The improvement and decrease in wet and dry angles respectively can be explained as in sections 4.5.2.1 and 4.5.2.2. More could be said about the observations only after studying the factors mentioned in the previous two sections.

The important feature of this method was that it simultaneously created cationic and anionic charges on cellulosic fibers in one step. The samples also showed improvements in wet WRA performance. The presence of these charges was evaluated by dyeing the treated samples with both, basic and acid dyes. The untreated samples were dyed as controls. The dyed treated samples were visually compared to the dyed controls. They showed darker shades than the untreated controls for both classes of dyes.

4.6 Basis weight and bending rigidity

Basis weight and bending rigidity were analyzed for Series 15 and Series 16 samples.

4.6.1 Basis weight and bending rigidity for samples obtained by CHTAC treatment of anionic cellulose (Series 15)

The basis weight data, bending length data and the stiffness data for Series 15 are shown in Table 8.16, Table 8.17 and Table 8.18 respectively in the Appendix. The tables also show data for untreated, DMDHEU treated, carboxymethylated only and cationized only samples. The effects of carboxyl content and nitrogen content on flexural rigidity are shown in Figure 4.21 and Figure 4.22.

Table 8.16 shows that the basis weight increased after the treatment. The increase could be due to the shrinkage involved in the treatment with NaOH during carboxymethylation, and addition of molecules during reaction with ammonium chloroacetate or CHTAC.

The basis weight of the samples increased after carboxymethylation. The increase did not change significantly as the carboxymethyl content of the samples increased. This indicated that the increase was mainly due to the shrinkage caused by NaOH treatment during carboxymethylation. Thus, the reaction of chloroacetate with cellulose did not contribute to the increase in basis weight. The basis weights of the cationized only samples were more than the untreated control and increased as the CHTAC concentration increased. This increase was mainly due to the reaction of cellulose chains with CHTAC. In almost all the cases, the basis weight of the samples that were subjected to carboxymethylation followed by cationization showed slightly more or equal weights as the carboxymethylated only samples. The slight increase over the carboxymethylated samples was due to reaction with heavier CHTAC molecules.

The cationized only samples showed higher stiffness values than the untreated control (Table 8.18). The stiffness increased as the nitrogen content of the fabric increased. The rise in stiffness was up to 4.54 times over the control. The carboxymethylation treatment alone increased the stiffness up to 37 times over the control. DMDHEU treated samples showed increase in stiffness by 1.5 times over control. The ionic cross-linked samples showed more stiffness than the control, cationized/carboxymethylated only or DMDHEU treated samples. It was 62 times over the control.

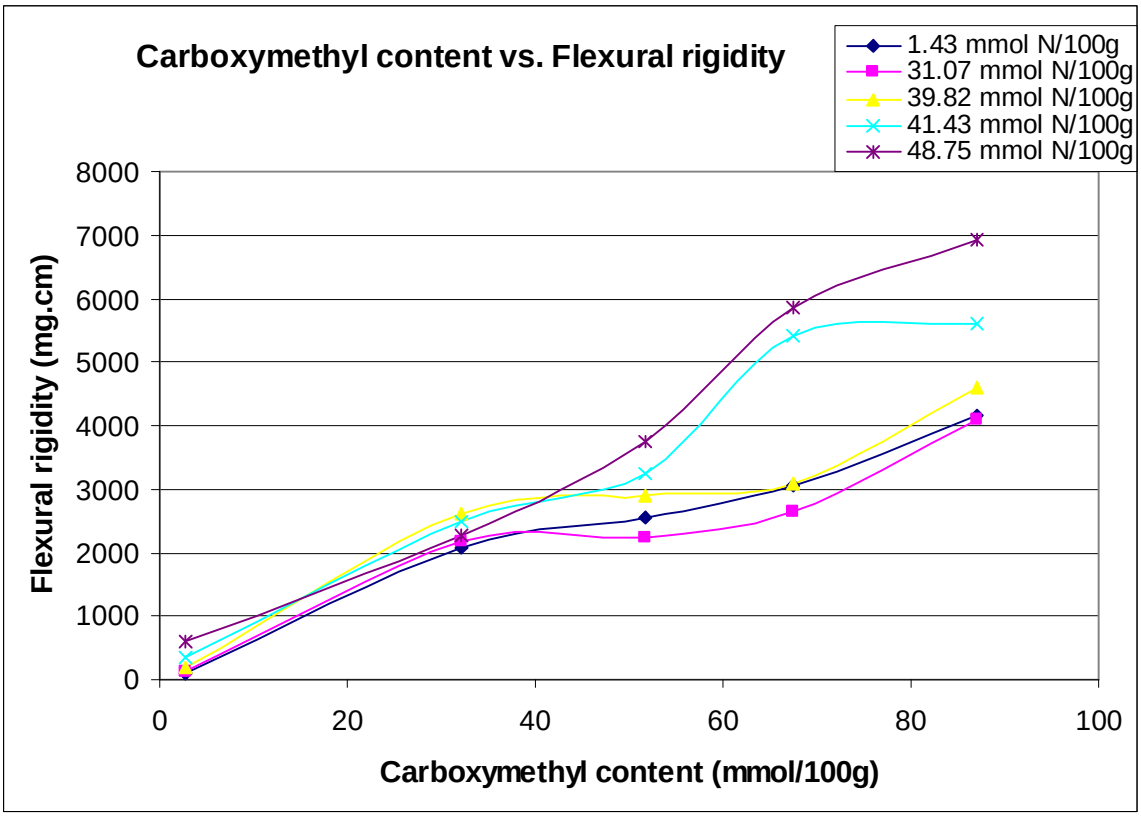


Figure 4.21 Effect of carboxymethyl content and nitrogen content on the stiffness of series 15 samples

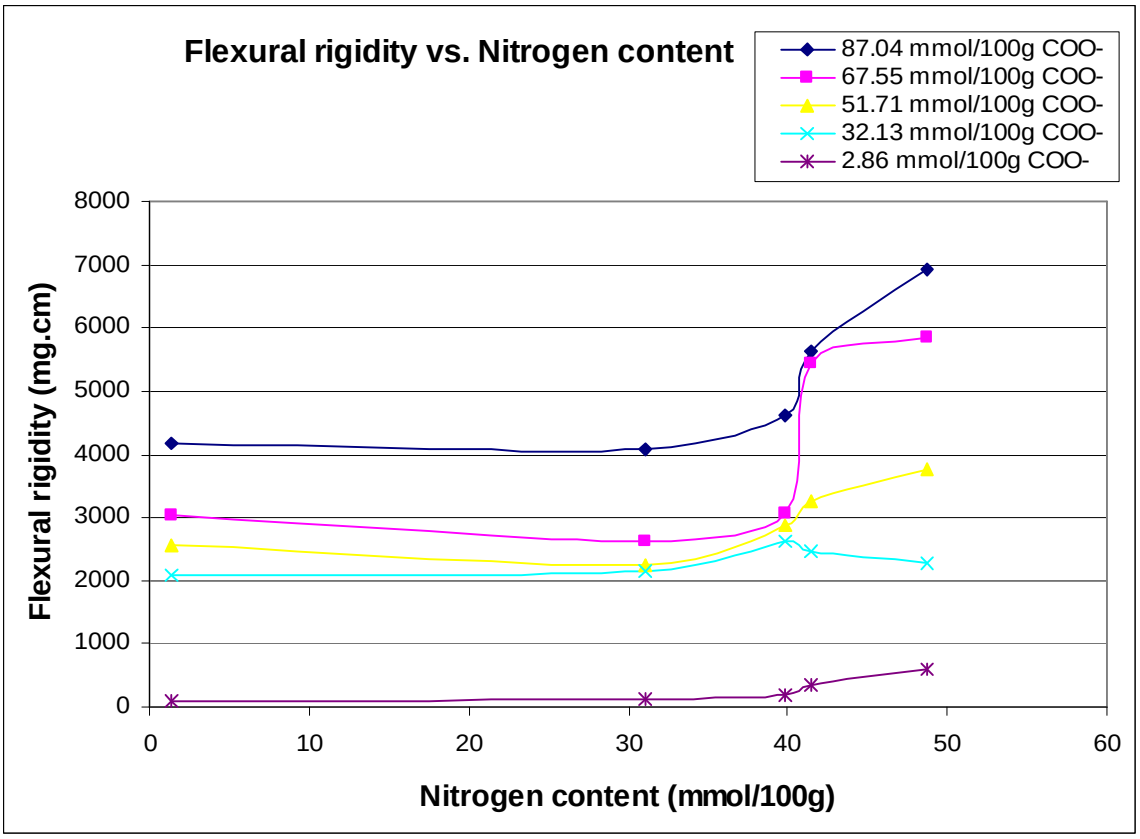


Figure 4.22 Effect of nitrogen content and carboxymethyl content on the stiffness of Series 15

Figure 4.21 shows that as the anionic contents of the samples increased the flexural rigidity, for the particular nitrogen content, increased. The increase up to 40 mmol/100g anionic contents was the same for all samples with different nitrogen contents. The rise in rigidity was steep at the highest values of carboxymethyl and nitrogen contents. For the higher carboxyl contents and lower nitrogen contents the stiffness values were lower than at the high nitrogen contents. These values were still more than those at low carboxyl and nitrogen contents.

The above observation can also be seen in Figure 4.22. It shows that for a specific value of anionic content, the stiffness values increased or remained same at lower nitrogen contents and increased at higher nitrogen contents. At higher nitrogen contents and lower

carboxymethyl contents, the values showed a smooth increase in all cases. The rise was steeper when the anionic and nitrogen contents were high.

A linear correlation was obtained between the carboxyl content and the stiffness values with the coefficient of determination (R^2) of 0.79 (Figure 4.23).

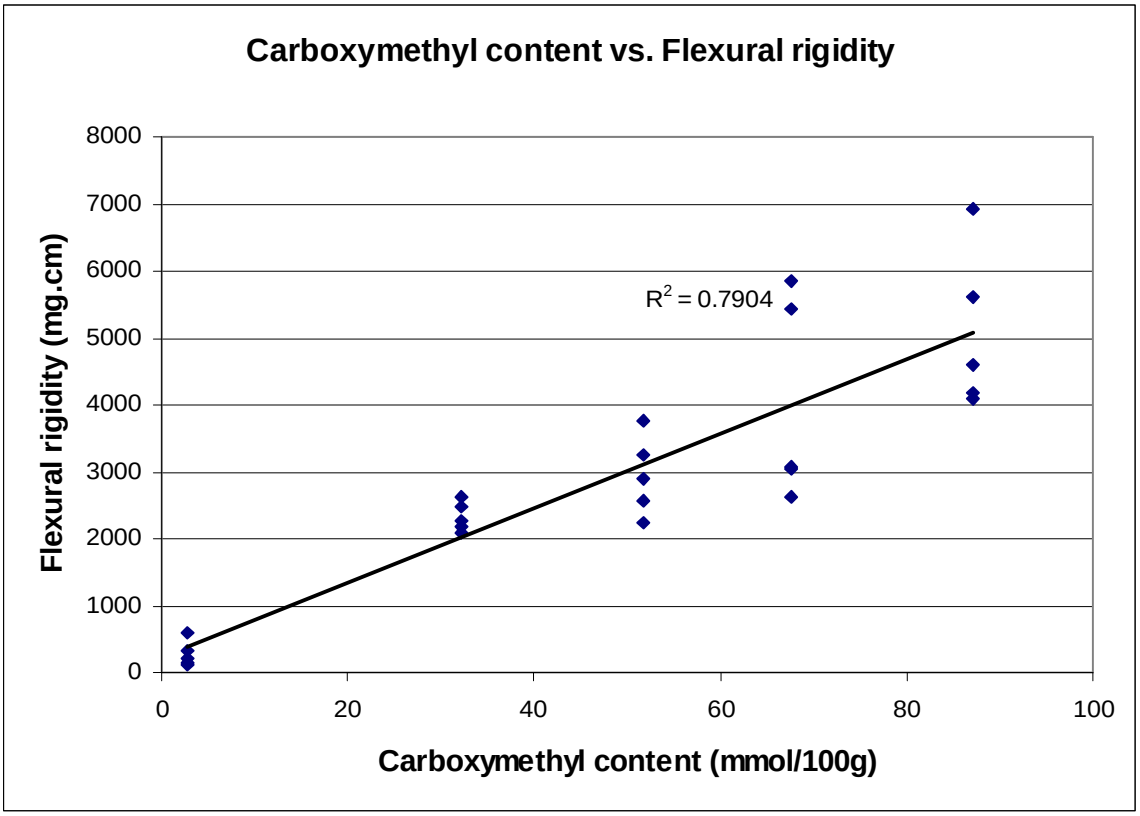


Figure 4.23 Correlation between flexural rigidity and carboxymethyl content for Series 15

The increase in stiffness values with the ionic content of the fabric could be explained as follows. At low concentration of ionic groups, the cellulose chains remain extended. As the concentration increases, they start coiling up and chains overlap forming entangled structures making fabric stiff. This reasoning explains the trends seen in the stiffness data at various combinations of low/high cationic and anionic levels.

4.6.2 Basis weight and bending rigidity for samples obtained by carboxymethylation of cationic cellulose (Series 16)

The basis weight data, bending length data and the stiffness data for Series 16 are shown in Table 8.19, Table 8.20 and Table 8.21 respectively in the Appendix. The tables also show data for untreated, DMDHEU treated, carboxymethylated only and cationized only samples. The effects of ammonium chloroacetate concentration and nitrogen content on flexural rigidity are shown in Figure 4.24 and Figure 4.25.

Table 8.19 shows that the basis weight increased after the treatment. The increase could be due to reaction with CHTAC, and/or due to shrinkage involved in the treatment with NaOH (during carboxymethylation) and addition of molecules during reaction with chloroacetate.

The basis weights of the samples were slightly more than the untreated control after reaction with CHTAC and increased with the increase in CHTAC concentration. This increase was mainly due to the reaction of cellulose chains with heavier CHTAC molecules. The basis weights of the samples increased enormously after carboxymethylation reaction following treatment with CHTAC. The increase for the specific CHTAC concentration did not change significantly as the chloroacetate concentration increased. This indicated that the increase was mainly due to the shrinkage caused by NaOH treatment during carboxymethylation. The reaction of chloroacetate with cellulose did not contribute significantly. In almost all the cases, the basis weights were slightly more or equal weights to the carboxymethylated only samples. The slight increase over the carboxymethylated samples was due to the synergistic effect caused by the reaction with bulkier CHTAC molecules. The basis weights were slightly more in few of the Series 16 samples than those

in Series 15 samples. This may be due to increased reaction of chloroacetate molecules caused by attraction of the existing quaternized groups on the fibers.

The cationized only samples showed higher stiffness values than the untreated control (Table 8.21). The stiffness increased as the nitrogen content on the fabric increased. The rise in stiffness was up to 4.54 times over the control. The carboxymethylation treatment alone increased the stiffness up to 37 times over the controls. The cross-linked samples showed more stiffness than the control, cationized/carboxymethylated only or DMDHEU treated samples. The stiffness increased up to 85 times over the blanks. The flexural rigidity values were more than the values obtained for Series 15 (Table 8.18)

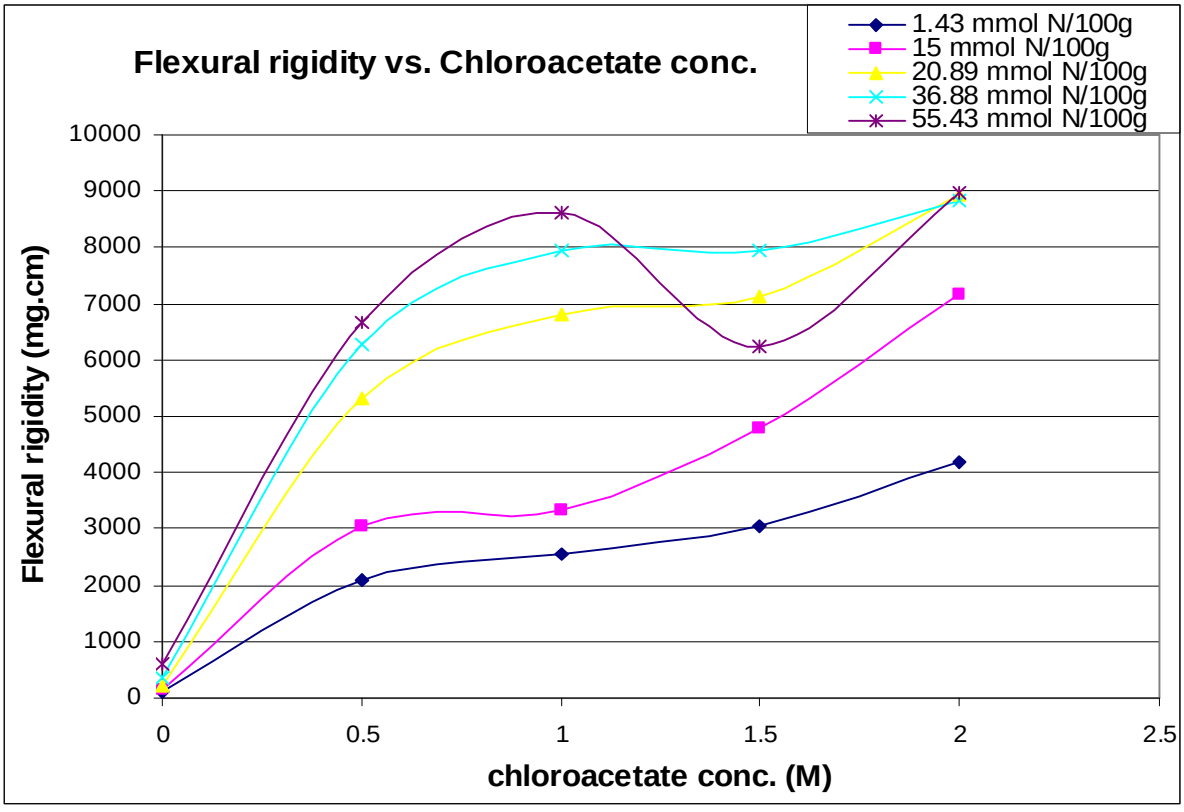


Figure 4.24 Effect of ammonium chloroacetate concentration and nitrogen content on the stiffness of Series 16 samples

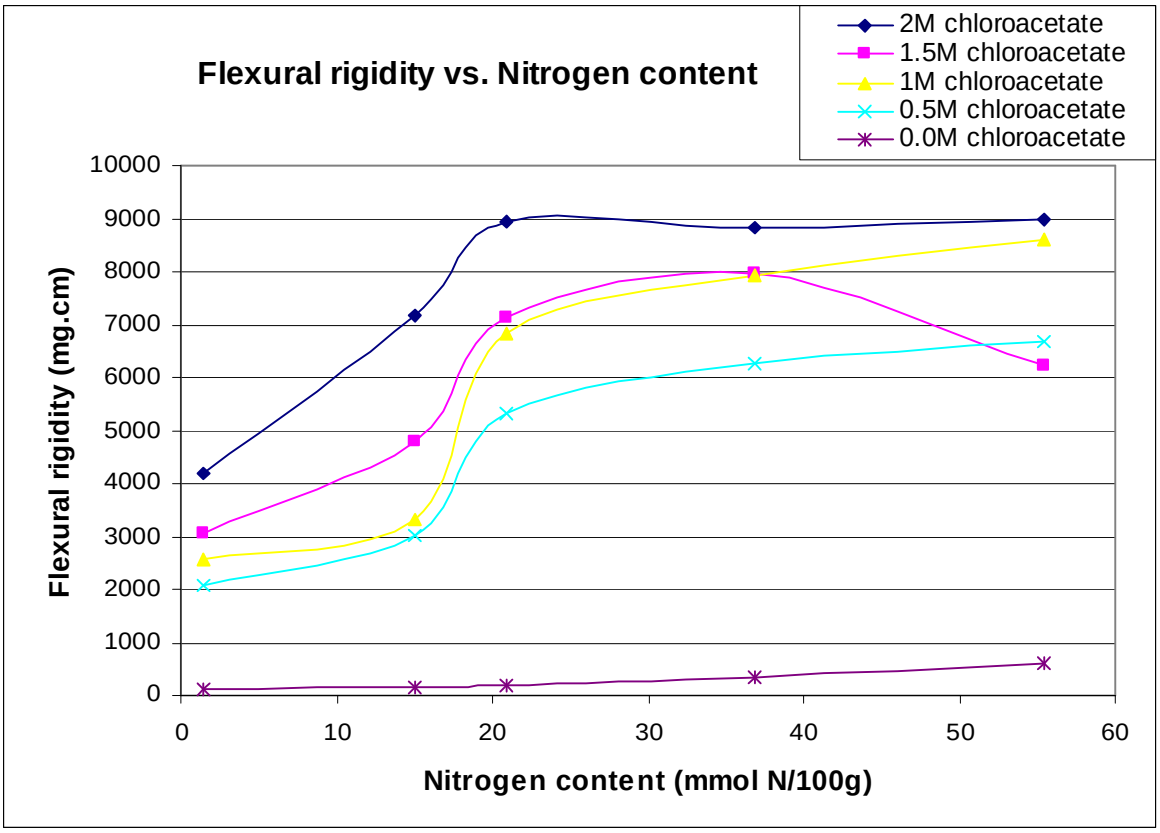


Figure 4.25 Effect of nitrogen content and carboxymethyl content on the stiffness of Series 16

Figure 4.24 shows that as the chloroacetate concentration of the samples increased the flexural rigidity, for the particular nitrogen content, increased. We assume that the anionic content of the samples would increase with the chloroacetate concentration. The rise in rigidity is steep at the low chloroacetate concentration and higher nitrogen content. It increases with lesser slope at low chloroacetate concentration and low nitrogen contents. At higher values of nitrogen content and higher chloroacetate concentration the rigidity values showed smooth increase. These values were more than the values at low nitrogen contents and high chloroacetate concentration.

The above observation can also be seen in Figure 4.25. It shows that as the chloroacetate concentration increased the stiffness values increased. For a specific value of chloroacetate concentration, the stiffness values increased as the nitrogen content increased.

At higher nitrogen contents and higher chloroacetate concentrations the values increased smoothly with a less steep slope.

The increase in stiffness values with the ionic content of the fabric could be explained as in 4.6.1 on the basis of extended and coiled structures of the cellulose chains. A method to find the anionic contents of the samples in Series 16 would further facilitate this explanation.

4.7 Tensile strength and Elongation at break

Tensile strength was tested for samples in Series 15 and Series 16. This test was carried to observe qualitatively if the samples performed better than the untreated control and the DHDHEU treated samples. Tensile strength tests of carboxymethylated/cationized only samples were also run.

4.7.1 Tensile strength and elongation at break of DMDHEU treated fabrics

Untreated control had the strength of 47.28 lbf. DMDHEU treated sample had strength of 31.15lbf. Thus it showed strength loss of about 34% compared to the control. It also showed reduction in elongation at break values by 72.72%.

4.7.2 Tensile strength and elongation at break for samples obtained by CHTAC treatment of anionic cellulose (Series 15)

The strength data for the samples that were untreated, carboxymethylated, cationized and DMDHEU treated is shown in Table 8.22 in the Appendix.

Since the test was performed with only two specimens in warp direction for each sample, the data was only qualitatively analyzed. The samples that were cationized only showed strength loss 2.64%-21.62% over blanks. Carboxymethylated samples not treated with CHTAC showed a strength gain up to 51.14% over control. The maximum strength of

the carboxymethylated sample was found to be 71.46 lbf. Samples 15C, 15E and 15H broke at the grips while testing and hence were not used for analysis. Most of the Series 15 samples showed either equal or slight increase in the strengths compared to the carboxymethylated (not treated with CHTAC) samples. The gain was up to 9.26% more over highest strength value of the carboxymethylated sample. This may be possibly due to ionic cross-linking. There was not very significant difference amongst all the strength values considering the standard deviations. The overall gain by the treatment was up to 65.14%. Table 8.23 and Figure 4.26 show the strength data for Series 15. Figure 4.26 also includes data for samples named in Table 8.22.

The samples that were only cationized showed reduction in elongation at break up to 45.45% over blanks. Carboxymethylated but not treated with CHTAC samples showed a gain in elongation at break from 64.34 to 92.2% over the untreated control. The maximum elongation at break of the carboxymethylated sample was found to be 14.8cm. Most of the Series 15 samples showed either equal or slight increase compared to the carboxymethylated (not treated with CHTAC) samples. The gain was up to 10.14% more over the highest value shown by the carboxymethylated samples. There was not very significant difference amongst all the samples for their breaking lengths considering the standard deviations. The overall gain due to the treatment was up to 111.69%. Table 8.23 and Figure 4.27 show the breaking lengths for Series 15. Figure 4.27 also includes data for samples named in Table 8.22.

The presence of carboxymethyl groups along with the changes in the physical crystalline structure of the fibers due to the action of strong alkali (NaOH) (during carboxymethylation) treatment explain the gain in strength and elongation at break. The strength gain (compared to the control sample) is very significant against the loss in strength

for the DMDHEU treated samples. In the DMDHEU treated samples rigid covalent bonds are formed which reduce the movement of yarns relative to each other leading to strength loss. Additionally, the strength loss is due to the depolymerization of cellulose chains in the presence of acid catalyst used in the treatment. In the above ionic cross-linked samples, the ionic bonds formed allow for the fibers to slide pass each other by breaking the ionic bonds. This leads to improvement in the strengths.

The ionic cross-linked samples show more elongation at break indicating improved flexibility over the untreated control. This flexibility additionally supports the relative movement of the cellulose chains to line up and become firmer under the applied force. This lining up resists much higher force giving higher strength gains to the treated samples.

Thus, in summary qualitatively strengths and elongation at break were improved compared to the untreated controls and DMDHEU treated samples.

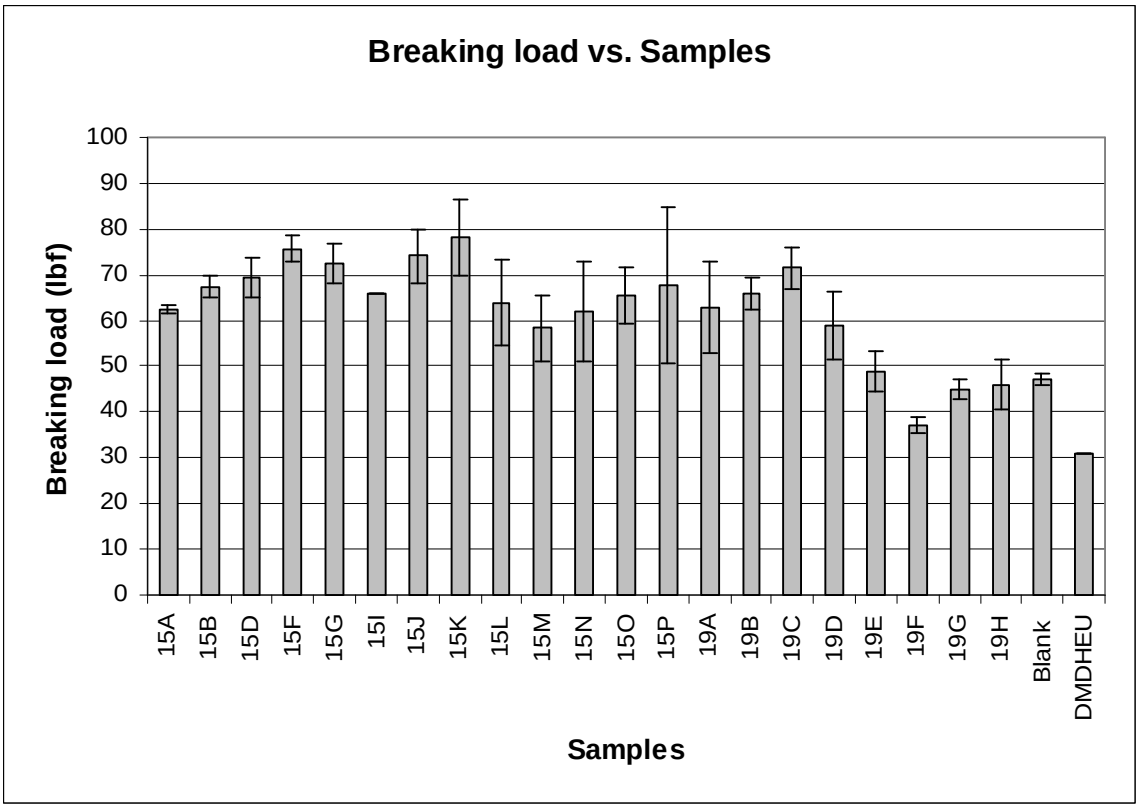


Figure 4.26 Tensile strength data for Series 15, and untreated, cationized, carboxymethylated and DMDHEU treated samples

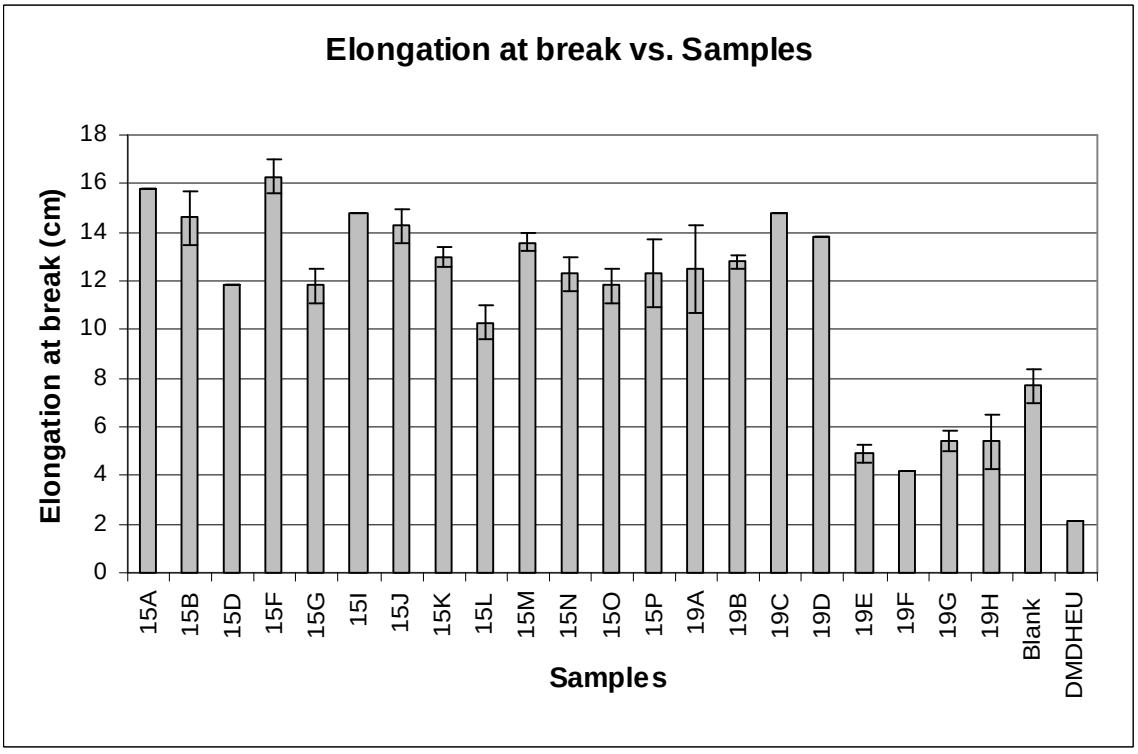


Figure 4.27 Elongation at break data for Series 15, and untreated, cationized, carboxymethylated and DMDHEU treated samples

4.7.3 Tensile strength and elongation at break for samples obtained by carboxymethylation of cationic cellulose (Series 16)

The strength data for the samples that were untreated, carboxymethylated, cationized and DMDHEU treated is shown in Table 8.22 in the Appendix.

Since the test was performed with only two specimens in warp direction for each sample, the data was only qualitatively analyzed. Samples 16C, 16D, 16F and 16H broke at the grips while testing and hence were not used for analysis. Most Series 16 samples showed either equal or slight increase in the strengths compared to the carboxymethylated (not treated with CHTAC) samples. The gain was up to 27.59% more over the highest strength value shown by the carboxymethylated sample. This may be possibly due to ionic cross-linking. This value is more than seen in Series 15. There was not very significant difference amongst all the strength values for the samples considering the standard deviations. The overall gain due to the treatment compared to the control was 92.85%. Table 8.24 and Figure 4.28 show the strength data for Series 16. Figure 4.28 also includes data for samples named in Table 8.22.

The samples that were only cationized showed reduction in elongation at break up to 45.45% over blanks. Carboxymethylated but not treated with CHTAC samples showed a gain in elongation at break from 64.34% to 92.20% over the untreated control. The maximum elongation at break of any carboxymethylated sample was found to be 14.8cm. All of the Series 16 samples showed increased values compared to the carboxymethylated (not treated with CHTAC) samples. The gain was up to 58.78% more over the highest value shown by the carboxymethylated samples. These values are much higher than those in Series 15. There was no significant difference amongst most samples, except a few, for their breaking lengths

considering the standard deviations. The overall gain due to treatment over control was up to 205.2%. Table 8.24 and Figure 4.29 show the breaking lengths for Series 16. Figure 4.29 also includes data for samples named in Table 8.22.

The behavior of the treated samples compared to the DMDHEU treated samples could be explained similarly as in section 4.7.2 based on the rigid covalent bonds vs. flexible ionic bonds, depolymerization of cellulose chains and improved elongation at break.

As seen in Series 15, all the samples in Series 16 showed better tensile strengths and elongation at break compared to the untreated control and DMDHEU treated samples.

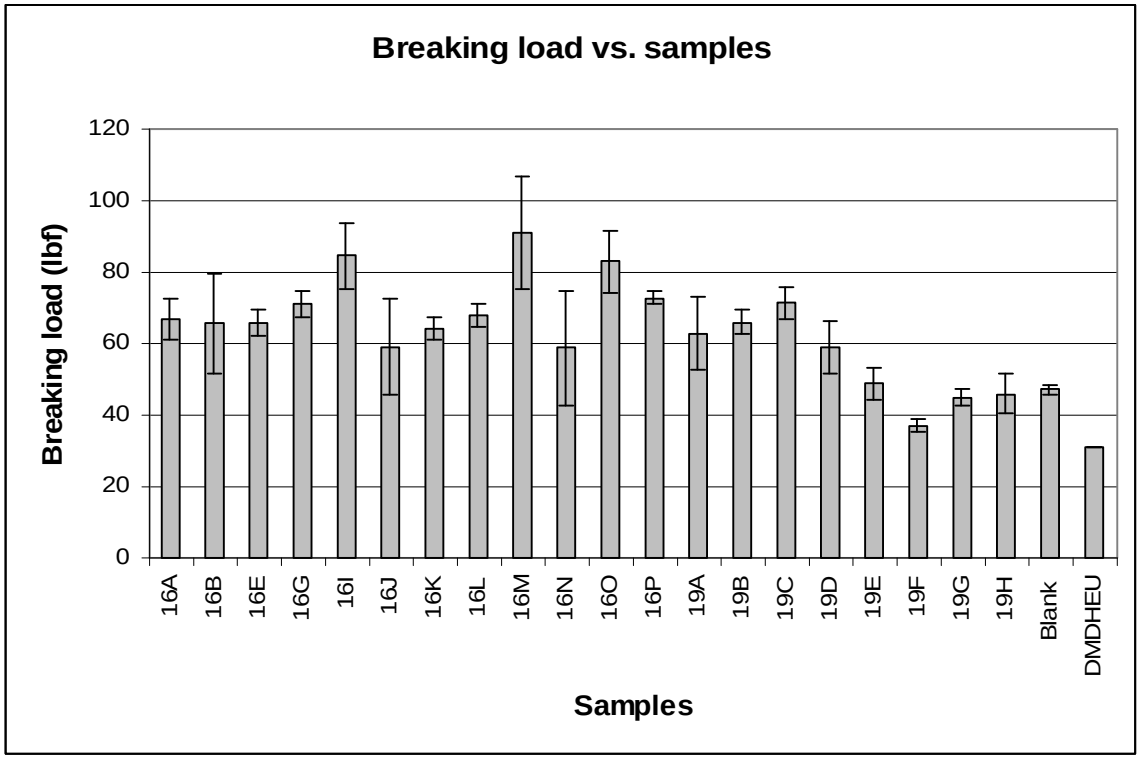


Figure 4.28 Tensile strength data for Series 16, and untreated, cationized, carboxymethylated and DMDHEU treated samples

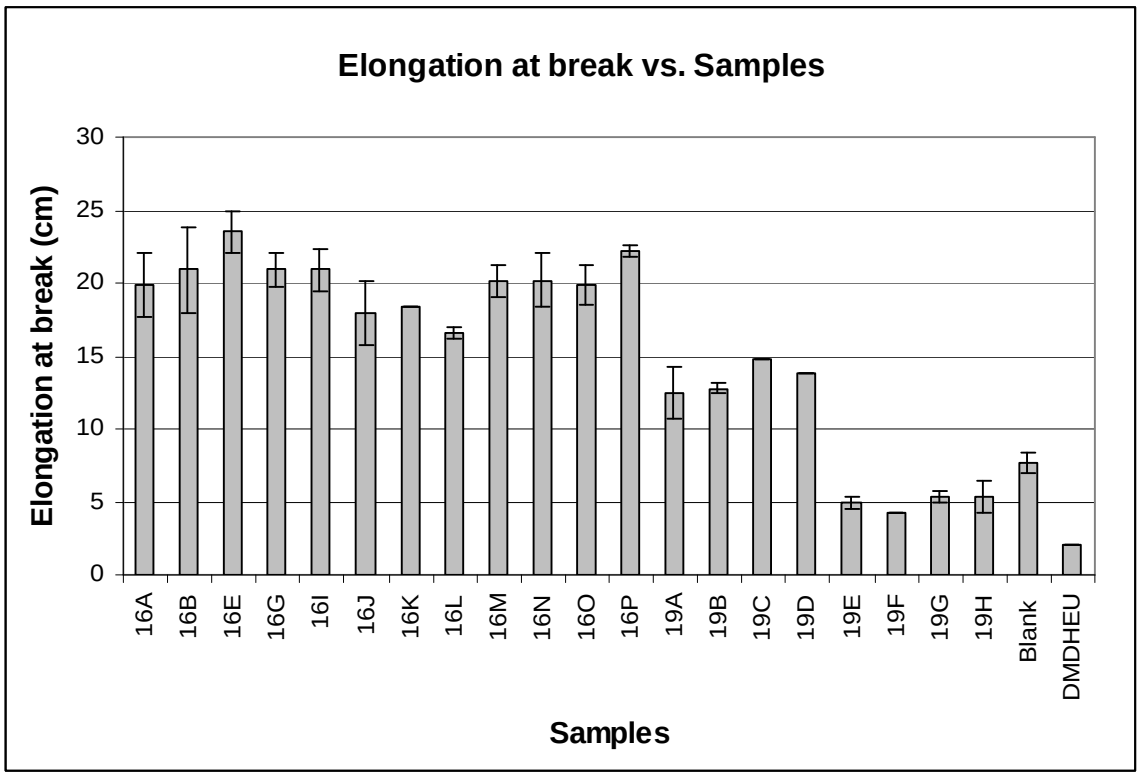


Figure 4.29 Elongation at break data for Series 16, and untreated, cationized, carboxymethylated and DMDHEU treated samples

4.8 CIE whiteness index (WI)

CIE whiteness index was measured for the untreated, carboxymethylated (not CHTAC treated), CHTAC treated (not ammonium chloroacetate treated), DMDHEU treated, and Series 15 and Series 16 samples.

4.8.1 CIE Whiteness index of DMDHEU treated samples

The CIE Whiteness index of the DMDHEU treated sample was found to be 73.15. The value for untreated control was 84.34. Thus the DMDHEU treatment reduced the whiteness index by 13.27%. This decrease was due to degradation of cellulose causing yellowing at high cure temperatures.

4.8.2 CIE Whiteness index for samples obtained by CHTAC treatment of anionic cellulose (Series 15)

The CIE whiteness index data of the untreated, DMDHEU treated, carboxymethylated/CHTAC treated, and CHTAC treated carboxymethylated samples are shown in Table 8.25 in the Appendix. Table 8.25 shows that the samples that were only CHTAC treated showed a decrease up to 79.52% over the untreated control. The WI decreased with the concentration of CHTAC. The treatment with the ammonium chloroacetate alone reduced the WI over control up to 23.8%. The WI reduced slightly with the anionic content. All the samples that were CHTAC treated following carboxymethylation showed lower values than the untreated control. All the samples that were cationized after carboxymethylation, showed higher WI than the cationized only samples with the few exceptions of 15H, 15L, 15O and 15P. The values were below the anionic (not CHTAC

treated) samples. Thus the chloroacetate treatment prevented the decrease in WI up to the values for cationized samples.

All the treated samples of Series 15 showed decrease in whiteness index. The decrease was up to 97.8%. The effect of carboxymethyl content and nitrogen content on WI is shown in Figure 4.30 and Figure 4.31. For specific nitrogen content, WI increased with the carboxymethyl content initially and then leveled off. As the nitrogen content increased, the WI decreased at a particular anionic content.

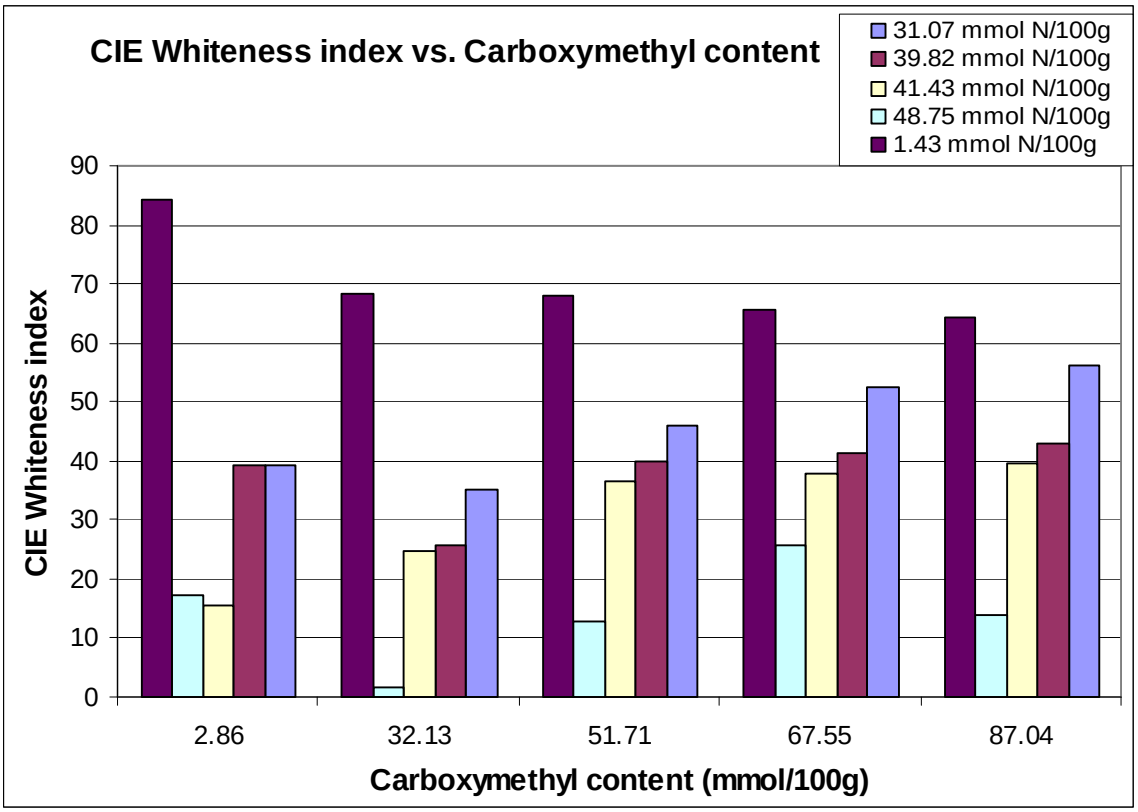


Figure 4.30 Effect of carboxymethyl content and nitrogen content on the WI of Series 15

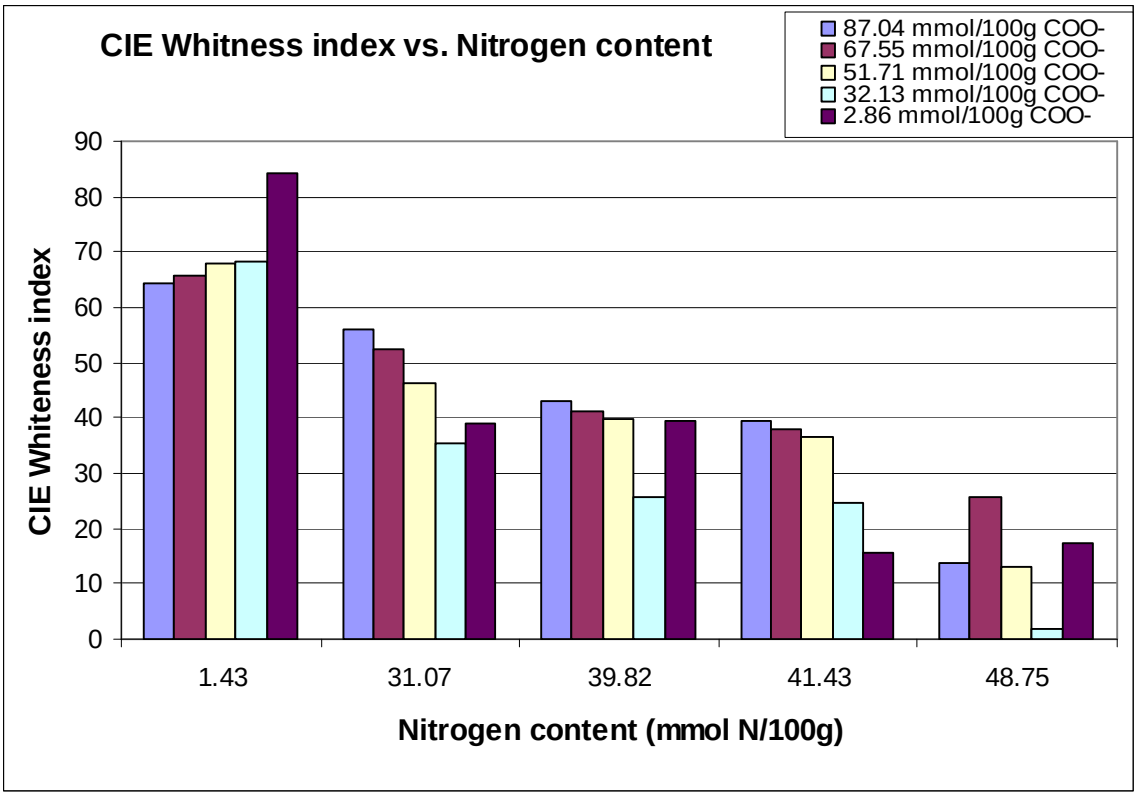


Figure 4.31 Effect of nitrogen content and carboxymethyl content on WI of Series 15

The WI of the treated samples was lower than the DMDHEU treated samples. The WI decreased as the total ionic content of the sample increased, that is, as the chloroacetate and CHTAC concentration increased. The decrease in WI was mainly due to CHTAC treatment, which causes fabric yellowing. The decrease was to some extent also due to the high curing temperatures employed for CHTAC application.

4.8.3 CIE Whiteness index for samples obtained by carboxymethylation of cationic cellulose (Series 16)

The CIE whiteness index data of the untreated, DMDHEU treated, carboxymethylated or CHTAC treated, and carboxymethylated CHTAC treated samples is shown in Table 8.26 in the Appendix. Table 8.26 shows that the samples that were only CHTAC treated showed a decrease up to 79.52% over the untreated control. The WI

decreased with the concentration of CHTAC. The treatment with ammonium chloroacetate alone reduced the WI over control as much as 23.8%. The WI reduced slightly with the anionic content. All the samples that were carboxymethylated following CHTAC treatment showed lower values than the untreated control. All these samples showed higher WI than the cationized (but not chloroacetate treated) samples. The values were lower than the carboxymethylated only samples. Thus the chloroacetate treatment improved the WI of the cationized samples.

All the treated samples of Series 16 showed decrease in whiteness index. The decrease was up to 44.64% compared to the untreated control. The decrease was lower than that shown by Series 15 samples. We assign this to the difference in nitrogen contents of the samples in Series 15 and 16 for the same concentration of CHTAC used. Nitrogen contents of Series 15 samples were slightly more than those of respective samples in Series 16 (except when 1.1M CHTAC was used). This was due to the effect of the anionic nature of the samples in Series 15 during treatment with CHTAC. The reaction with CHTAC increased due to the attraction of the quaternized groups to the anionic cellulose chains. For 1.1M CHTAC concentration in Series 16, the WI values were more than those for respective Series 15 samples, which had lower nitrogen contents. We believe that this was due to the sequence of treatment followed in preparing the samples. The lower nitrogen contents of Series 15 samples for 1.1M CHTAC also implies that as the CHTAC concentration increased the effect due to attraction from anionic groups subsided. This observation was supported from the no change in nitrogen content values (at higher CHTAC concentration used) as the anionic content increased.

Thus, the nitrogen content and the sequence of treatment play a critical role on WI values. The effect of chloroacetate concentration and nitrogen content on WI is shown in Figure 4.32 and Figure 4.33. Figure 4.32 shows that CHTAC treatment decreased the WI to large values below the value for untreated control. The values decreased as the CHTAC concentration (hence the nitrogen content) of the samples increased (Figure 4.33). The chloroacetate treatment improved the whiteness index of these cationic samples to certain value and then leveled off for all concentrations of chloroacetate used.

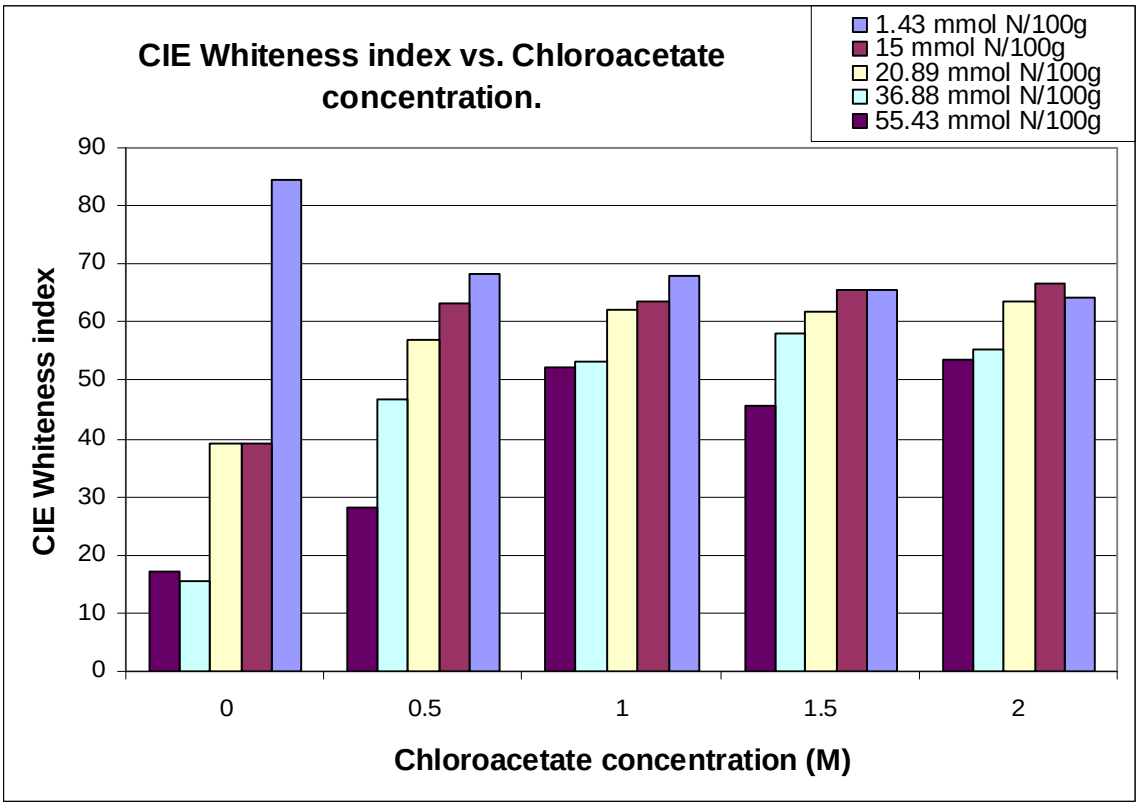


Figure 4.32 Effect of ammonium chloroacetate concentration and nitrogen content on the WI of Series 16

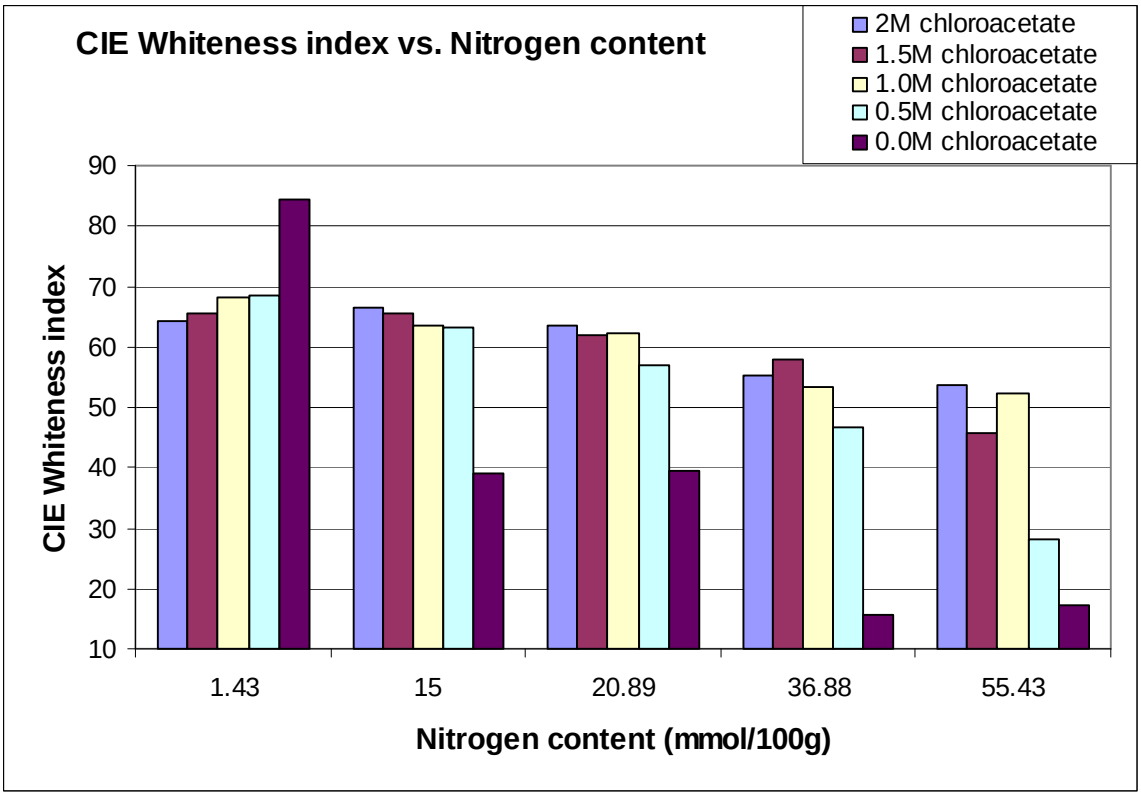


Figure 4.33 Effect of nitrogen content and ammonium chloroacetate concentration on WI of Series 16

The WI of the treated samples was lower than the DMDHEU treated samples. The WI decreased as the total ionic content of the sample increased, that is, as the chloroacetate and CHTAC concentration increased. The decrease in WI was mainly due to CHTAC treatment, which causes fabric yellowing. The decrease was to some extent also due to the high curing temperatures employed for CHTAC application.

5 Conclusions

Conventional DP finishes use formaldehyde-based chemicals, which are known for formaldehyde release and strength loss of the fabric. Ionic cross-linking of cotton cellulose can be a potential solution for DP finish free of formaldehyde and strength loss of the fabric. There are several alternatives to form ionic cross-links. For example, fabric can be made anionic with salt of mono chloroacetic acid (carboxymethylation) and then subjected to 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) (cationization) to form cationic sites (method 1) or by making the fabric cationic with CHTAC followed by reaction with salt of mono chloroacetic acid (method 2). Mixture of CHTAC and salt of mono chloroacetic acid (method 3) can also be used to make cellulose anionic and cationic simultaneously. Zwitter ionic cellulose chains are successfully formed in all the treatments. The adjacent oppositely charged sites on the cellulose chains bind to form inter or intra ionic bonds. The charged sites, being anchored to the cellulose backbone via covalent bonds, are durable to washing.

The ionic cotton cellulose from these treatments showed improvements in wet WRA and increase in tensile strength. Wet WRA improved up to 53° over the untreated fabric by method 3, whereas the values for method 1 and method 2 were 54° and 49° respectively. DMDHEU treatment showed an increase of 92°. Although, increases in angles were not comparable to DMDHEU treated samples, the process has shown promise towards improving the WRA performance via ionic cross-linking. The dry angles produced with ionic cross-linking were lower in all the cases compared to the untreated blanks. The improved performance in the wet form was assigned to the swollen state of the fabric imparting increased mobility to the ionic chains to form cross-links. The stiffness values for the treated

samples were higher than the untreated fabric. The values for DMDHEU treated fabric were 1.5 times of the untreated fabric. On the other hand, highest values for ionic cross-linked samples were over 85 times of the untreated fabric, the values for method 1 being lower by 25% than method 2. This was attributed to the stiffer entangled structure of the ionic cellulose chains against the extended conformation in the untreated form. DMDHEU treatment showed strength loss up to 34%, whereas all ionic cross-linked samples gained strength. A gain of 92% was shown by method 1. Method 2 showed an increase up to 65%. Ionic cross-linked samples showed higher elongation than the resin treated and untreated fabric. Resin treatment reduced the elongation at break by 72%, whereas improved values over 111% and 205% were observed for method 1 and method 2 respectively. The gains in tensile strengths and elongation at break were mainly due to the presence of carboxymethyl groups and the physical crystalline changes induced in the fibers by the NaOH treatment during carboxymethylation. The whiteness index of resin treated fabric was 13% lower than the untreated fabric. Treatments with method 1 and method 2 decreased whiteness over 97% and 44% respectively which is known to occur due to yellowing by CHTAC treatment.

Optimal conditions for fabric treatment using a 2-step pad-dry-pad-cure route were critical. Ammonium carbonate, due to its associated ease of ammonia liberation in the curing step, was selected as a neutralizing agent for mono chloroacetic acid. Drying after padding with NaOH in step 1 was necessary to prevent its wash off in following steps and it was further reduced with no soak in ammonium chloroacetate bath in step 2. Optimum NaOH concentration of 15-20% was a must for increased reaction efficiency. A linear increase in anionic content was observed with the ammonium chloroacetate concentration. Curing temperature was found to be a significant factor and curing time was not very critical. The

evaluation of the treatment with the confocal microscopy confirmed the occurrence of reaction in the fiber interior and the distribution of anionic sites across the fiber diameter. SEM images coupled with confocal microscopy were conclusive on the oval cross-sectional shape of the treated fibers by methods 1 and 2.

6 Recommendations for future work

The ionic cross-linking process has shown promise for a wrinkle resistant fabric as a replacement to the conventional formaldehyde based covalently bonded finishes.[2, 10, 34] The process is still far from commercialization. The inconsistencies in carboxymethylation and WRA results from person to person, poor dry WRA, and stiffness of the fabric are three main problems that need resolution. Though improvements in wet WRA are observed, they are not yet comparable to those produced with DMDHEU finished fabric, which dominates the DP finishing industry today.

The inconsistencies in results are observed mainly in the carboxymethylation treatment and in measurement of WRA. Carboxymethylation process needs training for consistency and reproducibility of results is difficult without practice. Well-defined procedures based on the results presented in this work and previous studies should be designed and followed to produce fabric with the desired anionic content, and process intricacies must be well understood. The inconsistency in WRA is mainly due to the test method used for the measurements. The method is susceptible to human variations and varies from person to person and time to time. In the work presented here, samples were tested with outmost care to eliminate the errors due to conditions of testing by following the AATCC test procedure strictly. Another method such as DP rating may be used as a replacement for WRA measurements. A more reliable method is the most urgent need for the characterization of future research on ionic crosslinking for wrinkle resistant fabric.

The problem of poor dry WRA is thought to be due to formation of ionic bonds in the wet state. An attempt was made in this research to form ionic bonds in the dry state using ammonium carbonate as neutralizing agent for mono chloroacetic acid, which would

eventually facilitate ammonia liberation during the curing step and aid formation of ionic bonds. The attempt was not very successful for being subdued by the increased stiffness of the fabric reducing the dry recovery angles. Another reason for the observed dry angles was thought to be the test method. The testing method for dry angles subjects the specimens to stresses that are thought to break the formed ionic bonds in the creased regions and form new ones which hold the fabric in the creased state. The validity of this hypothesis could be evaluated by designing a peel test. The reduced dry WRA may also be affected from the changes in crystalline structure of cellulose occurring in the treatment. Techniques like X-ray diffraction could be used to determine these changes and correlate them with the observations.

The ionic cross-linking process produced excellent results when a fabric with very low wet/dry WRA in the untreated state was used for the treatment.[3] The improvements were not significant if these WRA were high without treatment. The reasons for this behavior are unknown to us. The fabric performance also varies depending on factors such as weave structure. A plain weave fabric performed better than the one with a twill weave.[10] Based on this observation, it is suspected that factors such as fabric and yarn structure, which have not been focused on as significant parameters by us or any other research group to our knowledge, play key roles on the WRA performance. These factors need further evaluation.

In order to use the fabric produced by the ionic cross-linking process for apparel purposes, the stiffness of the fabric needs to be reduced. This may be achieved by applying cationic, anionic or non-ionic softeners to the treated fabric. Alternatively, a different approach of synthesizing a precondensate of softener and cationic/anionic agent may be considered.

The explanation of the trends observed in WRA performance in this research demands the knowledge of distribution of the charged species along and across the fiber, their density, location and their electrostatic behavior like repulsion and attraction. The distribution of charged species across the fiber cross-section could be determined by confocal microscopy, whereas their density on the surface and in the interior could be studied by using techniques[53] that employ polyelectrolytes that adsorb either on surface or penetrate into the bulk.

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Appendix

8 Appendix

Table 8.1 Design of experiment s for PDPC

Sample name.	NaOH Concentration (M)	Ammonium chloroacetate (CAA) concentration (M)	CAA soak time (min)	Curing temp. (°C)	Curing Time (min)	NaOH conc^2	C00$^-$ (mmol/100g)
13A	3	3	1	110	15	9	69.17
13B	9	3	20	50	5	81	39.7
13C	6	2	10.5	80	10	36	105.11
13D	3	1	20	110	15	9	35.4
13E	3	1	20	50	5	9	19.18
13F	9	3	1	110	5	81	129.22
13G	3	3	20	110	5	9	27.78
13H	3	3	1	50	5	9	17.72
13I	3	1	1	110	5	9	33.33
13J	9	1	20	50	15	81	46.33
13K	3	3	20	50	15	9	25.16
13L	3	1	1	50	15	9	22.63
13M	6	2	10.5	80	10	36	90.2
13N	9	1	20	110	5	81	70.52
13O	9	3	1	50	15	81	98.73
13P	9	1	1	50	5	81	22.32
13Q	9	1	1	110	15	81	73.66
13R	9	3	20	110	15	81	164.24

Table 8.2 Experimental design for the 'Method of Mixture'

Sample name	CHTAC concentration (M)	Ammonium chloroacetate concentration (M)	Cure temperature (°C)	mmol N/100g	Wet WRA (degrees)	Dry WRA (degrees)
17A	1.10	1.0	120	10.36	194	129
17B	0.71	0.5	120	12.14	191	110
17C	0.36	0.5	100	11.07	190	115
17D	0.71	0.5	100	13.21	178	125
17^{E}	1.10	0.5	100	06.43	122	139
17F	0.36	1.5	100	15.71	197	114
17G	1.10	0.5	070	03.21	198	146
17H	0.36	1.0	100	12.50	198	106
17I	0.71	1.0	120	14.64	213	116
17J	0.36	0.5	120	10.36	201	124
17K	0.36	1.0	070	12.14	184	104
17L	0.71	1.0	100	13.57	207	101
17M	0.71	0.5	070	13.93	178	137
17N	0.71	1.5	100	13.57	182	101
17O	0.71	1.0	070	15.35	198	133
17P	1.10	1.5	100	10.36	196	116
17Q	1.10	1.0	070	15.00	200	164
17R	1.10	1.5	070	06.43	180	148
17S	0.36	0.5	070	12.14	190	171
17T	1.10	0.5	120	10.36	181	177
17U	0.36	1.5	070	16.43	206	168
17V	0.36	1.5	120	14.29	191	178
17W	0.71	1.5	120	14.64	209	185
17X	0.36	1.0	120	14.29	198	169
17Y	1.10	1.0	100	16.79	199	169
17Z	1.10	1.5	120	16.07	212	169
17A'	0.71	1.5	070	12.50	193	167

Table 8.3 Effect of mole ratio of NaOH to sodium chloroacetate on carboxyl content

Sample	NaOH/sodium chloroacetate mole ratio	Carboxymethyl content (mmol/100g)
1A	6:1	28.36
1B	3:1	16.64
1C	1:1	10.78
Untreated fabric	Water	02.86

Table 8.4 Effect of delay time to soaking after mixed solution was prepared on carboxymethyl content

Sample name	Delay Time to soaking (min)	Carboxymethyl content (mmol/100g)
2A	0	60.49
2B	8	63.12
2C	15	60.65
2D	30	59.48
2E	60	61.91
2F	120	58.80
2G	240	55.99

Table 8.5 Effect of soaking time on carboxymethylation

Sample name	Soaking Time (min)	Carboxymethyl content (mmol/100g)
3A	0	61.75
3B	2	60.96
3C	4	56.24
3D	8	60.67
3E	16	53.93

Table 8.6 Effect of NaOH concentration on carboxymethyl content

Sample name	NaOH concentration (%) in step 1	Carboxymethyl content (mmol/100g)
8A	0	06.97
8B	5	16.14
8C	10	13.66
8D	15	81.08
8E	20	98.41
8F	25	77.81

Table 8.7 Effect of addition of NaOH in step 2 bath on carboxymethyl content

Sample name	Concentration of NaOH in step 1(%)	Concentration of NaOH in step 2 added to ammonium chloroacetate bath (%)	Carboxymethyl content (mmol/100g)
9A	0	20	91.68
9B	5	15	64.92
9C	10	10	60.12
9D	15	5	05.88
9E	20	0	04.81
7B	20	0 (no soaking of sample in ammonium chloroacetate solution)	98.41

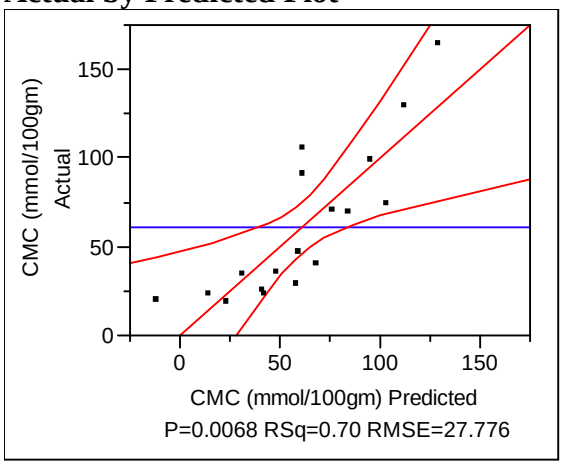
Table 8.8 Effect of curing time on carboxymethyl content

Sample name	Curing time (min)	Carboxymethyl content (mmol/100g)
10A	5	92.26
10B	10	97.62
10C	17	98.84
10D	25	99.78
10E	30	104.09

Table 8.9 Effect of ammonium chloroacetate concentration on carboxymethyl content (COO^-)

Day	Day 1 COO^- mmol/ 100g	Day 2 COO^- mmol/ 100g	Day 3 COO^- mmol/ 100g	Day 4 COO^- mmol/ 100g	Avg COO^- mmol/ 100g	COO^- Std Dev.
Concentrati -on of ammonium chloroaceta -te (M)						
2.0	85.77	86.95	87.5	87.95	87.04	0.94
1.5	61.56	68.07	70.84	69.78	67.56	4.17
1.0	50.35	50.76	49.07	56.66	51.71	3.38
0.5	30.41	32.77	29.15	36.19	32.13	3.10

Response carboxymethyl content (mmol/100gm)
Actual by Predicted Plot



Summary of Fit

RSquare	0.700562
RSquare Adj	0.575796
Root Mean Square Error	27.7756
Mean of Response	60.57778
Observations (or Sum Wgts)	18

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	21659.424	4331.88	5.6150
Error	12	9257.804	771.48	Prob > F
C. Total	17	30917.229		0.0068

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	11	9146.6504	831.514	7.4807
Pure Error	1	111.1540	111.154	Prob > F
Total Error	12	9257.8045		0.2784
				Max RSq
				0.9964

Parameter Estimates

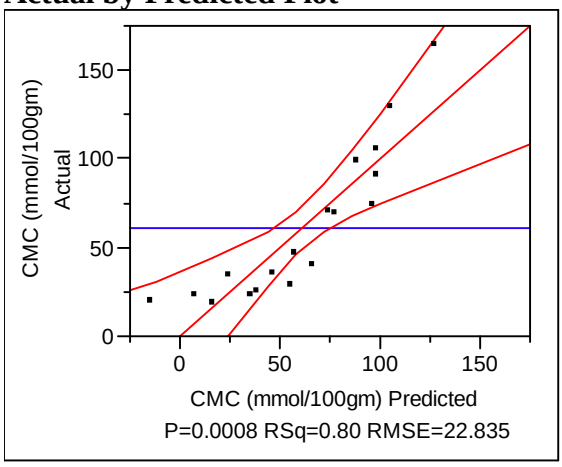
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	68.338715	7.410441	9.22	<.0001
NaOH concentration(3,9)	24.646875	6.943899	3.55	0.0040
CAA salt concentration(1,4)	23.282812	10.41585	2.24	0.0452
CAA soak time(1,20)	-2.404375	6.943899	-0.35	0.7351
Curing temp(50,110)	19.471875	6.943899	2.80	0.0159
Curing Time(5,15)	10.971875	6.943899	1.58	0.1401

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH concentration(3,9)	1	1	9719.4952	12.5984	0.0040
CAA salt concentration(1,4)	1	1	3854.8577	4.9967	0.0452
CAA soak time(1,20)	1	1	92.4963	0.1199	0.7351
Curing temp(50,110)	1	1	6066.4627	7.8634	0.0159
Curing Time(5,15)	1	1	1926.1127	2.4966	0.1401

Figure 8.1 Initial analysis of the effect of process parameters on the carboxymethyl content using Series 13 data

Response carboxymethyl content (mmol/100gm)
Actual by Predicted Plot



Summary of Fit

RSquare	0.797615
RSquare Adj	0.713288
Root Mean Square Error	22.83488
Mean of Response	60.57778
Observations (or Sum Wgts)	18

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	24660.049	4932.01	9.4586
Error	12	6257.180	521.43	Prob > F
C. Total	17	30917.229		0.0008

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	11	6146.0258	558.730	5.0266
Pure Error	1	111.1540	111.154	Prob > F
Total Error	12	6257.1799		0.3358
				Max RSq
				0.9964

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	272.26344	83.94924	3.24	0.0070
NaOH concentration(3,9)	191.49437	68.74209	2.79	0.0165
CAA salt concentration(1,4)	23.282812	8.563079	2.72	0.0186
Curing temp(50,110)	19.471875	5.70872	3.41	0.0052
Curing Time(5,15)	10.971875	5.70872	1.92	0.0787
NaOH concentration^2	-4.634653	1.902907	-2.44	0.0314

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
NaOH concentration(3,9)	1	1	4046.3554	7.7601	0.0165
CAA salt concentration(1,4)	1	1	3854.8577	7.3928	0.0186
Curing temp(50,110)	1	1	6066.4627	11.6342	0.0052
Curing Time(5,15)	1	1	1926.1127	3.6939	0.0787
NaOH concentration^2	1	1	3093.1209	5.9320	0.0314

Figure 8.2 Final analysis of the effect of process parameters on the carboxymethyl content using Series 13 data

Table 8.10 Effect of concentration of CHTAC on mmol N/100g fabric

CHTAC concentration (M)	**0.36**	**0.55**	**0.71**	**1.1**
Day 1	14.29	23.57	37.86	37.14
Day 2	15.71	17.50	39.64	35.36
Day 3	15.36	20.00	33.93	52.50
Day 4	14.64	22.50	36.07	59.28
Std. Dev.	0.65	2.71	2.45	11.70

Table 8.11 Nitrogen content (mmol/100g) for Series 15

CHTAC concentration (M)	**0.36**	**0.55**	**0.71**	**1.1**
Carboxymethyl content (mmol/100g)				
87.04	35.00	38.57	40.71	50.71
67.56	32.14	44.29	42.14	53.57
51.71	29.29	40.71	43.57	43.57
32.13	27.86	35.71	39.29	47.14
Std. dev.	3.17	3.61	1.84	4.34
Avg mmol N/100g	31.07	39.82	41.43	48.75

Table 8.12 Wet WRA (degrees) for Series 15 samples

CHTAC concentration (M)	**0.0**	**0.36**	**0.55**	**0.71**	**1.1**	**COO^- content (mmol/100g)**
Ammonium chloroacetate concentration (M)						
2.0	171	202	272	214	200	87.04
1.5	165	191	178	186	195	67.55
1.0	162	196	196	196	208	51.71
0.5	168	202	187	184	186	32.13
0.0	160	168	170	164	150	2.86
Avg mmol N/100g	1.43	31.07	39.82	41.43	48.75	

Table 8.13 Dry WRA (degrees) for Series 15 samples

CHTAC concentration (M)	**0.0**	**0.36**	**0.55**	**0.71**	**1.1**	**COO^- content (mmol/100g)**
Ammonium chloroacetate concentration (M)						
2.0	120	104	90	80	79	87.04
1.5	142	128	118	93	86	67.55
1.0	131	150	127	110	87	51.71
0.5	119	157	145	125	107	32.13
0.0	184	175	188	174	191	2.86
Avg mmol N/100g	1.43	31.07	39.82	41.43	48.75	

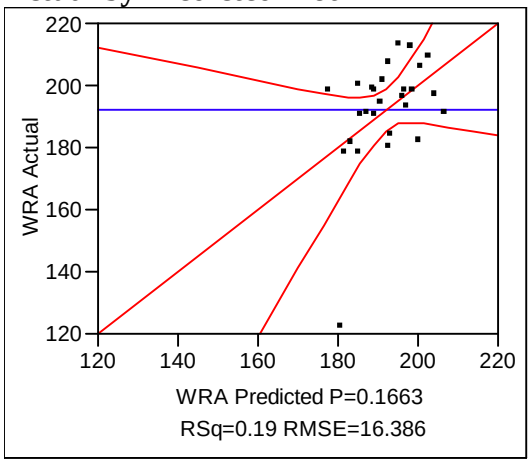
Table 8.14 Wet WRA (degrees) for Series 16 samples

CHTAC concentration (M)	0.0	0.36	0.55	0.71	1.1
Ammonium chloroacetate concentration (M)					
2.0	171	153	143	115	110
1.5	165	209	181	154	131
1.0	162	202	198	179	143
0.5	168	183	180	177	160
0.0	160	168	170	164	150
mmol N/100g	1.43	15	20.89	36.88	55.43

Table 8.15 Dry WRA (degrees) for Series 16 samples

CHTAC concentration (M)	0.0	0.36	0.55	0.71	1.1
Ammonium chloroacetate concentration (M)					
2.0	120	117	104	83	83
1.5	142	123	117	107	98
1.0	131	129	115	104	100
0.5	119	111	106	98	95
0.0	184	175	188	174	191
mmol N/100g	1.43	15	20.89	36.88	55.43

Response WRA
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.194425
RSquare Adj	0.08935
Root Mean Square Error	16.38586
Mean of Response	192.0741
Observations (or Sum Wgts)	27

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	1490.4347	496.812	1.8503
Error	23	6175.4171	268.496	Prob > F
C. Total	26	7665.8519		0.1663

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	174.06629	18.61844	9.35	<.0001
CR 2000 concentration	-11.11517	10.43326	-1.07	0.2978
CAA concentration	15.222222	7.724368	1.97	0.0609
Cure temp	0.1119883	0.153468	0.73	0.4729

Residual by Predicted Plot

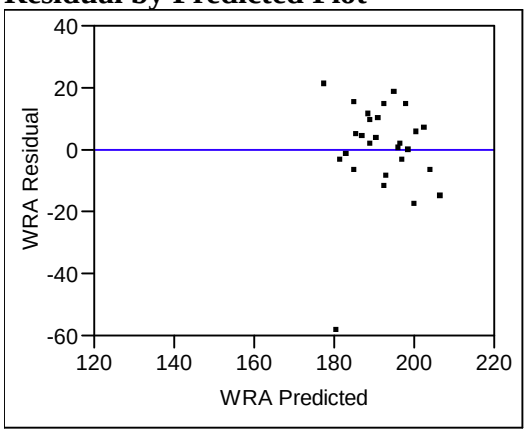


Figure 8.3 Analysis of the effect of process parameters on the WRA using Series 17 data

Table 8.16 Basis weight (mg/cm^2) data for Series 15

DMDHEU 12.76					
CHTAC concentration (M)	**0.0**	**0.36**	**0.55**	**0.71**	**1.1**
Ammonium chloroacetate concentration (M)					
2.0	17.51	18.90	18.43	18.67	18.15
1.5	17.34	17.19	18.47	19.32	17.83
1.0	17.18	18.40	16.42	18.07	17.83
0.5	17.20	16.81	17.13	17.10	17.66
0.0	11.90	12.14	12.01	12.53	12.81

Table 8.17 Bending length (cm) data for Series 15

DMDHEU 2.4					
CHTAC concentration (M)	**0.0**	**0.36**	**0.55**	**0.71**	**1.1**
Ammonium chloroacetate concentration (M)					
2.0	3.6	6.0	6.3	6.7	7.3
1.5	3.5	5.4	5.5	6.6	6.9
1.0	3.0	5.0	5.6	5.7	6.0
0.5	2.5	5.1	5.4	5.3	5.1
0.0	2.1	2.3	2.6	3.0	3.6

Table 8.18 Flexural rigidity (mg.cm) data for Series 15

DMDHEU 165.58					
CHTAC concentration (M)	**0.0**	**0.36**	**0.55**	**0.71**	**1.1**
Ammonium chloroacetate concentration (M)					
2.0	4172.01	4082.48	4607.28	5614.60	6918.25
1.5	3045.30	2631.65	3073.63	5428.27	5855.69
1.0	2557.11	2231.28	2883.68	3258.64	3754.75
0.5	2085.58	2164.64	2622.75	2474.20	2274.43
0.0	110.17	138.26	199.18	338.20	610.05

Table 8.19 Basis weight (mg/cm^2) data for Series 16

DMDHEU 12.76					
CHTAC concentration (M)	**0.0**	**0.36**	**0.55**	**0.71**	**1.1**
Ammonium chloroacetate concentration (M)					
2.0	17.51	19.60	21.63	21.75	21.71
1.5	17.34	18.74	21.24	22.69	21.71
1.0	17.18	19.00	19.05	20.00	22.11
0.5	17.20	20.39	18.45	20.36	20.75
0.0	11.90	12.14	12.01	12.53	12.81

Table 8.20 Bending length (cm) data for Series 16

DMDHEU 2.35					
CHTAC concentration (M)	**0.0**	**0.36**	**0.55**	**0.71**	**1.1**
Ammonium chloroacetate concentration (M)					
2.0	3.7	7.2	7.5	7.4	7.5
1.5	3.4	6.4	7.0	7.1	6.6
1.0	3.3	5.6	7.1	7.4	7.3
0.5	3.7	5.3	6.6	6.8	6.8
0.0	2.1	2.3	2.6	3.0	3.6

Table 8.21 Flexural rigidity (mg.cm) data for Series 16

DMDHEU 165.58					
CHTAC concentration (M)	**0.0**	**0.36**	**0.55**	**0.71**	**1.1**
Ammonium chloroacetate concentration (M)					
2.0	4172.01	7163.52	8944.79	8813.01	8972.83
1.5	3045.30	4797.23	7128.65	7949.99	6241.46
1.0	2557.11	3336.20	6816.65	7939.33	8599.97
0.5	2085.58	3035.93	5305.66	6262.63	6669.66
0.0	110.17	138.26	199.18	338.20	610.05

Table 8.22 Strength data for untreated, carboxymethylated, cationized and DMDHEU treated samples

Samples name	COO- content (mmol/100g)	N content (mmol/100g)	Tensile strength.(lbf)	Std dev.	Elong. At break (cm)	Std. dev.
19A	87.04	1.43	62.89	10.2	12.5	1.8
19B	67.55	1.43	65.95	3.31	12.8	0.3
19C	51.71	1.43	71.46	4.57	14.8	0.0
19D	32.13	1.43	58.94	7.42	13.8	0.0
19E	2.86	15.0	48.83	4.5	4.9	0.4
19F	2.86	20.89	37.06	1.63	4.2	0.0
19G	2.86	36.88	44.93	2.2	5.4	0.4
19H	2.86	55.43	46.03	5.57	5.4	1.1
Blank	2.86	1.43	47.28	1.27	7.7	0.7
DMDHEU	-	-	31.15	0.01	2.1	0.0

Table 8.23 Strength data for Series 15

Sample	Tensile strength.(lbf)	Std dev.	Elong. at break (cm)	Std. dev.
15A	62.4	0.72	15.8	0.0
15B	67.36	2.46	14.6	1.1
15C	60.01	2.57	11.8	0.0
15D	69.43	4.22	11.8	0.0
15E	50.86	0.46	17.1	0.4
15F	75.69	2.96	16.3	0.7
15G	72.54	4.48	11.8	0.7
15H	49.6	6.99	10.3	0.7
15I	65.99	0.0	14.8	0.0
15J	74.1	5.93	14.3	0.7
15K	78.08	8.41	13.0	0.4
15L	63.88	9.27	10.3	0.7
15M	58.34	7.13	13.6	0.4
15N	62.03	10.74	12.3	0.7
15O	65.32	6.1	11.8	0.7
15P	67.76	17.08	12.3	1.4

Table 8.24 Strength data for Series 16

Sample	Tensile strength.(lbf)	Std dev.	Elong. at break (cm)	Std. dev.
16A	66.88	5.62	19.9	2.2
16B	65.55	13.88	20.9	2.9
16C	65.42	1.67	24.5	0.7
16D	68.9	2.42	17.5	9.4
16E	65.79	3.84	23.5	1.4
16F	75.04	0.57	22.2	2.2
16G	71.1	3.55	20.9	1.2
16H	70.01	1.94	20.2	1.1
16I	84.69	9.22	20.9	1.4
16J	58.97	13.4	17.9	2.2
16K	64.39	3.11	18.4	0.0
16L	67.97	3.23	16.6	0.4
16M	91.18	15.68	20.2	1.1
16N	58.72	15.85	20.2	1.8
16O	82.98	8.65	19.9	1.4
16P	72.8	2.01	22.2	0.4

Table 8.25 CIE Whiteness index data for Series 15 samples, and untreated, DMDHEU treated and carboxymethylated or CHTAC treated samples

DMDHEU 74.22						
CHTAC concentration (M)	**0.0**	**0.36**	**0.55**	**0.71**	**1.1**	**COO^- content (mmol/100g)**
Ammonium chloroacetate concentration (M)						
2.0	64.27	56.05	42.96	39.49	13.71	87.04
1.5	65.62	52.4	41.33	37.88	25.6	67.55
1.0	68.12	46.12	39.78	36.48	12.9	51.71
0.5	68.38	35.26	25.59	24.56	1.86	32.13
0.0	84.34	39.14	39.28	15.59	17.27	2.86
Avg mmol N/100g	1.43	31.07	39.82	41.43	48.75	

Table 8.26 CIE Whiteness index data for Series 16 samples, and untreated, DMDHEU treated and CHTAC or carboxymethylated treated samples

DMDHEU 74.22					
CHTAC concentration (M)	**0.0**	**0.36**	**0.55**	**0.71**	**1.1**
Ammonium chloroacetate concentration (M)					
2.0	64.27	66.47	63.7	55.42	53.62
1.5	65.62	65.56	61.85	57.97	45.56
1.0	68.12	63.71	62.12	53.16	52.3
0.5	68.38	63.06	56.97	46.69	28.12
0.0	84.34	39.14	39.28	15.59	17.27
mmol N/100g	1.43	15	20.89	36.88	55.43