İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

IONIC CROSSLINKING OF COTTON FABRICS TO IMPROVE WRINKLE RECOVERY

Ph.D. Thesis by
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Department : Textile Engineering
Programme: Textile Engineering

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FOREWORD

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ABBREVIATIONS

AGU	: Anhydro Glucose Unit
ANOVA	: Analysis of Variance
BTCA	: 1,2,3,4-ButaneTetraCarboxylic Acid
CAA	: ChloroAcetic Acid
CC	: Cationized Chitosan
CG	: Cationic Glycerin
CH_4	: Methane
CHN	: Carbon Hydrogen Nitrogen
CHTAC	: 3-Chloro-2-Hydroxypropyl-Trimethyl Ammonium Chloride
CM	: Carboxymethyl
CO	: Carbon Monoxide
CO_2	: Carbon Dioxide
COO^-	: Carboxyl
DHDMI	: Dihydroxy Dimethyl Imidazolidinone
DMDHEU	: Dihydroxyethylene urea-formaldehyde
DMeDHEU	: Dimethyl Dihydroxy Ethylene Urea
DP	: Durable Press
EDTA	: Ethylene Diamine Tetraacetic Acid
EPTAC	: EpoxyPropyl Trimeethyl Ammonium Chloride
GTMAC	: GlycidylTriMethylAmmonium Chloride
H_2O_2	: Hydrogen Peroxide
HCl	: Hydro Chloric Acid
HEDTA	: N-(2-Hydroxyethyl) Ethylene Dinitrilo Triacetic Acid
HS+OD	: Hot Soaked and Oven Dried
HS+RT	: Hot Soaked and dried at Room Temperature
HTCC	: N-(2 Hydroxy) propyl-3-Trimethylammonium Chitosan
L.R.	: Liquor Ratio
NaOH	: Sodium Hydroxide
NTA	: Nitrilo riacetic acid Trisodium salt monohydrate
OT	: Optimum Treated
PB	: Pad-Batch
PC	: Pad-Cure
PCA	: PolyCarboxylic Acid
PDC	: Pad-Dry-Cure
PDPB	: Pad-Dry-Pad-Batch
PDPD	: Pad-Dry-Pad-Dry
S+OD	: Soaked and Oven Dried
SEM	: Scanning Electron Microscope
WRA	: Wrinkle Recovery Angle

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LIST OF SYMBOLS

C*	**:** Chroma value according to CIELAB Color Scale
h*	**:** Hue value according to CIELAB Color Scale
L*	**:** Lightness value according to CIELAB Color Scale
$\mathbf{N_{HCl}}$	**:** Normality of HCl used
$\mathbf{V_{blank}}$	**:** Volume of titrant used for blank
$\mathbf{V_{sample}}$	**:** Volume of titrant used for sample
$\mathbf{V_{titrant}}$	**:** Volume of titrant used
W,w	**:** Weight
$\mathbf{X_1}$, $\mathbf{X_2}$	**:** Design Factor Symbols

IONIC CROSSLINKING OF COTTON FABRICS TO IMPROVE WRINKLE RECOVERY

SUMMARY

Cotton fiber has a natural tendency to wrinkle. In order to overcome this undesired property of cotton several durable press finishes were proposed and have been used for a long while. However, most of these chemical finishes release formaldehyde, a suspected human carcinogen, and cause fabric to lose strength and to yellow. Non-formaldehyde alternatives to these finishes are expensive. Thus, a non-formaldehyde finish prepared by using common and more available chemicals is required. In this study, we prepared anionic cotton fabric by following 3 different carboxymethylation methods and further treated it with a novel crosslinker, namely cationic glycerin. We focused on optimizing ionic crosslinking process in terms of treated fabric's wrinkle recovery angle (WRA). We also tested our samples for strength, elongation, stiffness, smoothness, whiteness and nitrogen content. In order to investigate the effect of ionic crosslinking on dyeability, we dyed our treated samples with an acid and a basic dye. Our results showed that high WRA results may be achieved and strength of fabric may also be increased by ionic crosslinking. After ionic crosslinking treatment, elongation of cotton fabric was increased. Stiffness and smoothness of cotton fabric increased but to a limited extent. Dyeability of cotton with basic dyestuff got better as well. These results show that ionic crosslinking is a good alternative to conventional durable press finishes.

PAMUKLU KUMAŞLARIN BURUŞMAZLIK ÖZELLİKLERİNİN GELİŞTİRİLMESİ İÇİN İYONİK ÇAPRAZ BAĞLANMALARI

ÖZET

Pamuk lifinin buruşmaya karşı doğal bir eğilimi vardır. Pamuğun bu istenmeyen özelliğini gidermek için uzun süredir pek çok kalıcı ütü apreleri önerilmektedir ve kullanılmaktadır. Ancak, bu kimyasal aprelerin çoğu, kanser yapma ihtimali olduğundan şüphelenilen formaldehiti açığa çıkarırlar ve kumaşın mukavemet kaybetmesine ve sararmasına sebep olurlar. Bu aprelere alternatif olan formaldehitsiz kimyasallar pahalıdırlar. Bu nedenle, yaygın ve kolay ulaşılabilir kimyasallar kullanılarak hazırlanan bir formaldehitsiz apreye ihtiyaç vardır. Bu çalışmada, 3 farklı karboksimetilasyon yöntemi kullanarak anyonik pamuklu kumaş hazırladık ve daha sonra bunu katyonik gliserin adı verilen yeni bir çapraz bağlayıcı ile muamele ettik. Muamele edilen kumaşın buruşmazlık açısına göre iyonik çapraz bağlama işlemini optimize etmeye odaklandık. Numunelerimizi ayrıca mukavemet, uzama, sertlik, düzgünlük, beyazlık ve nitrojen miktarı için de test ettik. İyonik çapraz bağlamanın boyanabilirliğe etkisini incelemek için muamele ettiğimiz numunelerimizi bir asidik bir de bazik boya ile boyadık. Sonuçlarımız göstermektedir ki iyonik çapraz bağlama ile yüksek buruşmazlık açısı değerleri elde edilebilmektedir ve kumaş mukavemeti de artırılabilmektedir. İyonik çapraz bağlama muamelesinden sonra pamuklu kumaşın uzaması artmıştır. Pamuklu kumaşın sertliği ve düzgünlüğü artmıştır fakat bu sınırlı bir seviyededir. Ayrıca pamuğun bazik boyarmadde ile boyanabilirliği de artırılmıştır. Bu sonuçlara göstermektedir ki iyonik çapraz bağlama konvansiyonel kalıcı ütü aprelerine iyi bir alternatiftir.

1. INTRODUCTION

1.1 Introduction and Aim of Study

In this study, our aim was to show that ionic crosslinking could be a good alternative to conventional durable press finishing. We followed a designed experiment and optimized the ionic crosslinking process in terms of resulting fabric's wrinkle recovery angle (WRA). In previous studies, treating anionic cotton with cationic agents were shown to impart the highest WRA values on cotton fabric when ionic crosslinking was followed, but only one carboxymethylation method was used in these previous studies, a pad-dry-pad-batch (PDPB) method [1-3]. In our trials we used this method and two other alternative carboxymethylation processes, and investigated their effects on resulting WRA in an effort to decrease process time. One of these methods is pad-dry-pad-dry (PDPD) which is a shorter procedure. The other is pad-dry-cure (PDC) method, which is the shortest one but requires a high temperature step. We used cationic glycerin in our entire crosslinking trials. Cationic glycerin and cationic chitosan are the cationic agents that impart the highest WRA results but cationic glycerin has a lot of advantages when compared with cationic chitosan; it offers better breaking strength, whiteness and stiffness values [3]. It is also cheaper and more available. We also investigated the effects of ionic crosslinking on strength, elongation, stiffness, smoothness, whiteness, nitrogen content and dyeability with acid and basic dyes.

2. LITERATURE REVIEW

2.1 Cotton Chemistry

Cotton fibers are the purest form of cellulose which is the most abundant polymer in the nature. Almost 90% of the cotton fibers are cellulose. The cellulose in cotton fibers has the highest molecular weight among all plant fibers and the highest structural order, i.e., highly crystalline, oriented and fibrillar [4].

Cotton fibers are composed of mostly α-cellulose (88.0-96.5%). The noncellulosics are located either on the outer layers (cuticle and primary cell wall) or inside the lumens of the fibers whereas secondary cell wall is purely cellulose. The varieties of these are affected by growing environments (soil, water, temperature, pest, etc.) and maturity. The noncellulosics include proteins (1.3%), waxes (0.6%), pectins (1.2%), ash (1.2%), and other (1.7%) substances. In less developed or immature fibers, the non-cellulosic contents are much higher than the mature ones [4,5].

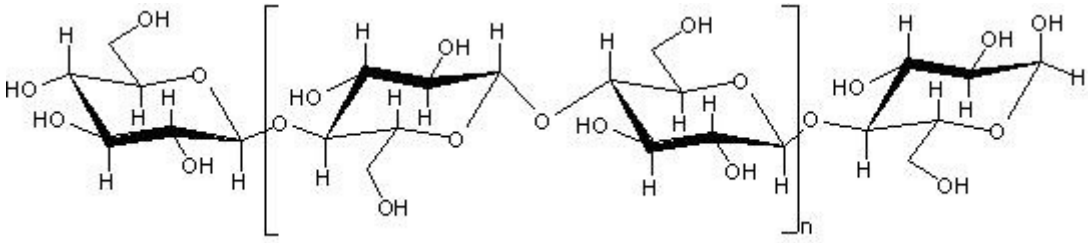

Figure 2.1 : Molecular structure of a cellulose polymer chain.

Cotton cellulose is highly crystalline and oriented. α-cellulose is distinct in its long and rigid molecular structure. The β-1,4-D(+)-glucopyranose building blocks in long cellulose chains are linked by 1,4-glucosidic bonds (see Figure 2.1). Free formation of the anhydrogluco-pyranose C-O-C link is prevented by steric effects. Each anhydroglucose contains three hydroxyl groups, one primary on C-6 and two secondary on C-2 and C-3. The abundant hydroxyl groups and the chain conformation allow extensive inter-molecular and intra-molecular hydrogen bonding to further improve the rigidity of the cellulose structure [4,6].

Effects of chemical reactions and heating on cellulose depends on the supermolecular structure and the activity of the C-2, C-3 and C-6 hydroxyl groups. Heat or reactions begin in the more accessible amorphous regions and the surfaces of crystalline domains. Chemical reactivity of the cellulose hydroxyl groups follows those of aliphatic hydroxyl groups, i.e., higher for the C-6 primary than the secondary on the C-2 and C-3. Etherification and esterification are the two main categories of reaction. Esterification reactions, such as nitration, acetylation, phosporylation, and sulfation, are usually carried out under acidic conditions. Etherification, on the other hand, is favored in an alkaline medium [4].

Oxidizing agents, such as hypochlorites, chlorus, chloric, and perchloric acids, peroxides, dichromates, permanganates, periodic acid, periodate salts, and nitrogen tetroxide readily attack cellulose. Most of these agents are not selective in the way they react with the primary and secondary hydroxyl groups. Oxidation of cellulose can result in two products, reducing and acidic oxycellulose. In reducing oxycellulose, the hydroxyl groups are converted to carbonyl groups or aldehydes, whereas in acidic oxycellulose, the hydroxyl groups are oxidized to carbonyl groups or acids. The oxycellulose can be further oxidized to acidic oxycellulose. Reducing oxycellulose is more sensitive to alkaline media and the chain lengths are often reduced. Periodic acid and periodate salts break the anhydroglucose ring between C-2 and C-3, converting the two secondary hydroxyl to aldehydes which can be further oxidized to carboxyl groups. Nitrogen tetroxide reacts specifically with the primary hydroxyl groups on C-6 and directly oxidizes it to carboxyl group or to polyglucuronic acid, an oxycellulose [4,6].

Dehydration and decomposition of cellulose are the general results of heating of cellulose. Presence of other compounds, the temperature and rate of heating affects these reactions. Presence of acid catalysts favor dehydration reactions whereas depolymerization reactions are favored by alkaline catalysts. Dehydration is favored by heating at low temperatures and subsequent char formation is enhanced. Higher temperature heating causes rapid volatilization via the formation of laevoglucosan and more gaseous combustible products are formed. Greater dehydration also reduces the yield of laevoglucosan and subsequently lowers the volatile species. For that reason, acid catalysts are especially important in order to impart flame retardancy to cellulose [4,5].

When cellulose is heated up to 120^{o}C, the moisture is driven off without affecting strength. Heating cellulose to 150^{o}C reduce viscosity and tensile strength which show that molecular weight is lowered. Between 200^{o}C and 300^{o}C, volatile products and liquid pyrolyzate, mainly 1,6-anhydro-β-D-glucopyranose, commonly known as levoglucosan, evolve. At 450°C, only char remains. 20% of total pyrolytic products is gaseous phase (CO, CO_2, and CH_4), 65% of them is the liquid phase (of which 80% is levoglucosan) and 15% of them is the char. The heating rate can influence the amount of char formation. Heating below 250°C only influences amorphous regions as no change in the crystalline structure has been found. The crystalline structure of cellulose has been shown to be lower when heated at 250^{o}C to 270^{o}C, and then disappear on further heating to 300^{o}C. Highly crystalline cellulose has been shown to decompose at higher temperatures, for instance 380^{o}C [4-6].

Depolymerization is prevented by blocking the primary hydroxyl groups of cellulose and production of volatiles are reduced as well. The reduction of flammable gases is accompanied by more complete intra-ring and inter-ring dehydration, giving rise to keto-enol tautomers and ethermic linkages, respectively. The carbonyl groups so formed can participate in a variety of reactions, leading to crosslinking, thus increasing char formation as well as carbon dioxide. The packing density of cellulose also affects the extent of levoglucosan formation. Higher yield of levoglucosan formation is reached when crystallinity in cotton is lowered by either mercerization or liquid ammonia. Cleavage of glucoside linkages form mono- and difunctional radicals. These radicals increases volatile products and levoglucosan [4].

2.2 Why does Cotton Wrinkle?

Wrinkles occur when fabrics are crushed during use and care like washing. Wrinkle recovery depends on crosslinks, which hold adjacent molecular chains together and pull them back into position after the fiber is bent, thus preventing the formation of a wrinkle. Fibers with strong intermolecular bonds have good molecular memory and resist wrinkling and creasing. Fibers with weak bonds wrinkle and crease readily.

Cellulosic fibers lack strong natural crosslinks. Their molecular chains are held together by weak hydrogen bonds and these bonds break with the stress of bending particularly when the fiber is wet. New hydrogen bonds are formed; they hold the fiber in this bent position and form a wrinkle as shown in Figure 2.2 [7].

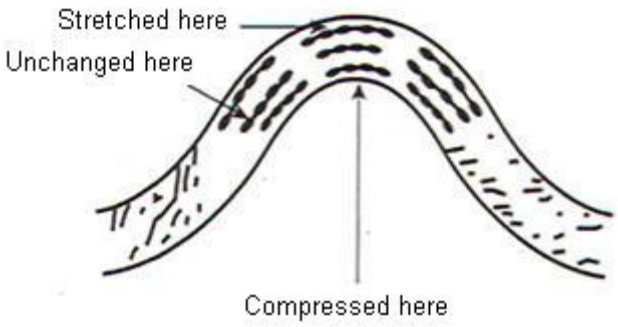

Figure 2.2 : Formation of wrinkle [7].

2.3 Anti-Wrinkle Finish of Cotton

2.3.1 Durable press finishing of cotton

Durable press finishes are an important treatment for cotton fabrics; they provide wrinkle resistant and permanent press performance for apparel. The cellulose chains are covalently bond together by crosslinking and these covalent bonds cannot be disrupted by water. The reaction steps of a typical crosslinking process are schematically shown in Figure 2.3. A dry fabric is impregnated with a mixture of crosslinking agents and reaction auxiliaries by means of a foulard. The fabric is mildly dried and then cured on special machines. The pre-polymers crosslink to form long chains of resin or link to the fiber surface. Initiation of condensation requires addition of acid and the reaction temperature has to be high [8].

Crosslinking processes may be classified into 2 groups according to the state of the fabric just before the reaction. First one of these is dry crosslinking process that is by far the most applied process. In dry crosslinking; a dry fabric is impregnated with a mixture of the polymer resin, auxiliaries and catalysts. It is then dried and cured to enable the condensation of the resins.

Second one is wet or moist crosslinking process, in which the cellulose fibers of the already wet fabric are swelled. The crosslinking agent is impregnated into the fabric in strong alkali or mineral acid medium. The overall product is left for nearly 24 hours in order to permit crosslinking. The effects of these 2 methods are quite different. The dry crosslinking reactions impart good constancy when wrinkled in the dry state but their stability is moderate after wetting. On the contrary, resin-free

crosslinking improves the wet wrinkle resistance, but the fabric tends to crease when dry [8].

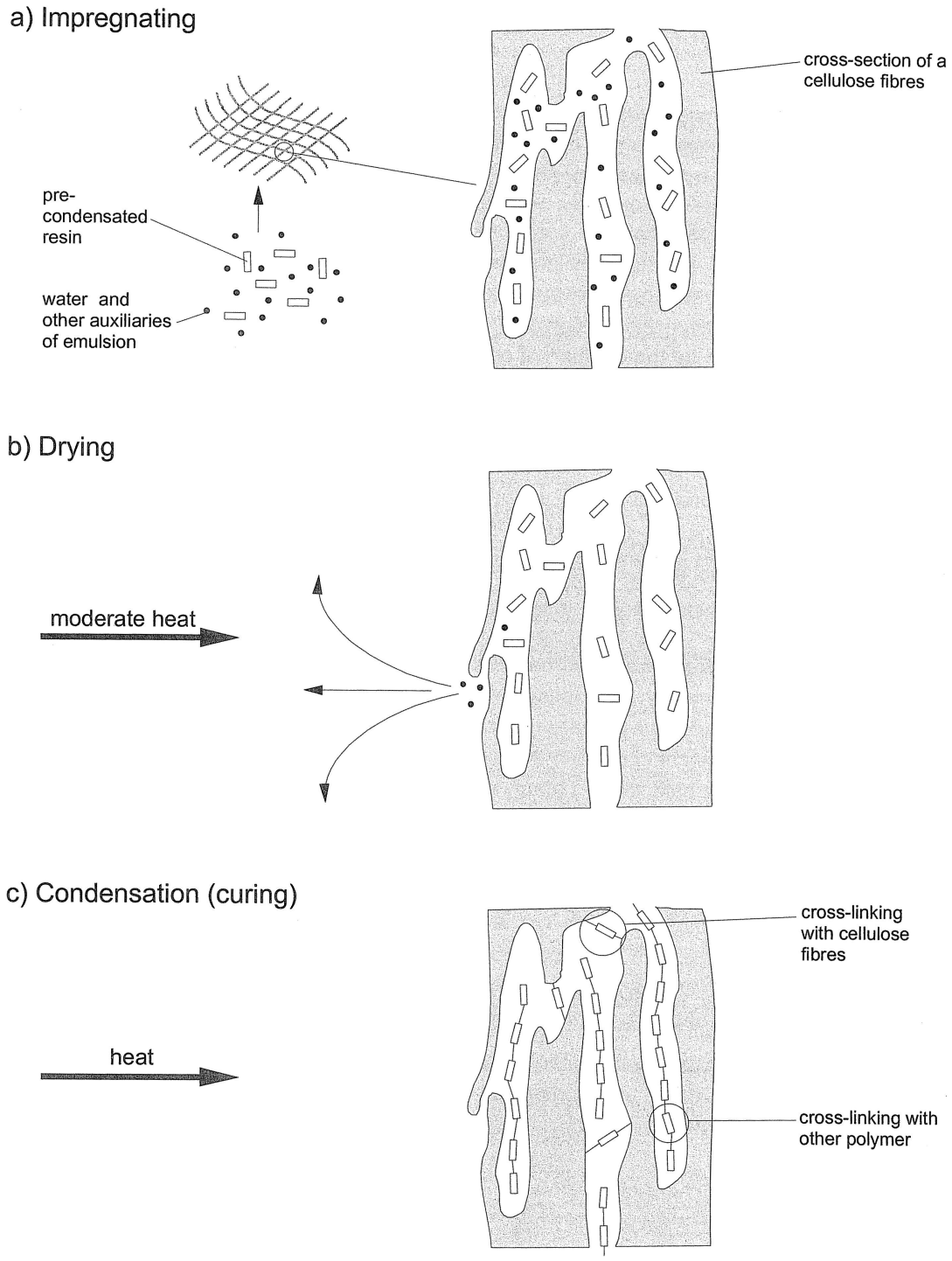

Figure 2.3 : Reaction scheme of a typical crosslinking process [8].

There are two types of products used in conventional durable press finishing; resin type and reactant type. Resin type products are the firstly commercialized ones.

2.3.1.1 Urea-formaldehyde derivatives

Use of amino resin finishing for the production of crease-resistant fabrics commenced in 1920s with the manufacture of simple urea-formaldehyde resins. After urea, a full range of products was developed. All of these products contain formaldehyde, such as urea-formaldehyde, highly condensated urea-formaldehyde, methylated urea-formaldehyde, melamine-formaldehyde, methylated melamine-formaldehyde, ethylene urea-formaldehyde, heterocyclic crosslinking agents based on melamine-formaldehyde, glycol based reactants and their derivatives. Urea-formaldehyde resins were very popular in 1940s. However, the fabric required washing off due to high free formaldehyde content of the resin. In 1950s methylated urea-formaldehyde resins came onto the market. They were applicable on nylon and when compared with urea-formaldehyde resins they had greater durability to washing, better shrink-stability of the treated fabric, and stability of the molecular size. Producing a stiff handle on synthetic fibers and giving high formaldehyde contents were some of the negative properties of urea-formaldehyde resins [9].

2.3.1.2 Melamine-formaldehyde derivatives

The next resin group commercialized was melamine resins. Among these, trimethylol melamins were the most popular ones. When compared with urea-formaldehyde resins, they give a fuller handle on cotton and viscose, but they were more expensive [9].

2.3.1.3 Methylol derivatives

To overcome the disadvantages of resin type products, reactant-type products were produced and they came in the market in the early 1960s. As a result of reacting only with the cellulose component, these products offered softer handle of blended fabrics. They had lower formaldehyde content, and required smaller amounts of resin to produce comparable results with resin formers. Unlike older resins that form a polymeric network within the fiber, reactant products actually react with the fiber. Some examples of reactant-type products are ethylene urea-formaldehyde, propylene urea-formaldehyde, methylated uron-formaldehyde and dihydroxyethylene urea-formaldehyde (DMDHEU). The most popular reactant-type product is the DMDHEU type and its modifications. DMDHEU resins are produced by a reaction of glyoxal, urea and formaldehyde. The low-formaldehyde versions of DMDHEU are widely

used. These have been modified to produce a low-formaldehyde resin by using diethylene glycol as a formaldehyde acceptor. The formaldehyde figure can be reduced by approximately 50%, compared with the original DMDHEU resin [9].

2.3.2 Alternatives to formaldehyde based DP applications

2.3.2.1 Non-formaldehyde DP applications

Durable press finishes free of formaldehyde or formaldehyde precursors have also been proposed. Some of these are dimethyl dihydroxy ethylene urea (DMeDHEU), dihydroxy dimethyl imidazolidinone (DHDMI), polycarboxylic acids such as citric acid and butane tetracarboxylic acid, with hyposphosphite salts, imidazoles or sodium maleate, sodium tartrate or sodium citrate as catalysts and citric acid as extender. Other systems based on polyacrylics, polyurethane and silicones are also offered. Reactive polymeric silicones appear to be interesting as they impart simultaneously non-creasing, waterproof, soil-release properties. These zero-formaldehyde finishing systems do not appear to compete with DMDHEU-type products because of their higher cost. By adding suitable additives such as polyhydric alcohols, phosphorous catalysts or sodium salt of hydroxyl acids, the cost of these finishing systems may be reduced. However, the molecular weight and thus the strength of the fabric decreases, yellowing of the fabric increases and the finish is less durable [8, 10].

2.3.2.2 Ionic crosslinking

It is apparent that a non-formaldehyde finish prepared by using common and more available chemicals is required. For this purpose researchers have been recently working on using ionic crosslinking as an alternative mechanism for producing durable press performance. Hashem, Hauser and Smith offered an ionic crosslinking process, in which an ionic site is imparted to cotton and then it is crosslinked by using a polyion of the opposite charge [1, 2]. In his study [3], Bilgen reacted cellulose with sodium salt of chloroacetic acid (CAA) and then crosslinked it with cationic chitosan, cationic glycerin (CG), calcium chloride, magnesium chloride, cationized ethylene glycol, cationized dextrose, cationized D-celobiose and cationized ß-cyclodextrin. He also reacted cellulose with 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride (CHTAC) and crosslinked it with polycarboxylic acid

(PCA), 1,2,3,4-butanetetracarboxylic acid (BTCA), ethylene diamine tetraacetic acid (EDTA), nitriloriacetic acid trisodium salt monohydrate (NTA), N-(2-hydroxyethyl) ethylene dinitrilotriacetic acid (HEDTA), oxalic acid, citric acid and maleic acid. All of these crosslinking agents demonstrated improvement in wrinkle resistance but the higher WRA results are gained when carboxymethylated (anionic) cotton is reacted with cationic agents synthesized by reaction of a quaternary compound, namely 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride (CHTAC), with chitosan or glycerin. There is no formaldehyde release or strength loss unlike conventional methods and WRA results for such treated cotton fabric are promising but yet an optimized procedure for ionic crosslinking is still needed.

2.4 Studies on Imparting Cotton an Ionic Character

Many studies have been made on cationic and anionic agents to be used in imparting cotton an ionic character, some of which are briefly reviewed below.

2.4.1 Studies on cationic agents

Rupin studied on reactive and direct dyeing of cotton, which was aminated by an epoxy quaternary ammonium compound, namely glycidyl trimethyl ammonium chloride. He listed some advantages of amination as; not needing a fixing agent in dyeing because of the ionic bond formed, savings of rinse water and wastewater treatment, and savings in the amount of the dye needed. He added that the cost due to addition of necessary nitrogen content could be balanced with these savings [11].

Ungeful and Sello used divalent cations to form ionic crosslinks that increased the strength properties of the acrylic polymer film used in acrylic sizes. They increased the tensile strength of these copolymer films while reducing their moisture sensitivity [12].

Evans, Shore and Stead studied on reactive quaternary agents used to modify cotton. They compared epoxypropyl type agents with chlorotriazine ones, and gave detailed information on preparation and evaluation of chlorotriazine-type quaternary agents [13].

Lewis and Lei made a literature review about modifying cellulose by reactive compounds to covalently bind secondary amino, tertiary amino, quaternary amino,

thiol or disulfide residues. Some of those chemicals were 2-aminoethylsulfate, glycidil-trimethyl ammonium chloride (or its precursor 1-trimethyl-ammonium-2-hydroxy-3-chloropropane chloride), β-chloroethyl-diethylamino hydrochloride, and 2,4-difluoromonochloropyrimidine. They suggested that as a result of increased cellulose hydroxyl ionization due to the proximity of strong basic groups, the neutral fixation was improved in chemicals that introduce tertiary and quaternary amino groups [14].

Wu and Chen pretreated cotton by using polyepichlorohydrin-dimethylamine to investigate its dyeability properties with reactive dyes. They stated that dyeability of cotton was increased by introducing amino groups, and added that only one tenth of normal amount of salt was needed when exhaust dyeing such treated cotton under neutral condition with low-reactivity dyes and no salt was needed with high-reactivity dyes [15].

Kim, Choi and Yoon synthesized a quaternary ammonium derivative of chitosan, namely N-(2 hydroxy) propyl-3-trimethylammonium chitosan (HTCC), to be used as an antimicrobial finish, by reacting chitosan with glycidyltrimethylammonium chloride (GTMAC). They gave details on the reaction of GTMAC with chitosan to give HTCC (Reaction occurred between GTMAC and NH_2 groups in chitosan). They investigated the antimicrobial activity of cotton fabrics treated with HTCC, and the laundering durability of HTCC [16].

Kamel, Youssef and Shokry studied the dyeing conditions and dyeing properties of cationized cotton using 1,1-dimethyl-3-hydroxy-azetidinium chloride and 1,1-diethyl-3-hydroxy-azetidinium chloride [17].

Kanik and Hauser investigated the effect of cationic pretreatment on reactive printing of cotton. They treated cotton with aqueous solution of N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride in the presence of alkali (sodium hydroxide) and printed it with different pastes. They concluded that color yield of the prints was increased especially with medium dye concentrations, steaming time was reduced and washing-off procedure was shortened [18].

Hauser gave a detailed background of conventional dyeing procedures and reactions of cationic reactant 2,3-epoxypropyltrimethylammonium chloride. He compared commercial dyeing procedures for conventional and cationic cotton [19].

Hauser and Tabba studied on improving the affinity of anionic dyes for cotton by adding cationic dye sites to this fiber. They used 2,3 epoxypropyl trimethylammonium chloride for the modification of cotton, and they dyed modified cotton using direct, reactive and acid dyes. They concluded that cotton treated with such a reactant gives excellent color yields and color fastness values with direct and reactive dyes without the need for the electrolyte in the dyebath. They added that dyeing procedures for cationic cotton are shorter, use less water and chemical auxiliaries, and require less energy. They concluded that dyeings with acid dyes resulted in darker shades when compared to acidic dyeings of untreated cotton [20].

Hauser and Tabba studied on cationized cotton and applied a non-salt and non-afterscour dyeing procedure. They used 2,3 epoxypropyl trimethylammonium chloride to impart a cationic charge on cotton fibers. They basically used 3 different reactive dyeing procedures, and reached equivalent fastness values with higher color yields with cationic cotton when compared with fabrics dyed according to supplier recommendations [21].

Hashem, Refaie and Habeish investigated the effects of NaOH concentration, reaction time and temperature, quaternizing agent concentration, material to liquor ratio and method used for quaternization on quaternization reaction of partially carboxymethylated cotton fabric with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride. They concluded that ionic crosslinking of cotton fabric significantly improved its wet crease recovery angle, tensile strength, and elongation at break with a little improvement in dry recovery angle compared with that of untreated cotton fabric. They also concluded that cold pad-batch method yielded higher N% and fixation % results than those obtained with exhaustion method [22].

2.4.2 Studies on anionic agents

Kim, Yoon and Son synthesized an anionic agent containing a dichloro-s-triazinyl reactive group by a 3-step reaction, and treated this chemical on cotton fibers to be able color cotton fibers with cationic Berberine colorant. They found that the exhaustion of Berberine to the cotton fibers was 23 times higher than that of the untreated sample and 10 times higher than that of tannic acid pretreated samples [23].

2.4.3 Studies on both cationic and anionic agents

Hashem, Hauser and Smith studied on synthesis and application on cotton of a cationized chitosan (CC). CC was synthesized in alkaline conditions and the substitution was made on the hydroxyl sites. Furthermore, they offered 5 different methods for ionic crosslinking cellulosic fabric, and applied two of those. They concluded that crease angle recovery was imparted on cotton fabric by ionic crosslinking, generally with strength gain [1].

Hashem, Hauser and Smith investigated the reaction efficiency for cellulose cationization using CHTAC and concluded that fixation of CHTAC on cellulosic fabrics varied greatly with the choice of method, CHTAC concentration used, alkali amount, time, temperature, and other parameters of the method [2].

2.5 Carboxymethylation

The primary aim of wet processing of textile materials is to increase their usefulness and added values while preserving their natural properties. One of these widely used processes is called carboxymethylation in which carboxyl (COO^-) groups are attached to the primary alcohol of anhydroglucose unit.

The process generally consists of treating the material with solutions of monochloroacetic acid and sodium hydroxide. The order of application of these solutions may alternate [24-27] or a mixture of these may be used [28, 29] according to the procedure, always followed by acidification in a dilute aqueous hydrochloric, sulfuric or acetic acid solution. The resulting material is very swellable and has highly acidic carboxyl groups [30] giving enhancements in water retention, moisture regain, soil release, tensile strength and elongation at break [26, 28, 31]. A very good review of studies on carboxymethylation is given by Racz, Deak and Borsa [29].

2.6 Use of Quaternary Compounds in Textile

Use of quaternary compounds in modification of cotton for further use in finishing and dyeing started in mid 70s with amination prior to dyeing, which brought savings in fixing agent, rinse water and dye needed [11]. Many researchers worked with cationic agents and reported positive results, some of which are increase in dyeability [15], decrease in amount of electrolyte needed [15, 20], higher color yield [20, 21],

shorter processing time, less need for water and chemicals and thus energy savings [20] in dyeing, increased wash fastness and processing speed in printing [32], and increase in antimicrobial activity [16]. Detailed information on reactions of 2,3 epoxypropyl trimethyl ammonium chloride and comparison of commercial dyeing procedures for conventional and cationic cotton is given by Hauser [19].

3. EXPERIMENTAL

3.1 Materials

3.1.1 Fabric

The fabric used in this study was a 100% standard plain weave cotton fabric (style 400, 44"- 45", 78 X 76, ISO 105/F02) supplied from Testfabrics Inc. The fabric weight was measured as 102 g/m^2. The fabric did not have absorbency for an observation time of 60 seconds.

3.1.2 Chemicals

All solution percentages are expressed as weight on weight.

Reagent used for synthesis of the cationic crosslinkers:

- N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHTAC): 69%, CR2000, Dow Chemicals Company

Alcohols used for synthesis of the cationic crosslinkers:

- Glycerin: 99%, Fisher Chemicals Company
- Ethylene Glycol: Laboratory grade, Fisher Chemicals Company
- Ethyl Alcohol: Denaturated, Fisher Chemicals Company
- 1,2-Propanediol: 99%, Acros Chemical Company
- 1,3-Propanediol: 98%, Acros Chemical Company
- 1,2-Butanediol: 99%, Aldrich Chemicals Company
- 2,3-Butanediol: 98%, Aldrich Chemicals Company
- 1,4-Butanediol: 99%, Aldrich Chemicals Company

Chemicals used for carboxymethylation:

- Chloroacetic Acid (CAA): Flakes, Fisher Chemicals Company

- Sodium Hydroxide: 50%, Fisher Chemicals Company
- Sodium Carbonate: Reagent grade

Chemicals used for titration:

- Silver Nitrate: 1N solution, Fisher Chemicals Company
- Phenolphthalein: Powder, Baker and Adamson Chemicals Company
- Hydrochloric Acid: 0.09%, Fisher Chemicals Company
- Sodium Hydroxide: 0.2%, Fisher Chemicals Company

Chemical used for washing:

- Nonionic Surfactant: Kieralon MFB, BASF Chemicals Company

Chemicals used for bleaching:

- Sodium Hydroxide: 50%, Fisher Chemicals Company
- Ethylene Diamine Tetraacetic Acid (EDTA): Questal Special, BASF Chemicals Company
- Wetting agent: Nonionic surfactant, Kieralon N-F, BASF Chemical Company
- Stabilizer: Sodium silicate, Prestogen N-D, BASF Chemicals Company

Chemicals used for durable press (DP) finishing:

- Modified Ethylene Urea Resin: Freerez 900 Reactant, Noveon Chemicals Company
- $MgCl_2$ and $AlCl_3$ catalyst: Freecat Accelerator, Noveon Chemicals Company
- Wetting Agent: Renex 36, Noveon Chemicals Company

Chemicals used for dyeing:

- Acid Dyestuff: CI Acid Red 114, Polar Red RS 125%, Ciba Chemical Company
- Basic Dyestuff: CI Basic Blue 3, Maxilon Blue 5G 200%, Ciba Chemical Company
- Acetic Acid: Glacial, 99.8%, Fisher Chemicals Company
- Soaping agent: Apollo Scour SDRS, Apollo Chemical Company

3.2 Equipment for Preparation

3.2.1 Stirring hot plate

A Fisher Hot Plate was used to control the heating and stirring during synthesis of cationic crosslinker.

3.2.2 pH meter

A Fisher Scientific Co. model 600-pH meter was equipped with a standard combination pH electrode for measuring and adjusting pH before and after all synthesis reaction steps.

3.2.3 Padding machine and oven

Wet application of chemical materials was performed using a 35 cm laboratory pad machine manufactured by Werner Mathis AG. For drying and curing, samples were pinned on 18 X 30 cm metal pin frames and put in a forced air oven manufactured by Werner Mathis AG.

3.3 Testing

3.3.1 CIE whiteness index and dyeability

CIE Whiteness Index and CIE L*, C*, h* measurements of the fabrics were performed according to AATCC Standard Test Method 110 by using a Spectraflash SF600X, a double beam spectrophotometer, manufactured by DataColor, with 16mm area view, CIE standard illuminant D_{65} and 10^{o} observer [33].

3.3.2 Titration

Titrations were carried out to find the carboxymethyl content of the fabrics by following the method offered by Hashem, Hauser and Smith in their previous study [1]. Anionic cotton fabric was cut into small pieces; 100mL of 0.5% aqueous HCl solution prepared and fabric samples were steeped in it for 16 hours. The samples were then washed several times with cold deionized water until free from HCl and having a pH of 7. Silver nitrate drop test was performed to make sure there was no presence of chloride on the samples. The samples were dried at 105^{o}C for 3 hours in laboratory type oven. Samples weighing approximately 0.25g were soaked in 25mL

of 0.05N aqueous NaOH solutions at room temperature for 4 hours. First, a blank solution was titrated with 0.05N aqueous HCl solution. Phenolphthalein pH indicator was used. The volume of HCl solution (mL) spent was recorded for the blank. Then, each of the solutions with different carboxymethylated samples was titrated in the same way as the blank. The carboxymethyl (CM) contents of samples were calculated as follows:

$$\text{CM content (mmoles/100 grams)} = 100 \cdot (V_{blank}-V_{sample})_{HCl} \cdot N_{HCl}/0.25 \quad \textbf{(3.1)}$$

where V_{blank} is the volume of HCl used for titration of blank solution, V_{sample} is the volume of HCl used for titration of sample solution, and N_{HCl} is the normality of HCl titrant.

Carboxymethyl content is a measure of anionic sites in the cellulose chain. Knowing the mmole CM content per 100 grams of cotton and as molecular weight of anhydro glucose unit is 162g/mole, we can easily calculate the average amount of anionic sites per anhydro glucose unit (AGU) as follows:

$$\text{Average Number of anionic sites per AGU} = \quad \textbf{(3.2)}$$
$$= \text{CM content (mmole/100g)} \cdot 162\text{(g/mole)}/(1000\text{mole/mmole}*100\text{g})$$

and thus,

$$\text{Average Number of AGUs per Anionic Site} = 1/(\text{CM content} \cdot 0.00162) \quad \textbf{(3.3)}$$

where CM content is the carboxymethyl content in mmole/100g cotton.

3.3.3 Wrinkle recovery angle

WRA tests were done according to AATCC Test Method 66, option 2 [34]. 12 specimens of 40 x 12mm are cut, six with their long dimension parallel to the warp direction of the fabric and six with their long dimension parallel to the filling direction. Warp specimens are cut from sample locations with different warp yarns and filling specimens are cut from sample locations with different filling yarns. We used a template for cutting the specimens and tweezers for handling them. Prior to testing samples are brought to moisture equilibrium in a standart atmosphere having a relative humidity of 65±2% at 21±1^{o}C.

Each specimen is placed between the leaves of the metal holder with one end aligned under the 18mm marks using the tweezers. The free end of the specimen is lifted up and over to the 18mm mark taking care to loop back rather than flatten the specimen. The edge of the specimen is firmly hold in place with a thumbnail. The jaws of the plastic press is opened with the other hand. The holder with the specimen is inserted between the long and short jaws, releasing the thumbnail when bringing the end edge of the long jaw into contact with the specimen. The 18mm mark on the metal holder, the unfolded end of the specimen and the end edge of the plastic press are aligned before releasing the specimen. A fold should be formed 1.5mm from the end of the short metal leaf. The plastic press should be in firm contact with the folded specimen but should not be squeezed. The press-holder combination is inverted on a flat surface with the small platform up. 500g of weight is gently applied to the platform. After 5 minutes, the weight is removed and the press-holder combination is picked up by the plastic press and the exposed end of the specimen holder is inserted in the clip mount on the face of the recorder device. Jaws are opened and press is removed rapidly taking care to avoid rolling the exposed end of the specimen or pulling it out of the holder. The holder is aligned with the front edge of the clip mount shelf. The specimen fold should line up with the spot at the center of the recorder disc leaving the free hanging leg of the specimen aligned with the vertical guide line on the scale. To eliminate gravitational effects, the free hanging leg of the specimen is kept aligned with the recorder's vertical guide line during the 5 minutes recovery period. Adjustments are made once every 15 seconds in the first minute and once every minute thereafter during the remaning recovery period. The final adjustment is made 15 seconds before the 5 minutes recovery period ends. The recovery angle is red from the scale and recorded. If the free end of a specimen twists, a vertical plane through its center is sighted and it is aligned with the vertical mark on the recorder scale.

3.3.4 Stiffness

Stiffness was determined using ASTM D 1388-96 [35]. A Fabric Development Drape-Flex Stiffness Tester was used. This test method involves sliding a 2.5 cm by 15 cm specimen off the edge of a planar surface. The distance is recorded at which the fabric bends under its own weight to touch a surface extending at a 41.5^{o} from the

edge. From this distance and the basis weight (average weight of the test fabrics) of the fabric, the bending rigidity is calculated.

3.3.5 Breaking strength, elongation and energy to peak load

Breaking strength tests were done with a Syntech tensile strength tester according to ASTM D5034 [36]. Elongation and energy to peak load values were recorded as well.

3.3.6 Absorbency

The cotton fabric was tested for absorbency according to AATCC Test Method 79-1986 before and after bleaching [37]. Prior to testing samples are brought to moisture equilibrium in a standart atmosphere having a relative humidity of 65±2% at 21±1^{o}C. Fabric is mounted in the embroidery hoop so that the surface is free of wrinkles, but without distorting the structure of the material. The hoop is placed 10mm below the tip of the burette and one drop of distilled water at 21±3^{o}C is allowed to fall on the fabric. Using the stopwatch, the time required, up to 60 seconds, for the surface of the liquid to lose its specular reflectance is measured. 5 reading are taken and their average is calculated.

3.3.7 Scanning electron microscope (SEM)

In order to investigate the effect of ionic crosslinking on breaking behavior of the fiber, we broke cotton yarn samples and had images of broken fibers by using SEM.

3.3.8 Nitrogen content

As the crosslinking agent comprised nitrogen, it is expected that the nitrogen content of ionic crosslinked fabric compared to that of untreated fabric would be higher. The nitrogen content of ionic crosslinked sample is a measure of the amount of crosslinks it has.

In order to determine the nitrogen content of our ionic crosslinked samples, a LECO TruSpec® CHN analyzer is used with the following settings; Air pressure: 40psi; He pressure: 35psi; O_2 pressure: 38psi; Furnace Temperature: 950^{o}C; After Burner Temperature: 850^{o}C.

For calibration of this analyzer a standard EDTA (supplied by LECO) having 41.03±0.12% of carbon, 5.55±0.03% of hydrogen, and 9.57±0.04% of nitrogen is used.

Fabric samples are wrapped in capsules (supplied by Leco) of 8.0mm diameter and 20mm height. The samples are burned by using He and O_2. After burning, the gaseous product is analysed in order to determine the carbon, hydrogen and nitrogen content of the sample.

3.3.9 Smoothness

The ionic crosslinked samples were tested for smoothness according to AATCC Test Method 128-1999 [38]. An M272 SDL Atlas AATCC Wrinkle Recovery Tester is used. This test method involves wrapping a 15 cm by 28 cm specimen around the tester, lowering the top flange of the tester and placing 3500 grams weight on the top flange for 20 minutes. After the weights are removed, the specimen is hung vertically in the long (warp) direction in standard conditioned atmosphere for 24 hours prior to evaluation by three trained observers.

3.4 Synthesis of Cationic Agents

8 different cationic agents are synthesized using different alcohols. These alcohols are reacted with CHTAC (N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride) in 1:8 mole ratios. Additionally glycol is reacted with CHTAC in 1:4 mole ratio using the same procedure and the final product was called Glycerin 1:4. The general procedure for synthesis of cationic agent is as follows (see Figure 3.1):

- Weigh CHTAC and add 5% NaOH dropwise into CHTAC while stirring to adjust pH value between 10 to 11 at room temperature (Solution A).
- Weigh alcohol and add 5% NaOH dropwise into this alcohol while stirring at room temperature to adjust the same pH value with Solution A (Solution B).
- Add Solution A dropwise into Solution B while stirring at room temperature. Measure and record the pH of the mixture.
- Filter the mixture by using vacuum, weigh and remove all the salt formed.

- Fix water bath temperature at 50°C and stir this mixture for 16 hours in constant temperature at water bath, cool down to room temperature, adjust pH with 5% acetic acid to between 6 to 8.
- To find solid content, weigh 3g of this product, dry in oven at 70°C for 24 hours and weigh it again.

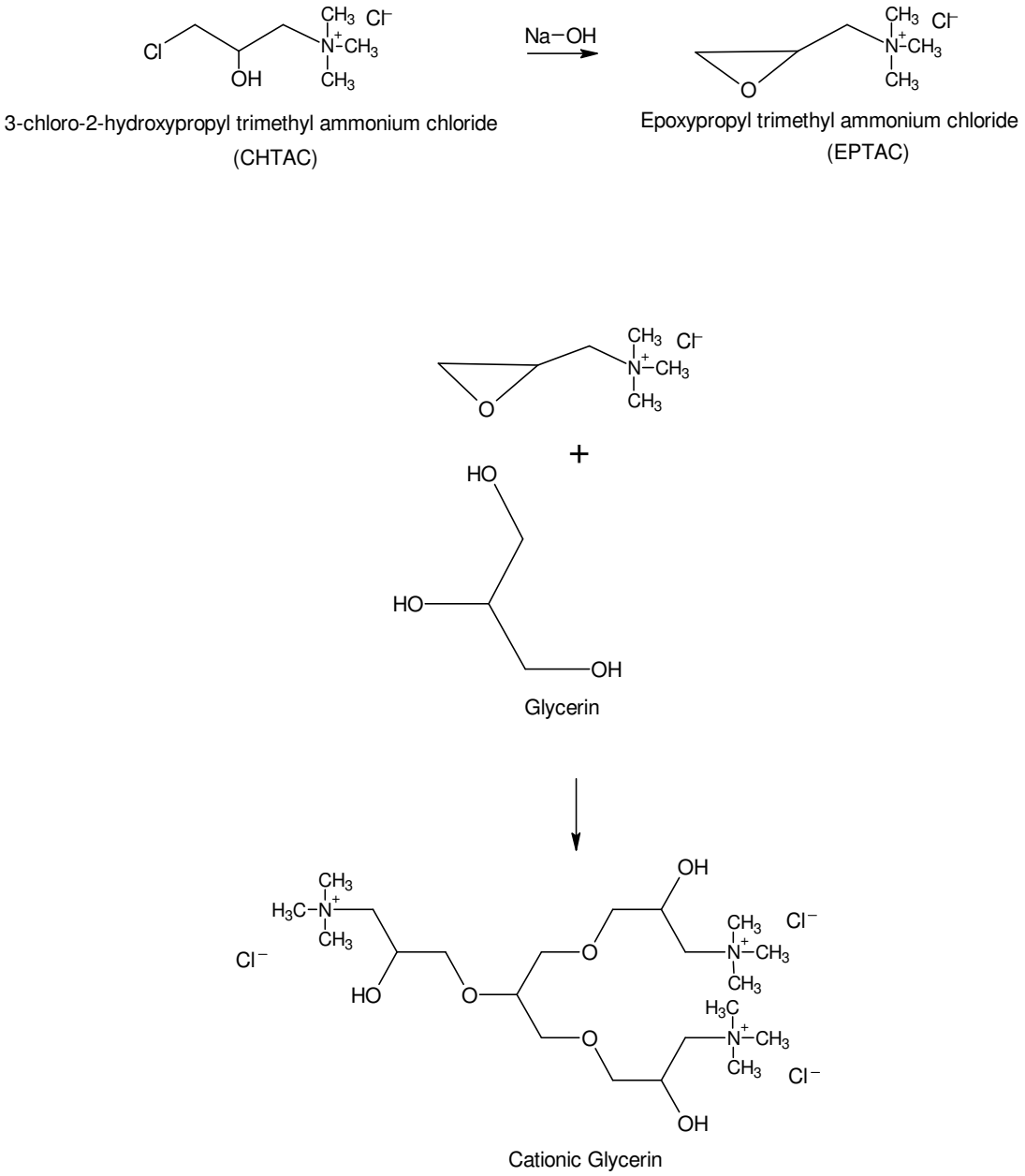

Figure 3.1 : Synthesis of cationic glycerin.

We offered an alternative procedure for cationic agent preparation. According to this procedure, CHTAC and glycerin are weighed and mixed before setting pH at room temperature. The resulting product was called Glycerin New.

We also tried reacting CHTAC with its hydrolyzed form to reach a cationic agent. The procedure we offered was as follows:

- Add 1:1.5 mole ratio 50% NaOH dropwise into CHTAC, stir at 80^{o}C for 4 hours to hydrolyze CHTAC.
- Add equal mole of NaOH into CHTAC dropwise in ice bath while stirring.
- Add this second solution dropwise into first one in ice bath, measure pH; if pH value is not between 10 to 11, add NaOH to set pH to between 10 to 11.
- Adjust water bath temperature to 80^{o}C and stir for 2 hours, cool down to room temperature, measure pH, adjust pH with acetic acid to between 6 to 8.

3.5 Applied Processes

3.5.1 DMDHEU crosslinking

For comparison of effect of conventional durable press finishing on cotton fabric with that of ionic crosslinking, we prepared samples with a common durable press finish (DMDHEU). 1L of pad bath composed of 250g/L modified ethylene urea resin, 62.5g/L catalyst, 1g/L wetting agent and 686.5mL deionized water. Softener was not used. Fabric samples were padded to 80-90% wet pick up. Samples were dried for 5 minutes and cured for 2 minutes at 105C^{o} and 177C^{o}, respectively.

3.5.2 Bleaching

We bleached the fabric by using 3g/L NaOH, 6g/L H_2O_2, 1g/L ethylene diamine tetraacetic acid (EDTA), 1g/L surfactant and 1g/L stabilizer in a Jet dyeing machine with a liquor ratio (L.R.) of 1:8. All chemicals were added to bleaching liquor and reaction was started at 30^{o}C by a temperature increase of 3°C/min. After the reaction temperature of 98^{o}C was reached, bleaching was followed for 1 hour. Bleached fabric was rinsed for 10min. Bleaching procedure is shown in Figure 3.2.

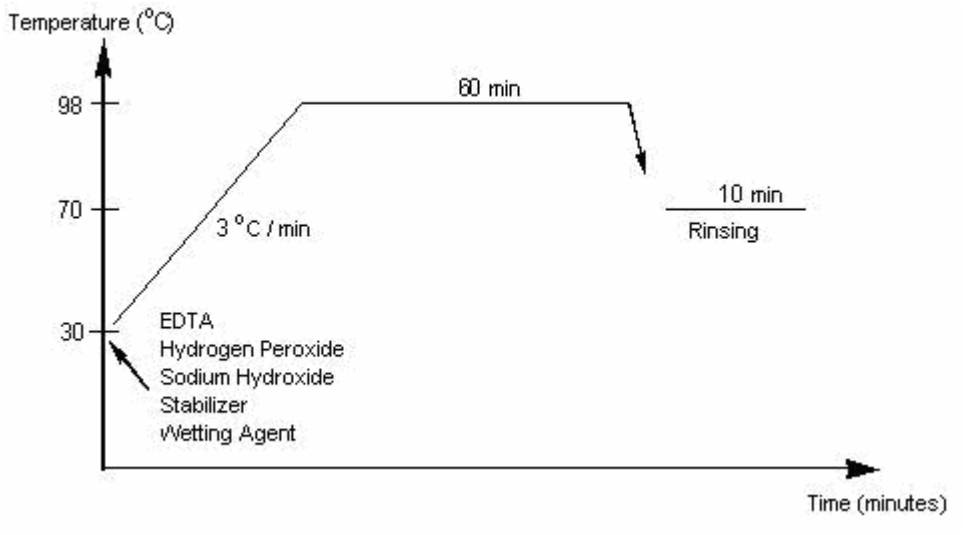

Figure 3.2 : Bleaching procedure.

3.5.3 NaOH treatment

In order to open up the fabric to prepare it for further wet processing, and only before carboxymethylation by following pad-dry-pad-batch (PDPB) and pad-dry-pad-dry (PDPD) methods, the fabric was soaked in 17.14% NaOH (L.R. 1:30) for 10 minutes, padded to a wet pick up of 100%, and dried at 60°C for 10 minutes.

3.5.4 Carboxymethylation

We conducted trials in order to find the better carboxymethylation procedure. Details on each procedure are given below. Note that at the end of each carboxymethylation procedure all these different fabrics were acidified together in 2g/L acetic acid solution for 5 minutes in room temperature, and rinsed twice for 5 minutes with deionized water. All samples were then centrifuged, and dried in tumble drier at 85°C for 5 minutes.

3.5.4.1 Pad-dry-pad-batch

The NaOH treated fabric was soaked in Na salt of CAA (L.R. 1:30) for 5 minutes, and padded to a wet pick-up of 100%. The wet fabric was placed in a plastic bag and kept in the oven at 70°C for 1 hour.

3.5.4.2 Pad-dry-pad-dry

The NaOH treated fabric was soaked in Na salt of CAA (L.R. 1:30) for 5 minutes, and padded to a wet pick-up of 100%. The wet fabric was pinned to a frame and dried in the oven at 70°C for 10 minutes.

3.5.4.3 Pad-dry-cure

The fabric was soaked in a mixture of equal volumes of 17.14% NaOH and Na salt of CAA for only 30 seconds (L.R. 1:30). The fabric was padded to 100% wet pick up, dried in the oven at 35°C for 12 minutes, and cured in the oven at 115°C for 10 minutes.

3.5.4.4 Pad-batch

The fabric was soaked in a mixture of equal volumes of 17.14% NaOH and Na salt of CAA for only 30 seconds (L.R. 1:30). The fabric was padded to 100% wet pick up and placed in a plastic bag and kept in the oven at 70°C for 1 hour.

3.5.4.5 Pad-cure

The fabric was soaked in a mixture of equal volumes of 17.14% NaOH and Na salt of CAA for only 30 seconds (L.R. 1:30). The fabric was padded to 100% wet pick up and cured in the oven at 115°C for 10 minutes.

3.5.5 Crosslinking

All carboxymethylated fabrics were separately soaked in cationic glycerin solutions for 1 hour (L.R. 1:30) and padded to 100% wet pick up. They were then dried in the oven at 85°C for 5 minutes followed by curing at 140°C for 90 seconds. Finally, they were hot washed (≅95°C) in 2g/L solution of nonionic surfactant in order to get rid of the unattached cationic agent for 10 minutes, and rinsed until no foam was observed on the rinsing water. The fabrics were centrifuged, dried in tumble dryer at 85°C for 5 minutes and kept in the conditioning room for 24 hours before testing for WRA.

3.5.6 Dyeing with acid and basic dyes

In order to determine the effect of ionic crosslinking on dyeability of cotton, we dyed our ionic crosslinked samples with an acid and a basic dye by using Nuance Top Speed model infrared heat laboratory dyeing machine supplied by Ahiba datacolor.

As mentioned before, in order to attach as many as possible dyestuff to our samples, we prepared very saturated dye baths with Polar Red RS 125% (Acid Red 114, Color Index Constitution No: 23635, molecular weight 830.82g/mole) and Maxilon Blue 5G 200% (Basic Blue 3, Color Index Constitution No: 51004, molecular weight 359.89g/mole) supplied by Ciba Chemical Company. The dyeing procedure we followed is shown in Figure 3.3. We used acetic acid to set the pH of the dyebath to pH 4. Dyeing was started at 23.5°C with 1°C/min heating speed. After reaching 100°C, we continued dyeing for 60 minutes and finally cooled down to 40°C with 2°C/min cooling speed (L.R. 1:20). After dyeing, all samples were hot soaped (≅95°C) with 1g/L soaping agent for 45 minutes and dried in an Isotemp® 500 series Lab-type oven supplied by Fisher for 1 hour at 70°C before testing.

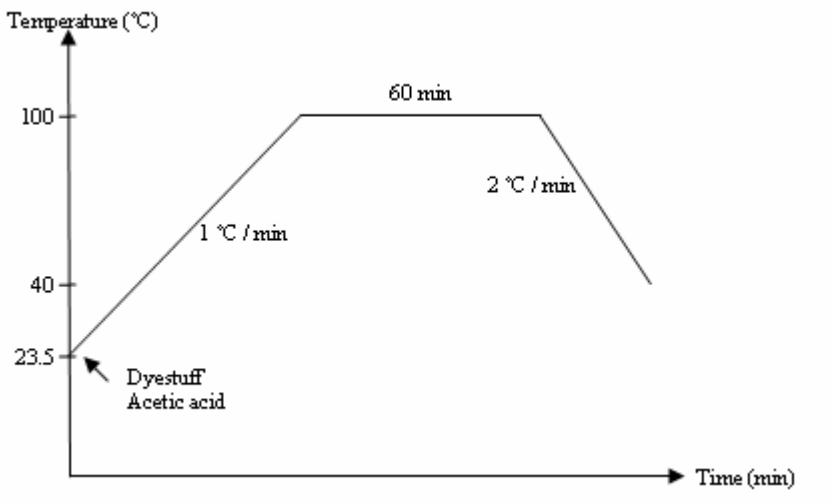

Figure 3.3 : Dyeing procedure.

3.6 Experimental Design

3.6.1 Full factorial experimental design

In multi-level designs, in order to systematically vary experimental factors, each factor is assigned a discrete set of levels.

Table 3.1: Coded and actual design levels for full factorial experimental design.

Variable symbol	Variable	Coded levels of the variables					
		-2	-1	0	+1	+2	+3
X_1	Na salt of CAA (M)	0	0.5	1	1.5	2	2.5
X_2	Cationic glycerin (%)	0	1	3	5	7	9

Full factorial design measure response variables using every treatment which is the combination of the factor levels. A full factorial design requires one experimental run for each treatment. While advantageous for separating individual effects, full factorial designs can make demands on data collection. In order to find out the individual effects as well as interaction effects of the factors we studied, we used full factorial experimental design.

Table 3.2: Full factorial experimental design of the study.

Coded ID	Carboxymethylation method	Na salt of CAA (M)	CG (%)
111	PDPD	0	0
112	PDPD	0	1
113	PDPD	0	3
114	PDPD	0	5
115	PDPD	0	7
116	PDPD	0	9
121	PDPD	0.5	0
122	PDPD	0.5	1
123	PDPD	0.5	3
124	PDPD	0.5	5
125	PDPD	0.5	7
126	PDPD	0.5	9
131	PDPD	1	0
132	PDPD	1	1
133	PDPD	1	3
134	PDPD	1	5
135	PDPD	1	7
136	PDPD	1	9
141	PDPD	1.5	0
142	PDPD	1.5	1
143	PDPD	1.5	3
144	PDPD	1.5	5
145	PDPD	1.5	7
146	PDPD	1.5	9
151	PDPD	2	0
152	PDPD	2	1
153	PDPD	2	3
154	PDPD	2	5
155	PDPD	2	7
156	PDPD	2	9
161	PDPD	2.5	0
162	PDPD	2.5	1
163	PDPD	2.5	3
164	PDPD	2.5	5
165	PDPD	2.5	7
166	PDPD	2.5	9
211	PDPB	0	0
212	PDPB	0	1
213	PDPB	0	3
214	PDPB	0	5
215	PDPB	0	7
216	PDPB	0	9
221	PDPB	0.5	0
222	PDPB	0.5	1
223	PDPB	0.5	3
224	PDPB	0.5	5
225	PDPB	0.5	7
226	PDPB	0.5	9
231	PDPB	1	0
232	PDPB	1	1
233	PDPB	1	3
234	PDPB	1	5
235	PDPB	1	7
236	PDPB	1	9
241	PDPB	1.5	0

Table 3.2 (continued): Full factorial experimental design of the study.

Coded ID	Carboxymethylation method	Na salt of CAA (M)	CG (%)
242	PDPB	1.5	1
243	PDPB	1.5	3
244	PDPB	1.5	5
245	PDPB	1.5	7
246	PDPB	1.5	9
251	PDPB	2	0
252	PDPB	2	1
253	PDPB	2	3
254	PDPB	2	5
255	PDPB	2	7
256	PDPB	2	9
261	PDPB	2.5	0
262	PDPB	2.5	1
263	PDPB	2.5	3
264	PDPB	2.5	5
265	PDPB	2.5	7
266	PDPB	2.5	9
311	PC	0	0
312	PC	0	1
313	PC	0	3
314	PC	0	5
315	PC	0	7
316	PC	0	9
321	PC	0.5	0
322	PC	0.5	1
323	PC	0.5	3
324	PC	0.5	5
325	PC	0.5	7
326	PC	0.5	9
331	PC	1	0
332	PC	1	1
333	PC	1	3
334	PC	1	5
335	PC	1	7
336	PC	1	9
341	PC	1.5	0
342	PC	1.5	1
343	PC	1.5	3
344	PC	1.5	5
345	PC	1.5	7
346	PC	1.5	9
351	PC	2	0
352	PC	2	1
353	PC	2	3
354	PC	2	5
355	PC	2	7
356	PC	2	9
361	PC	2.5	0
362	PC	2.5	1
363	PC	2.5	3
364	PC	2.5	5
365	PC	2.5	7
366	PC	2.5	9

In this study, experiments with 3 different carboxymethylation methods were conducted using a 2-level full factorial, which included 6 levels of each variable (-2, -1, 0, +1, +2, +3). Two variables of ionic crosslinking were examined (as shown in Table 3.1). The other parameters (concentration of NaOH, liquor ratio, treatment time and temperature, liquor ratio for washing, drying time and temperature) were kept constant. Dry, wet and total WRA response results were used to express the effectiveness of ionic crosslinking. Coded identification numbers (ID), carboxymethylation methods and chemical levels are given in Table 3.2.

3.6.2 Central composite design

Optimization means the study of problems when trying to minimize or maximize a real function by systematically choosing the values of real or integer variables from within an allowed set. It practically means to reach a desired result by using as few as possible resources which means that the final response value that one tries to reach determines the level of factors that are effective on this response in optimization. There are generally more than one combination of factors to reach optimum response and one picks the factor levels that are more beneficial. Since 1980s, increasing ecological concerns brought the need for using less chemicals and energy in all industries. This resulted in studies on developing eco-friendly processes often with optimization.

Table 3.3: Central composite design in coded level.

Coded ID	Na salt of CAA (M)	CG (%)
22	-1	-1
24	-1	+1
42	+1	-1
44	+1	+1
23	-α	0
43	+α	0
32	0	-α
34	0	+α
33	0	0
33	0	0

Response surface methodology is the process of adjusting predictor variables to move the response to an optimum. There are two types of response surface design; Box-Wilson (also known as Central Composite Design) and Box-Behnken. In this study, we used Box-Wilson Design as we had 2 factors, namely Na salt of CAA and CG, and Box-Behnken Design requires a minimum of 3 factors. The central composite design permits a more accurate mathematical model to be produced than the full factorial model and is appropriate for optimization [39].

Face centered central composite designs provide relatively high quality prediction over the entire design space and do not require using points outside the original factor range. For that reason we conducted a face centered central composite design.

Coded levels of central composite design are given in Table 3.3. Actual levels of central composite design are given in Table 3.4.

Table 3.4: Central composite design in actual level.

Coded ID	Na salt of CAA (M)	CG (%)
22	0.5	1
24	0.5	5
42	1.5	1
44	1.5	5
23	0.5	3
43	1.5	3
32	1	1
34	1	5
33	1	3
33	1	3

4. RESULTS AND DISCUSSION

4.1 Bleaching

Gray cotton fabric has hydrophobic characteristic and pretreatment is needed in order to increase hydrophility of cotton which is necessary for subsequent wet processes. Either scouring or bleaching can be used to increase hydrophilic properties of cotton fabric. Scouring is preferred when cotton fabric will subsequently be dyed to dark shades. When vivid or light shades are required, the fabric must be either bleached or scoured and then bleached prior to dyeing. As the fabric we used in our study is a shirting fabric and shirts are generally dyed to vivid or light shades, we preferred bleaching process instead of scouring to prepare the fabric for further wet processes (ionic crosslinking and dyeing).

The gray fabric was tested for absorbency according to AATCC Test Method 79-1986 and no absorbency was observed for an observation time of 60 seconds [37]. After bleaching the fabric was absorbent having an absorbency time smaller than 1 second which showed that the fabric is ready for further wet treatment.

4.2 Ionic Crosslinking

4.2.1 Preliminary experiments

4.2.1.1 Preliminary experiments to choose NaOH percentage used in preparation of the fabric before carboxymethylation

To find the optimum NaOH% needed to reach the desired carboxymethylation level, we set a series of trials by using NaOH from 8% to 20% and 1M of Na salt of chloroacetic acid. The carboxymethyl contents of the fabrics are measured and the results are shown in Table 4.1. Second order (see Figure 4.1) and third order (see Figure 4.2) polynomials showed with high R^2 values (around 0.915 for all three graphs below) that the maximum carboxymethylation level is reached with 17.14%

NaOH. After measuring carboxymethyl content, we crosslinked our samples using 3% cationic glycerin. Total WRA of samples are shown in Figure 4.3.

Table 4.1: Carboxymethylation levels of samples treated by using different levels of NaOH prior to treatment with 1M Na salt of CAA.

NaOH (%)	Weight (g)	Volume of HCl used (mL)	Carboxymethyl content (mmoles/ 100g cotton)
Blank	-	24.95	-
Blank	-	24.95	-
Blank	-	24.9	-
8	0.2377	24.6	7.36
9	0.245	24.65	6.12
10	0.2393	24.2	15.67
11	0.2415	24	19.67
12	0.2423	23.8	23.73
13	0.2496	23.7	25.04
14	0.2359	23.4	32.85
15	0.2398	23.6	28.15
16	0.2383	23.3	34.62
17	0.2392	23.4	32.40
18	0.2376	23.7	26.30
19	0.2291	23.5	31.65
20	0.2433	23.45	30.83

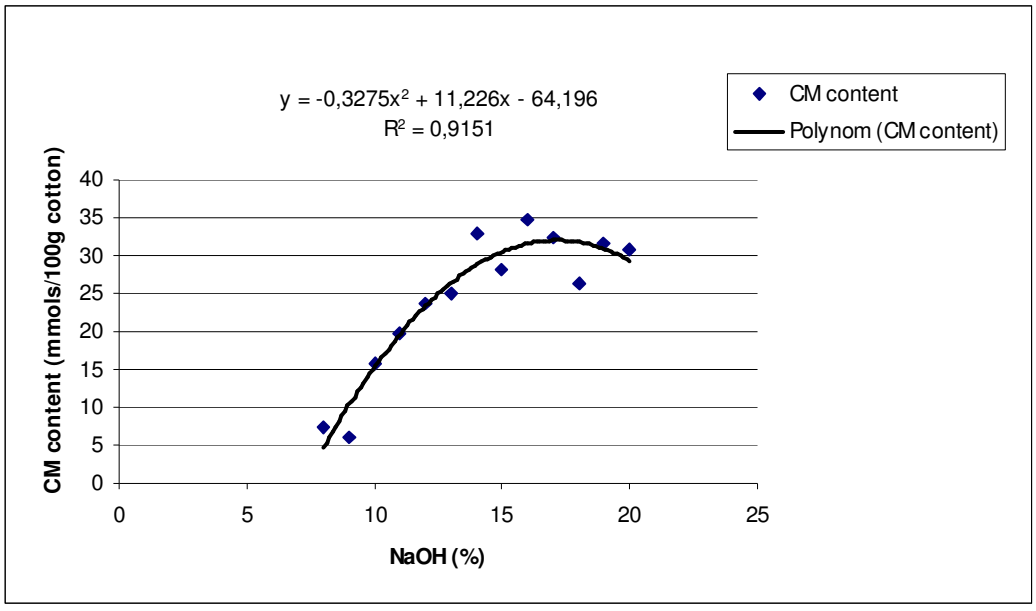

Figure 4.1 : Second order polynomial fit for NaOH% vs. CM content.

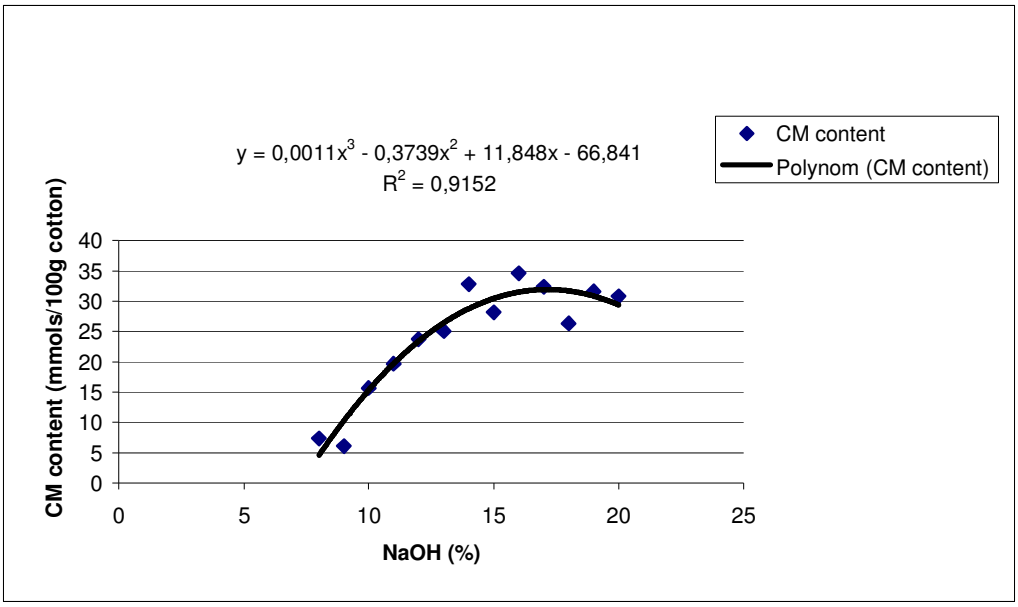

Figure 4.2 : Third order polynomial fit for NaOH% vs. CM content.

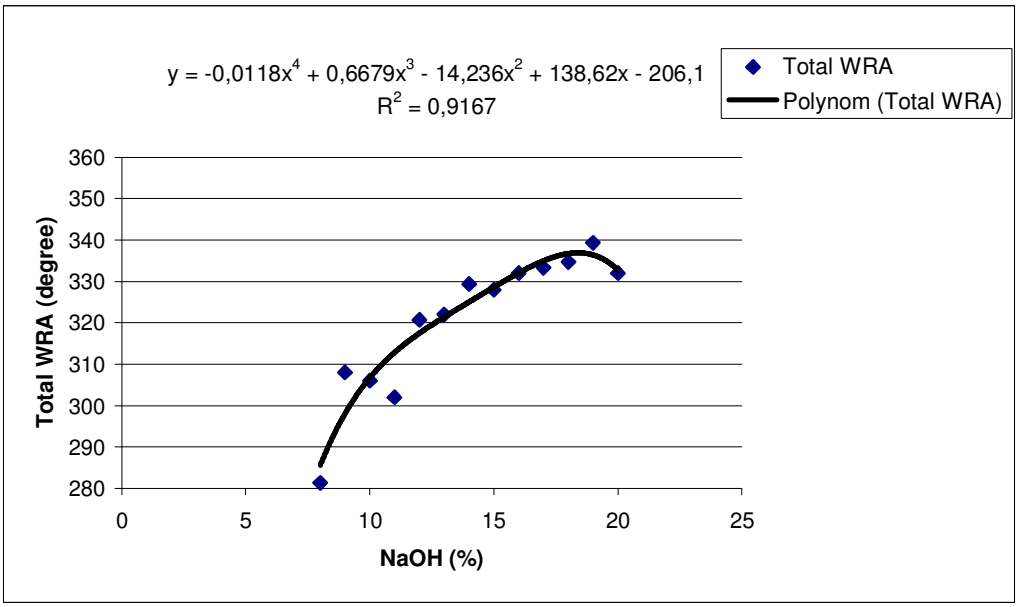

Figure 4.3 : Fourth order polynomial fit for NaOH% vs. total WRA.

17.14% NaOH level which gives the maximum carboxymethylation causes to impart the highest total WRA to cotton fabric. For this reason, 17.14% NaOH level is chosen for our full factorial and central composite designed experiments.

4.2.1.2 Preliminary experiments to choose cationic agent type

Bleached cotton fabric was treated with 17.14% NaOH and carboxymethylated by using 1M Na salt of chloroacetic acid. After that, it is ionic crosslinked by using 3%

of 11 different cationic agents. (The synthesis of these agents are explained in section 3.4 of this study in detail).

Table 4.2: WRA results for various alcohol groups of cationic agent.

Alcohol used	Average total WRA (^{o})	Average wet WRA (^{o})	Average dry WRA (^{o})
Untreated	255	127	128
Glycerin	360	218	142
Glycerin 1:4	306	190	116
Glycerin New	310	199	111
Ethanol	286	165	121
CHTAC agent	331	221	110
Ethylene Glycol	322	199	123
1.2Propane Diol	325	202	123
1.3 Propane Diol	347	231	116
1.2 Butane Diol	351	220	131
2.3 Butane Diol	315	169	146
1.4 Butane Diol	358	205	153

Total, wet and dry WRA values for durable press finished fabric are 555^o, 275^o and 280^o respectively. As we see in Table 4.2, all ionic crosslinked samples have lower WRA than DP treated one. Only butane diols and glycerin caused an increase in dry WRA performance. The wet WRA values of ionic crosslinked samples are more comparable to that of durable press treated one, but there seems to be no direct relation between the alcohol type used and wet WRA. Use of glycerin imparted the highest total WRA score (360^o) among ionic crosslinked samples followed by 1,4 butane diol.

As it is well known, one of the biggest handicaps about durable press treatment is to cause strength loss. Breaking strength, elongation, energy to peak load, and stiffness values for DP finished cotton fabric are 5.65 Kgf, 6.13%, 7.52 Kg.mm and 55.11 mg.cm respectively. As we can see from Table 4.3, DP treated sample is less than 1/4 times as strong as untreated one, but all ionic crosslinked samples gained some strength in an extent of % 2.6- 35.8. 1,2 propane diol imparted the highest strength gain followed closely by glycerin.

Table 4.3: Breaking strength, elongation, energy to peak load and stiffness results for various alcohol groups of cationic agent.

Alcohol used	Breaking strength (Kgf)	Elongation (%)	Energy to peak load (Kg.mm)	Stiffness (mg.cm)
Untreated	23.86	22.12	66.48	48.8
Glycerin	31.62	22.79	168.54	122.8
Glycerin 1:4	24.69	24.12	140.56	345.5
Glycerin New	26.96	23.46	141.25	305.4
Ethanol	24.49	27.46	145.00	258.9
CHTAC agent	27.40	24.13	155.28	317.6
Ethylene Glycol	29.01	26.12	174.80	365.6
1.2 Propane Diol	32.40	28.79	219.01	375.7
1.3 Propane Diol	31.05	30.79	220.29	255.9
1.2 Butane Diol	31.26	30.13	226.08	392.9
2.3 Butane Diol	27.21	28.12	170.63	365.0
1.4 Butane Diol	28.64	31.45	208.16	287.0

Based on these results, it is apparent that glycerin is superior to other cationic agents in terms of increasing desired fabric qualities. It imparts the highest total WRA value, second highest strength value and best stiffness value among the alcohols studied. It is also cheaper and easier to reach than the other alcohols. For this reason, we will be using this agent in our studies on optimizing ionic crosslinking process.

4.2.1.3 Preliminary experiments to choose application process of cationic agent

In order to investigate the effect of soaking our samples in a hot cationic glycerin solution, we conducted a set of trials by using anionic samples treated with 1M Na salt of CAA by following PDPB method. HS+OD was soaked at 70^{o}C for 1 hour and oven dried at 85^{o}C for 5 minutes and conditioned, S+OD was soaked at room temperature for 1 hour and oven dried at 85^{o}C for 5 minutes and conditioned, and HS+RT was soaked at 70^{o}C for 1 hour and oven dried at room temperature.

Table 4.4: Effect of hot soaking and drying processes on WRA.

Sample ID	Dry WRA (^{o})	Wet WRA (^{o})
HS+OD	104	176
S+OD	109	192
HS+RT	101	170

It is apparent from Table 4.4 that all three samples had low dry and wet WRA results. We will carry on with pad-dry-cure method for CG treatment.

4.2.1.4 Preliminary experiments to choose the final drying

In order to investigate the effect of drying method on WRA we conducted trials at a Na salt of CAA level of 1M and a CG level of 3%. Tumble drying resulted in higher dry and wet WRA values as shown in Table 4.5. Thus, after washing our crosslinked samples, we will dry them in the tumble dryer.

Table 4.5: Effect of drying method on WRA.

Drying procedure	Total WRA (°)	Dry WRA (°)	Wet WRA (°)
In oven at 85°C for 5min	288	117	170
Line at room temperature overnight	302	121	182
Flat at room temperature overnight	300	119	181
In tumble dryer at 85°C for 5min	313	129	183

4.2.1.5 Preliminary experiments to choose base levels for the experimental design

Five different carboxymethylation procedures (PDPB, PDPD, PDC, PB, PC) were followed using the same Na salt of CAA concentration (1M). Crosslinking was carried out using a pad-dry-cure method. All carboxymethylated fabrics were separately soaked in 3% cationic glycerin solutions for 1 hour (L.R. 1:30).

Table 4.6: Titration results for five different carboxymethylation procedures.

Carboxymethylation method	Carboxymethyl content (mmoles/ 100g cotton)
Untreated	10.76
Pad-dry-pad-batch	28.77
Pad-dry-pad-dry	70.29
Pad-dry-cure	54.95
Pad-batch	14.59
Pad-cure	28.13

The titration results are as shown in Table 4.6. It is apparent that 1 step pad-cure and 1 and 2 step pad-batch methods did not help to increase the carboxymethyl content of cotton fabric as much as the other 2 step methods did in the chemical level studied. On the other hand, 2 step reactions resulted in carboxymethylation levels of almost 2 times than 1 step ones. We believe this is a matter of treating cotton fabric with NaOH before carboxymethylation. Treating cotton fabric with NaOH opens up the

fabric which helps it to get more available for further wet processing. Our results showed that NaOH treatment must be a separate step of the process.

The WRA and breaking strength results are as shown in Table 4.7 and Table 4.8 respectively. As seen in Table 4.4, highest total WRA results are reached after crosslinking 1- or 2-step pad-batch carboxymethylated cotton fabrics. These two fabrics are the only ones that resulted in an increase in dry WRA values. It is obvious that 1 step pad-cure treatment did not have enough of available negative sites for further crosslinking, and thus it has a poor dry WRA.

Table 4.7: WRA results for five different carboxylethylation procedures.

Carboxymethylation method	Average total WRA (^{o})	Average wet WRA (^{o})	Average dry WRA (^{o})
Bleached	294	127	167
Pad-dry-pad-batch	386	213	173
Pad-dry-pad-dry	331	182	149
Pad-dry-cure	323	186	137
Pad-batch	360	187	173
Pad-cure	318	185	133

Table 4.8: Breaking strength results for five different carboxymethylation procedures.

Carboxymethylation method	Breaking strength after carboxymethylation (Kgf)	Breaking strength after crosslinking (Kgf)
Bleached	22.48	22.48
Pad-dry-pad-batch	33.72	34.87
Pad-dry-pad-dry	33.10	31.22
Pad-dry-cure	22.90	23.60

2-step pad-dry-pad-batch method caused an increase in wet WRA values 10% more when compared to other four trials. When compared with bleached (untreated) fabric, 2-step pad-dry-pad-batch method caused an increase in dry WRA by 5% and in wet WRA by 68%.

As seen in Table 4.8, all three samples tested versus bleached cotton fabric gained some strength after crosslinking; pad-dry-pad-batch had +55.12%, pad-dry-pad-dry had +38.88%, and pad-dry-cure had +4.98%. It is apparent from these results that the trend in increased strength is consistent with total WRA values.

In order to investigate the effect of Na salt of CAA concentration on WRA and set the base levels of CAA treatment, carboxymethylation trials were conducted by

varying the molarity of Na salt of CAA, and these samples were crosslinked to see the effect of Na salt of CAA level on WRA performance. The carboxymethyl contents, WRA and breaking strength results are as shown in Table 4.9.

Table 4.9: Titration and WRA results for various pad-batch trials.

Na salt of CAA (M)	CM content (mmoles/ 100g cotton)	Average total WRA (°)	Average wet WRA (°)	Average dry WRA (°)	Breaking strength after CM (Kgf)	Breaking strength after crosslinking (Kgf)
Untreated	15.09	294	127	167	22.48	22.48
0	17.67	343	204	139	26.31	29.37
0.5	19.92	350	209	141	28.98	29.18
1	28.22	386	213	173	33.72	34.87
1.5	38.61	321	192	129	34.14	35.45
2	52.43	310	184	126	35.54	34.20
2.5	63.41	293	185	108	34.39	32.62

It is apparent from Table 4.9 that the yield point of Na salt of CAA level for highest dry WRA performance is around 1M. When molarity of Na salt of CAA is higher than 1M, wet WRA starts to decrease slightly. The highest strength result reached for carboxymethylated cotton is at 2.0M Na salt of CAA, and that for crosslinked cotton is at 1.5M Na salt of CAA. Strength decreases slightly after these concentration levels.

Based on these results, it is apparent that carboxymethyl content is not the only factor affecting WRA performance of cotton fabric. Rather, carboxymethylation method and Na salt of CAA level have a greater effect on WRA performance. One possible explanation for this may be the distribution of carboxymethyl sites throughout the fabric. In pad-dry and pad-cure methods, heat in oven is directly applied to fabric and it is dried rapidly, not allowing much time for cotton to react with chemicals, especially for those fibers far from the fabric and yarn surface. But in pad-batch, fabric is kept in the oven in a wet state for a longer period of time giving enough time for the cotton-Na salt of CAA reaction to form carboxymethyl sites. The solution is not dried out of the fabric, probably giving a more even distribution of reaction and thus evenly distributed carboxymethylated sites. Another reason for low dry WRA may be the increased stiffness of the fabric which badly affects the ability to recover. The experimental data shows that ionic crosslinking generally increases the strength of cotton fabric, especially for pad-batch carboxymethylated fabric, but

high strength results for carboxymethylated fabric brings the question if the reason for that increase is all about carboxymethylation or not.

4.2.2 Results of full factorial designed experiments

4.2.2.1 Carboxymethyl content

Carboxymethyl contents of anionic cotton samples treated with 3 different carboxymethylation methods by using 6 different concentrations of Na salt of chloroacetic acid are given in Table 4.10. It is apparent from these results that increasing the amount of Na salt of chloroacetic acid after 2M did not result in an increase in the carboxymethylation level of fabrics treated by using PDPD and PDC methods. The highly concentrated solutions of Na salt of chloroacetic acid is unable to react with cotton fabric when the reaction is not conducted in wet state (as in PDPB) resulting in a decrease in carboxymethyl levels but for PDPB treatment the carboxymethyl levels are directly proportional with the concentration of Na salt of CAA. The highest carboxymethyl content is reached by using PDPB treatment which shows that when very high amounts of carboxymethylation is required, PDPB treatment can be preferred rather than PDPD or PDC.

Table 4.10: Carboxymethyl contents of anionic cotton samples (mmole/100g cotton).

Carboxymethylation method	Carboxymethyl content (mmoles/100g) at 6 different levels of Na salt of CAA (M)					
	0M	0.5M	1M	1.5M	2M	2.5M
Pad-Dry + Pad-Batch	13.80	24.87	35.17	70.51	97.27	165.42
Pad-Dry + Pad-Dry	20.43	34.74	65.48	95.39	133.52	123.34
Pad-Dry-Cure	23.29	42.77	64.69	81.40	94.32	89.10

4.2.2.2 Nitrogen content

The carboxymethylated samples were ionic crosslinked by using cationic glycerin of 6 different concentrations. As cationic glycerin is synthesized using CHTAC it contains nitrogen. For this reason, increase in nitrogen content of fabrics is a measure of the effectiveness of ionic crosslinking procedure. The higher the nitrogen content the more cationic glycerin is attached and thus the higher the amount of ionic

crosslinks. Average nitrogen content values of ionic crosslinked samples are given in Table 4.11.

Table 4.11: Coded ID and average nitrogen content values.

Coded ID	Nitrogen content (%)
111	0.19035
112	0.20183
113	0.18547
114	0.16653
115	0.20013
116	0.38831
121	0.19510
122	0.26429
123	0.25466
124	0.37576
125	0.19342
126	0.21377
131	0.25567
132	0.32495
133	0.32200
134	0.21792
135	0.35513
136	0.34577
141	0.27881
142	0.25489
143	0.45311
144	0.51320
145	0.44914
146	0.41701
151	0.36618
152	0.50428
153	0.56256
154	0.54766
155	0.50156
156	0.47465
161	0.36362
162	0.63269
163	0.72393
164	0.73323
165	0.77869
166	0.68820
211	0.05649
212	0.06589
213	0.25508
214	0.17494
215	0.23099
216	0.17021
221	0.20009
222	0.25018
223	0.22176
224	0.10349
225	0.20912
226	0.25049
231	0.23238
232	0.36179
233	0.23135
234	0.38101
235	0.49632
236	0.46705
241	0.26775
242	0.36654
243	0.54901
244	0.50128
245	0.50967
246	0.48312
251	0.34596
252	0.43793
253	0.62497
254	0.66903
255	0.66956

Table 4.11 (continued): Coded ID and average nitrogen content values.

Coded ID	Nitrogen content (%)
256	0.63413
261	0.38252
262	0.70816
263	0.77998
264	0.66146
265	0.67882
266	0.67263
311	0.03422
312	0.20706
313	0.17606
314	0.19364
315	0.19479
316	0.16146
321	0.18404
322	0.33966
323	0.28628
324	0.27490
325	0.14572
326	0.30164
331	0.28984
332	0.46408
333	0.40102
334	0.25948
335	0.36738
336	0.39452
341	0.33428
342	0.42192
343	0.53152
344	0.48629
345	0.38140
346	0.47767
351	0.35743
352	0.44839
353	0.51040
354	0.48536
355	0.50188
356	0.49161
361	0.29431
362	0.48970
363	0.54127
364	0.53862
365	0.48346
366	0.49744

The interaction of the Na salt of CAA and CG on nitrogen content for PDPD, PDPB and PDB treated samples are shown in Figures 4.4 to 4.6. Contour lines represent nitrogen content.

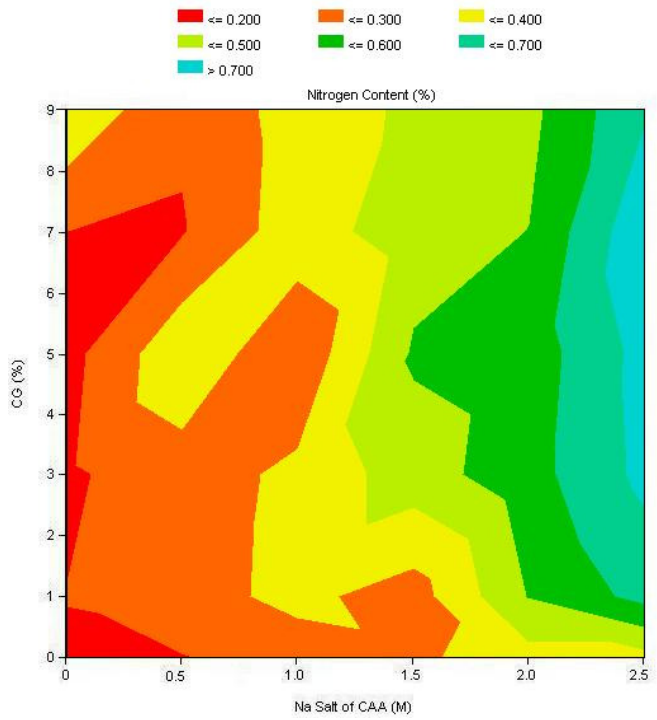

Figure 4.4 : The effects of Na salt of CAA and CG on nitrogen content for PDPD treated samples.

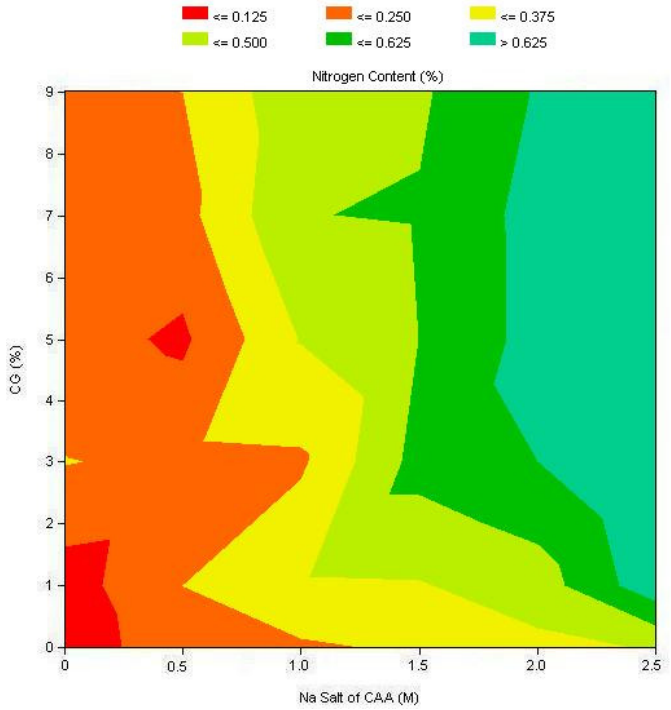

Figure 4.5 : The effects of Na salt of CAA and CG on nitrogen content for PDPB treated samples.

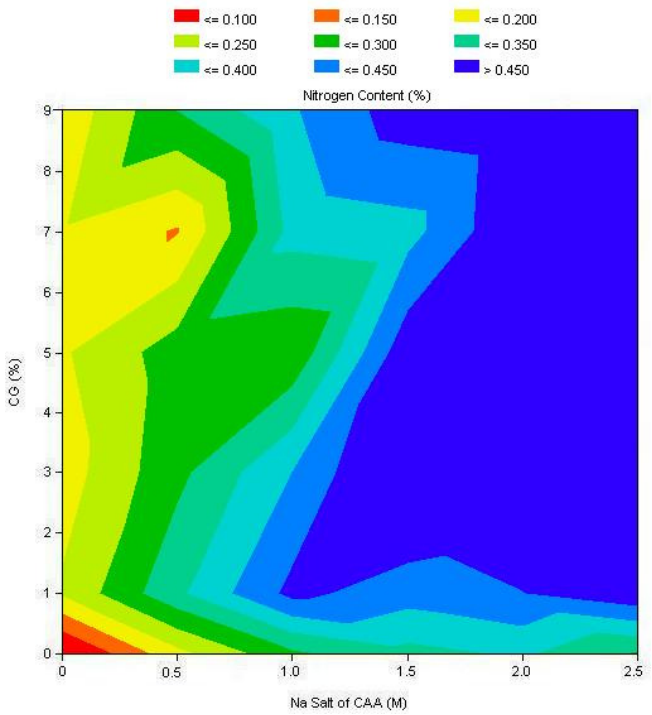

Figure 4.6 : The effects of Na salt of CAA and CG on nitrogen content for PDC treated samples.

The Prob > F results of the ANOVA analysis are shown in Table 4.12. The Prob > F is a good measure for significance. Prob > F is the probability of obtaining a greater F value by chance alone if the specified model fits no better than the overall response mean. Significance probabilities of 0.05 or less are often considered evidence that there is at least one significant regression factor in the model. As shown in Table 4.12, Prob > F values are all lower than 0.0001 which means that they are very highly significant.

Table 4.12: Prob > F values for nitrogen content responses of PDPD, PDPB and PDC trials.

Response	Prob > F for trial		
	PDPD	PDPB	PDC
Nitrogen content	< 0.0001	<0.0001	<0.0001

An increased amount of Na salt of CAA was shown to increase nitrogen content for all samples regardless of the carboxymethylation method as shown in Figures 4.4, 4.5 and 4.6. For PDC samples, after certain chemical levels (1M Na salt of CAA and 1% CG), nitrogen content was not increased at all showing that number of ionic crosslinks were unable to increase even if more chemicals were used. For PDPD and

PDPB samples nitrogen content increased as molarity of Na salt of CAA was increased. It is apparent that the increase in nitrogen content was a direct result of carboxymethyl content and thus the number of available anionic sites that CG can crosslink. It is also seen from Figure 4.5 and 4.6 that using 3% CG is enough to reach the highest nitrogen content levels and thus highest number of ionic crosslinks.

4.2.2.3 WRA

Table 4.13: Coded ID and average WRA values.

Coded ID	Dry WRA (°)	Wet WRA (°)	Total WRA (°)
111	164	131	295
112	159	141	300
113	148	139	287
114	150	149	299
115	156	149	305
116	157	164	321
121	158	135	293
122	155	152	307
123	154	171	325
124	142	163	305
125	139	160	299
126	144	160	304
131	120	144	264
132	148	162	310
133	176	198	374
134	163	180	343
135	160	157	317
136	155	167	322
141	118	148	266
142	135	142	277
143	112	164	276
144	125	168	293
145	95	155	250
146	118	159	277
151	91	138	229
152	114	154	268
153	100	150	250
154	96	164	260
155	99	148	247
156	99	138	237
161	110	140	250
162	107	182	289
163	98	155	253
164	47	177	224
165	65	176	241
166	64	172	236
211	162	144	306
212	146	138	284
213	122	147	269
214	154	166	320
215	155	160	315
216	152	155	307
221	154	139	293
222	133	187	320
223	189	200	389
224	170	181	351
225	146	162	308
226	128	178	306
231	151	128	279
232	158	220	378
233	198	226	424
234	195	202	397
235	165	180	345
236	94	163	257
241	114	141	255
242	113	161	274

Table 4.13 (continued): Coded ID and average WRA values.

Coded ID	Dry WRA (°)	Wet WRA (°)	Total WRA (°)
243	190	208	398
244	174	180	354
245	124	168	292
246	71	171	242
251	93	149	242
252	97	157	254
253	87	181	268
254	89	171	260
255	72	181	253
256	55	161	216
261	94	138	232
262	85	181	266
263	63	175	238
264	76	172	248
265	75	187	262
266	63	168	231
311	183	133	316
312	187	127	314
313	176	133	309
314	173	150	323
315	179	139	318
316	175	149	324
321	182	130	312
322	180	139	319
323	181	142	323
324	176	148	324
325	177	145	322
326	184	155	339
331	182	129	311
332	187	128	315
333	185	133	318
334	169	130	299
335	182	143	325
336	167	143	310
341	184	121	305
342	186	131	317
343	175	133	308
344	190	148	338
345	169	140	309
346	168	148	316
351	175	138	313
352	182	136	318
353	169	140	309
354	180	137	317
355	165	148	313
356	153	147	300
361	168	132	300
362	180	143	323
363	174	136	310
364	160	138	298
365	167	153	320
366	152	145	297

The average dry, wet and total WRA values of ionic crosslinked samples are given in Table 4.13.

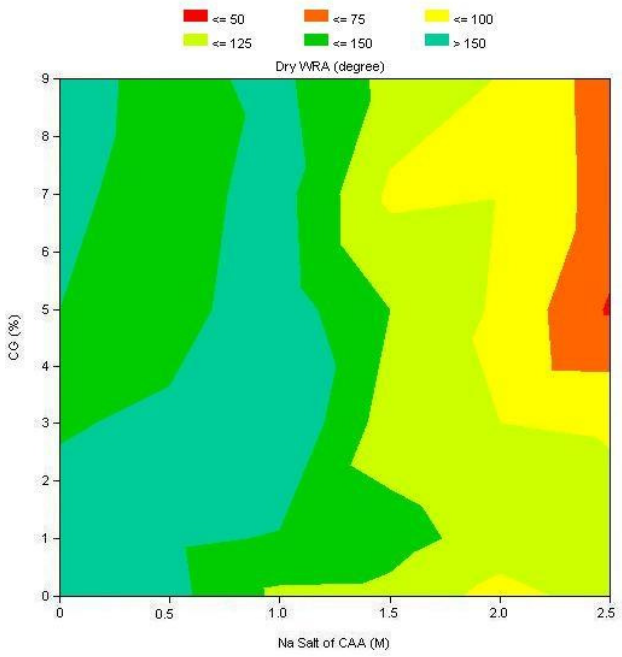

Figure 4.7 : The effects of Na salt of CAA and CG on dry WRA for PDPD treated samples.

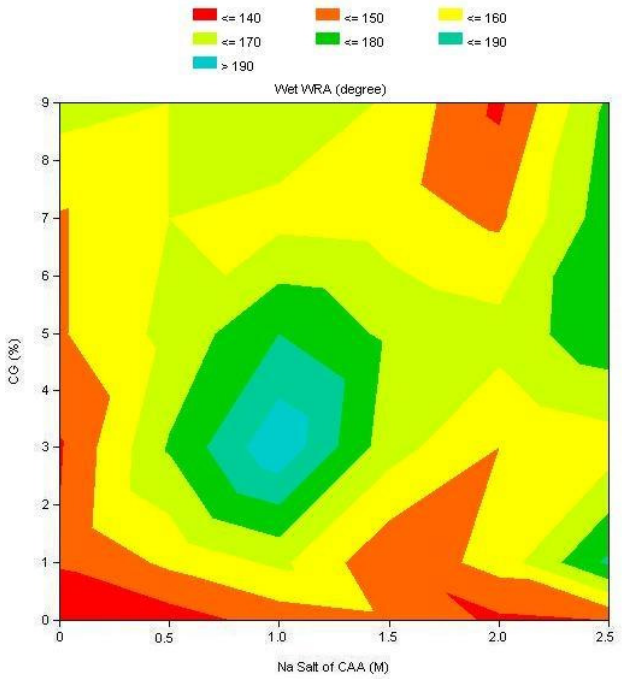

Figure 4.8 : The effects of Na salt of CAA and CG on wet WRA for PDPD treated samples.

The interaction of the Na salt of CAA and CG on dry and wet WRA values for PDPD, PDPB and PDB treated samples are shown in Figures 4.7 to 4.12. Contour

lines represent WRA. Note that WRA values for DMDHEU treated samples and untreated samples are 280°/275° (dry/wet) and 128°/127° (dry/wet) respectively.

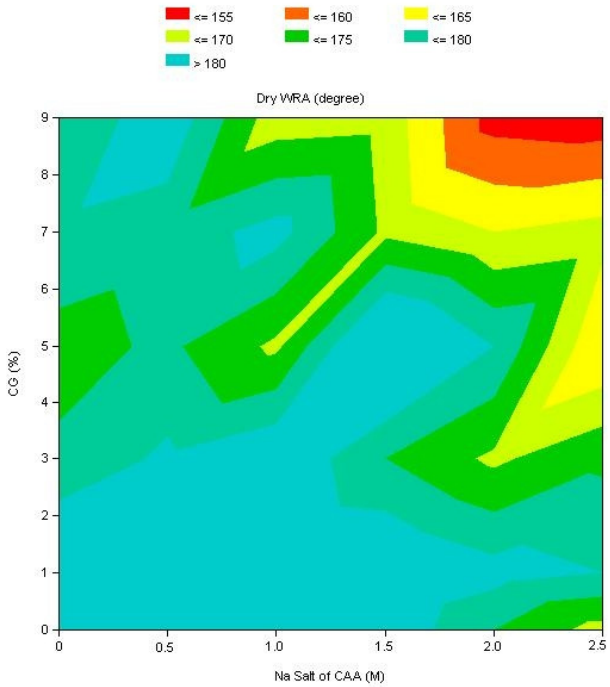

Figure 4.9 : The effects of Na salt of CAA and CG on dry WRA for PDC treated samples.

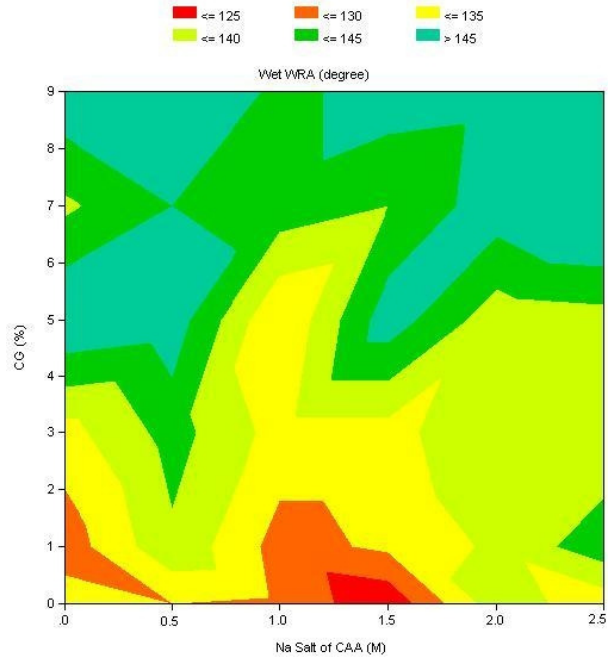

Figure 4.10 : The effects of Na salt of CAA and CG on wet WRA for PDC treated samples.

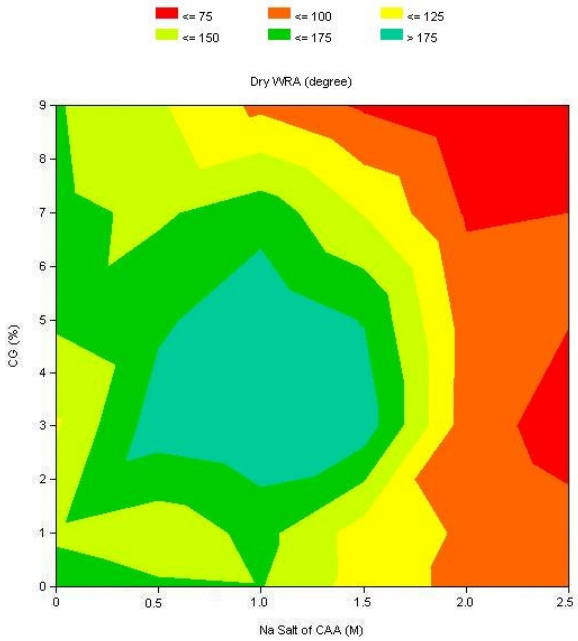

Figure 4.11 : The effects of Na salt of CAA and CG on dry WRA for PDPB treated samples.

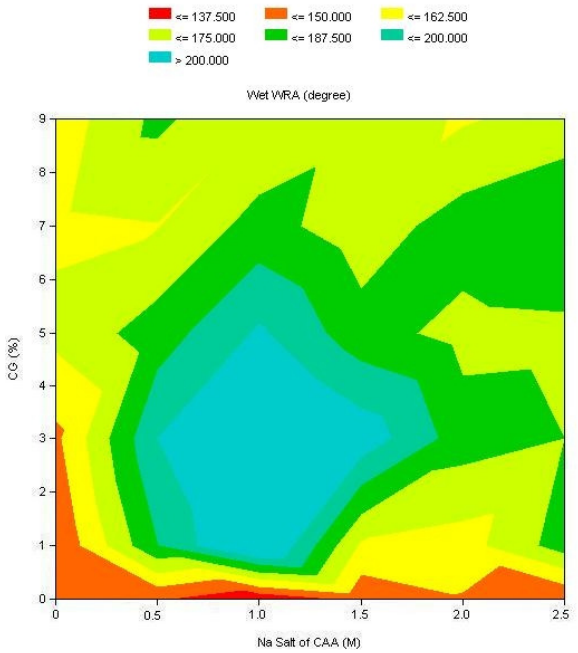

Figure 4.12 : The effects of Na salt of CAA and CG on wet WRA for PDPB treated samples.

The Prob > F results of the ANOVA analysis are shown in Table 4.14. As shown in Table 4.14, Prob > F values which ranged between 0.0001-0.0402 are significant.

Table 4.14: Prob > F values for dry and wet WRA responses of PDPD, PDPB and PDC trials.

Response	Prob > F for trial		
	PDPD	PDPB	PDC
Dry WRA	< 0.0001	<0.0001	<0.0001
Wet WRA	0.0004	0.01236	0.0402

An increased amount of Na salt of CAA was shown to decrease dry WRA for all samples as shown in Figures 4.7, 4.9 and 4.11. After certain chemical levels, CG concentration had more effect on dry WRA values of PDC (see Figure 4.9) and PDPB (see Figure 4.11) samples, and had almost no effect on dry WRA values for PDPD samples (see Figure 4.7). Figure 4.9 shows that dry WRA values for PDC samples started to decrease after 1.5M Na salt of CAA and 5% CG levels, while the same values started to decrease for PDPB samples after 1M Na salt of CAA and 5% CG levels (see Figure 4.11). It is apparent from Figures 4.7, 4.9 and 4.11 that a molarity of Na salt of CAA of 1M is enough to reach an anionic cotton fabric that will give the higher dry WRA values after being treated with CG. Samples treated with Na salt of CAA of molarities higher than 1M gets very stiff and they can hardly open up during dry WRA testing, thus giving lower dry WRA results.

As shown in Figure 4.10, PDC treated samples had very poor wet WRA results. Increase in %CG and molarity of Na salt of CAA increased wet WRA results but very weakly. Figure 4.8 and Figure 4.12 shows that PDPD and PDPB treated samples followed the same trend; their wet WRA results increased with increasing %CG and molarity of Na salt of CAA until base levels. After those levels, increase in amounts of both CG and Na salt of CAA negatively affected the resulting wet WRA of the samples.

It is apparent from Figures 4.7 to 4.12 that the highest WRA values (as a total of dry WRA and wet WRA) among ionic crosslinked ones are gained by PDPB treated samples. PDPB treated samples were also shown to reach higher WRA values with lower levels of chemicals than PDC and PDPD samples. PDPB treated samples had a more continuous trend in increase in wet and dry WRA values around the base levels of chemicals and reached to as high as $198^{o}/226^{o}$ for dry/wet WRA, while the other two methods offered local maximum WRA trends among the chemical levels studied. Highest WRA values for PDC treated samples were $184^{o}/155^{o}$ (dry/wet

WRA) and that for PDPD treated samples were 176°/198° (dry/wet WRA). For these reasons we picked PDPB treatment for our optimization trials.

4.2.2.4 Stiffness

The ionic crosslinked samples are tested for stiffness. Stiffness values in warp and filling directions for ionic crosslinked samples are given in Table 4.15.

Table 4.15: Coded ID and stiffness values in warp and filling directions for ionic crosslinked samples.

Coded ID	Stiffness in warp direction (mg.cm)	Stiffness in filling direction (mg.cm)
111	162.08	53.89
112	176.76	48.35
113	200.24	56.43
114	150.01	58.13
115	154.64	55.28
116	140.37	60.97
121	179.45	73.54
122	189.79	81.23
123	244.05	91.01
124	197.52	82.01
125	288.25	62.90
126	218.67	71.57
131	311.74	185.39
132	372.48	85.94
133	405.66	128.25
134	283.67	81.34
135	269.37	113.04
136	369.45	90.61
141	498.48	236.41
142	312.40	134.54
143	400.20	225.08
144	298.00	108.09
145	304.09	105.58
146	350.45	131.43
151	469.07	186.57
152	708.41	335.72
153	821.46	410.33
154	724.43	324.00
155	555.72	190.54
156	403.17	219.43
161	195.54	311.40
162	490.42	182.68
163	1676.45	1112.51
164	1004.33	1135.78
165	462.65	514.78
166	682.84	693.44
211	165.00	53.72
212	190.71	68.57
213	176.23	47.44
214	199.97	50.32
215	184.13	64.30
216	186.26	56.85
221	229.49	88.62
222	244.19	125.24
223	196.31	50.16
224	230.21	107.44
225	230.39	79.04
226	263.16	76.90
231	284.22	97.79
232	329.22	103.97
233	430.23	187.41
234	314.92	124.44
235	294.43	116.32
236	339.63	97.67
241	345.48	128.18

Table 4.15 (continued): Coded ID and stiffness values in warp and filling directions for ionic crosslinked samples.

Coded ID	Stiffness in warp direction (mg.cm)	Stiffness in filling direction (mg.cm)
242	440.85	170.16
243	470.99	116.83
244	422.12	178.48
245	522.60	255.39
246	411.55	171.59
251	978.30	521.71
252	1095.15	451.75
253	929.66	409.23
254	1101.47	551.22
255	1723.04	1011.79
256	1507.78	774.30
261	1144.64	558.23
262	761.29	469.26
263	985.40	361.64
264	1300.15	494.48
265	1046.16	486.79
266	1776.49	643.42
311	107.31	35.24
312	116.10	35.90
313	118.56	42.65
314	106.06	39.63
315	105.80	41.67
316	109.82	39.96
321	106.82	41.24
322	107.57	47.79
323	111.97	38.45
324	113.98	36.72
325	122.63	41.34
326	91.65	37.14
331	139.03	54.25
332	125.42	68.47
333	116.01	39.37
334	113.16	68.58
335	104.65	48.49
336	111.46	66.93
341	181.09	52.63
342	182.19	156.34
343	317.57	95.99
344	138.31	132.12
345	122.99	169.03
346	121.27	136.01
351	357.96	83.79
352	205.90	144.75
353	150.66	90.65
354	184.29	74.98
355	172.91	76.38
356	176.09	78.45
361	292.21	72.47
362	220.93	187.45
363	209.68	112.44
364	207.51	78.42
365	139.60	142.30
366	154.84	69.94

The effects of the Na salt of CAA and CG on stiffness in warp and filling directions for PDPD, PDPB and PDC treated and crosslinked samples are shown in Figures 4.13 to 4.18. It is apparent that increase in stiffness depends highly on the concentration of Na salt of chloroacetic acid and crosslinking does not decrease stiffness at all.

When effects of carboxymethylation procedures on resulting stiffness of ionic crosslinked cotton fabric are compared it is obvious that PDPB and PDPD treatments

resulted in almost two times higher stiffness values at any chloroacetic acid level when the sample is tested in either warp or filling direction. Stiffness in warp direction is almost two times that in filling direction at any Na salt of CAA concentration. This may be due to application of tension in warp direction during drying step of carboxymethylation. As the WRA results of both PDPB and PDPD treated samples are higher than that of PDC samples, we can conclude that increase in stiffness does not have a sharp decreasing impact on cotton fabric's WRA.

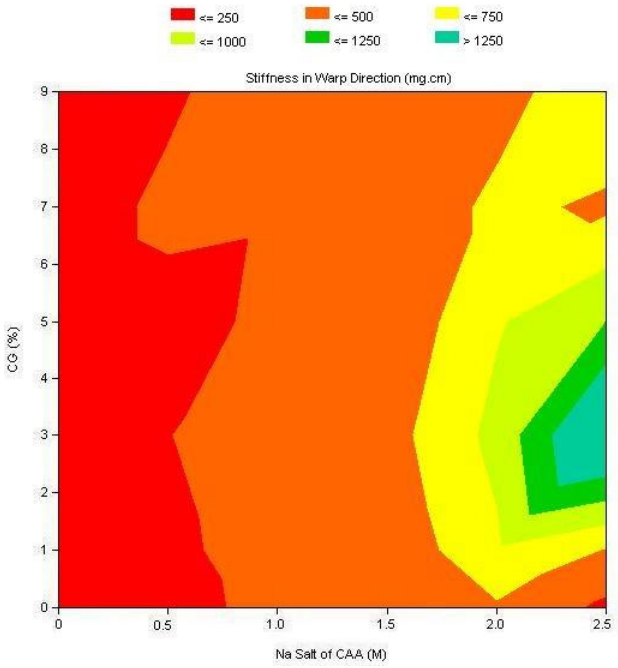

Figure 4.13 : The effects of Na salt of CAA and CG on stiffness in warp direction for PDPD treated samples.

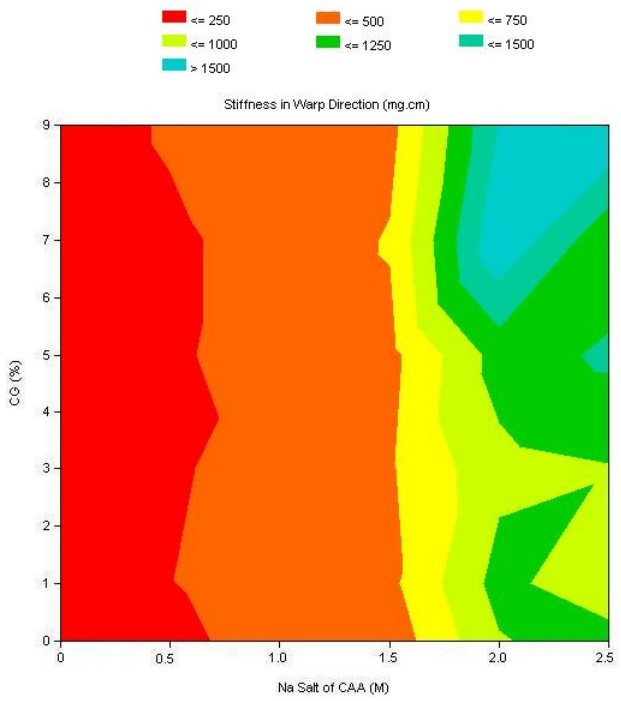

Figure 4.14 : The effects of Na salt of CAA and CG on stiffness in warp direction for PDPB treated samples.

As mentioned before, stiffness values for DMDHEU treated sample are 97.39 mg.cm in warp direction and 55.09 mg.cm in filling direction, and those for untreated sample are 117.67 mg.cm in warp direction and 52.30 mg.cm in filling direction respectively. This means that stiffness values of PDPB treated (with 1M Na salt of CAA) and ionic crosslinked (with 3% CG) sample which gives highest dry and wet WRA values are comparable with those of durable press finished fabric.

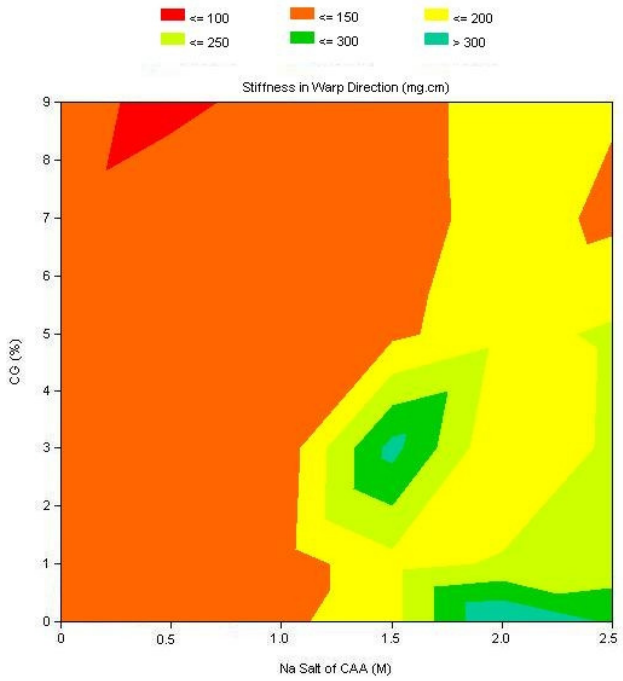

Figure 4.15 : The effects of Na salt of CAA and CG on stiffness in warp direction for PDC treated samples.

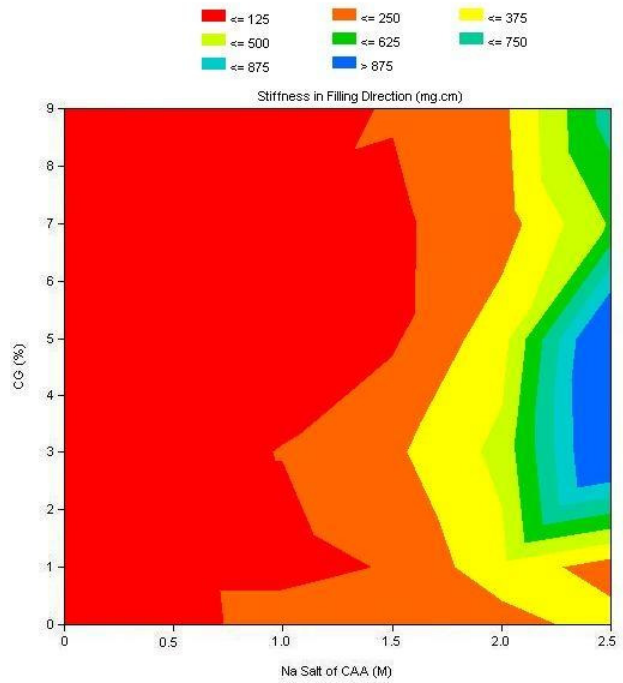

Figure 4.16 : The effects of Na salt of CAA and CG on stiffness in filling direction for PDPD treated samples.

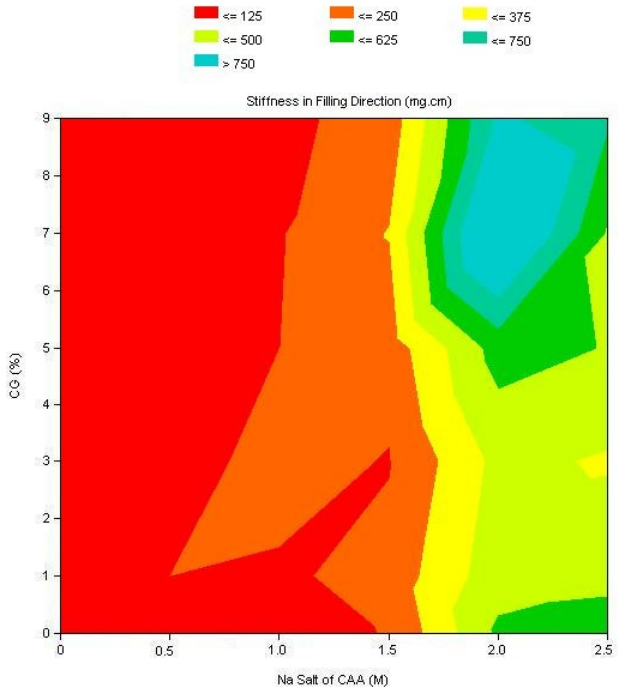

Figure 4.17 : The effects of Na salt of CAA and CG on stiffness in filling direction for PDPB treated samples.

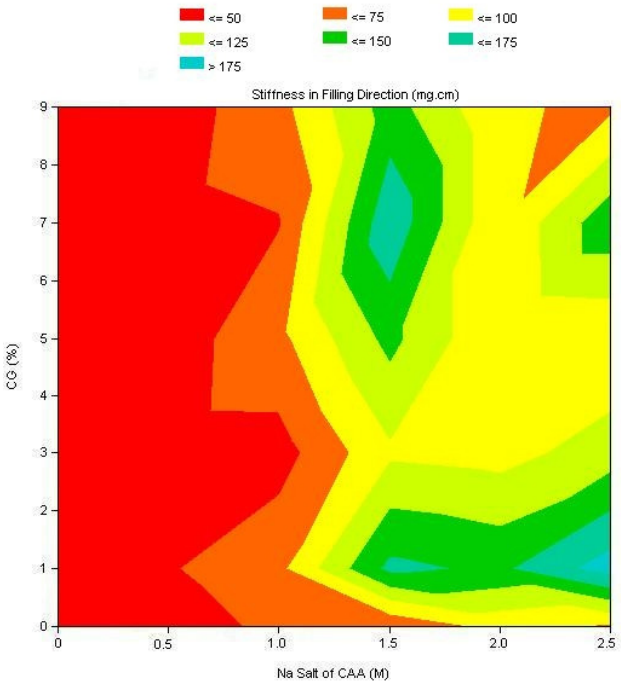

Figure 4.18 : The effects of Na salt of CAA and CG on stiffness in filling direction for PDC treated samples.

The Prob > F results of the ANOVA analysis are shown in Table 4.16. It is apparent from data on Table 4.16 that the effect of Na salt of CAA and CG on stiffness is very significant regardless of the test direction of the samples.

Table 4.16: Prob > F values for stiffness in warp direction and stiffness in filling direction responses of PDPD, PDPB and PDC trials.

Response	Prob > F for trial		
	PDPD	PDPB	PDC
Stiffness (warp)	<0.0001	<0.0001	<0.0001
Stiffness (filling)	<0.0001	<0.0001	<0.0002

When stiffness is taken into consideration, we can say that Na salt of CAA and stiffness (in terms of flexural rigidity) in warp and filling directions correlate well, showing R^2 values of 0.8808, 0.6673, and 0.5419 for PDPB, PDPD, and PDC respectively in warp direction and R^2 values of 0.8499, 0.8012, and 0.5839 for PDPB, PDPD, and PDC respectively for filling direction (see Figures 4.19 and 4.20).

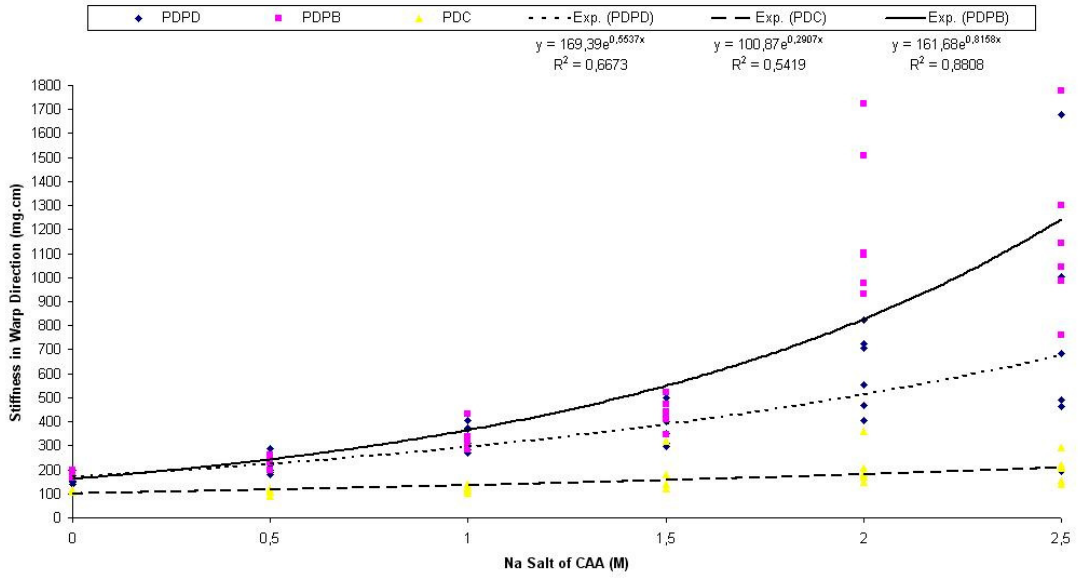

Figure 4.19 : Interaction between Na salt of CAA and stiffness in warp direction.

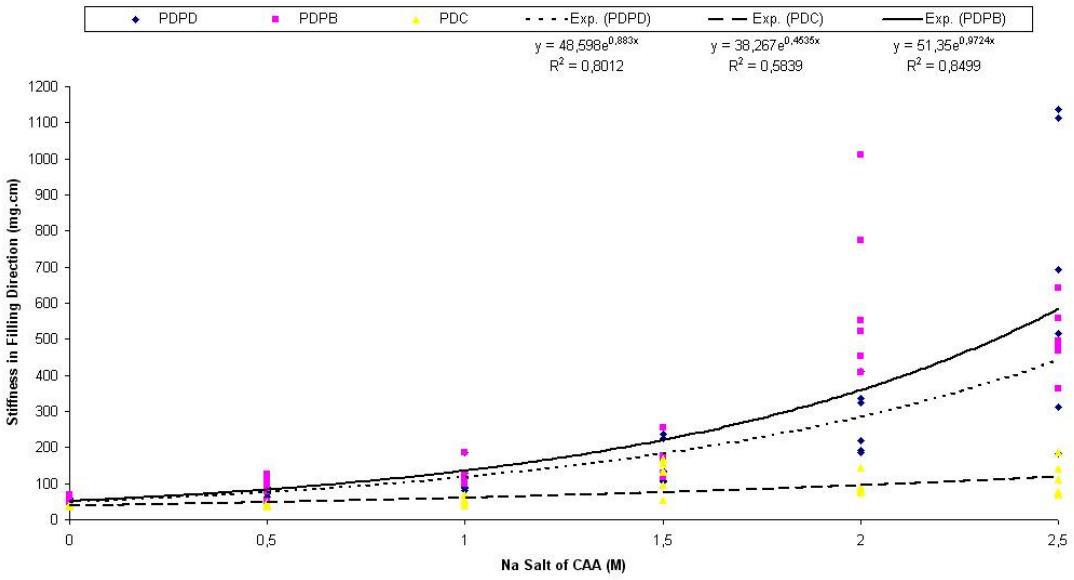

Figure 4.20 : Interaction between Na salt of CAA and stiffness in filling direction.

It is apparent from Figures 4.13 to 4.18 that CG% has almost no effect on the resulting stiffness characteristics of the fabric. As shown in Figures 4.21 and 4.22, PDPD and PDPB have positive but not strong correlation values between dry WRA and stiffness, and PDC had almost no correlation.

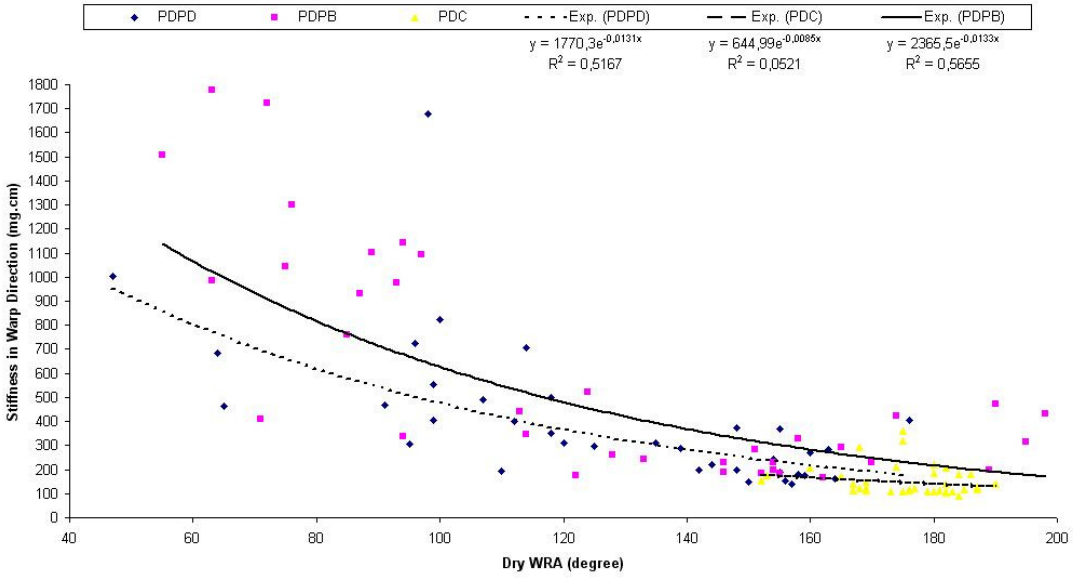

Figure 4.21 : Interaction between dry WRA and stiffness in warp direction.

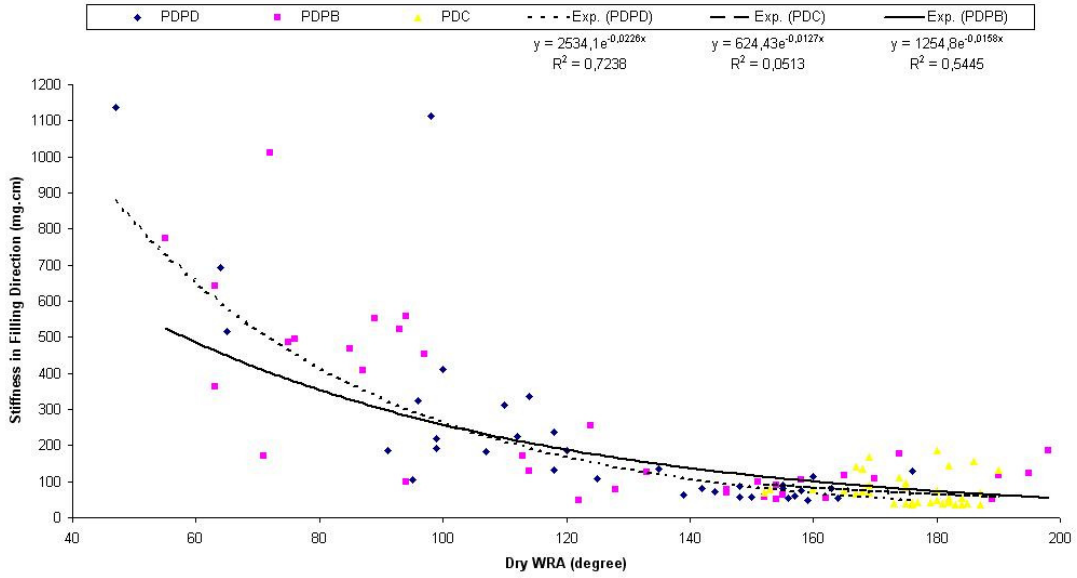

Figure 4.22 : Interaction between dry WRA and stiffness in filling direction.

As shown in Figures 4.23 and 4.24, wet WRA results have almost no correlation with stiffness.

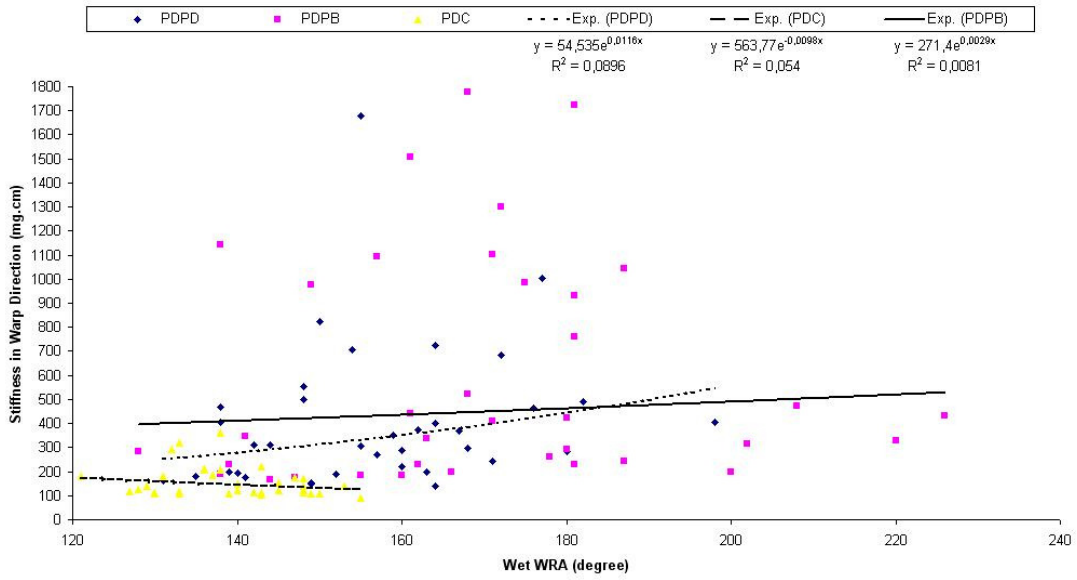

Figure 4.23 : Interaction between wet WRA and stiffness in warp direction.

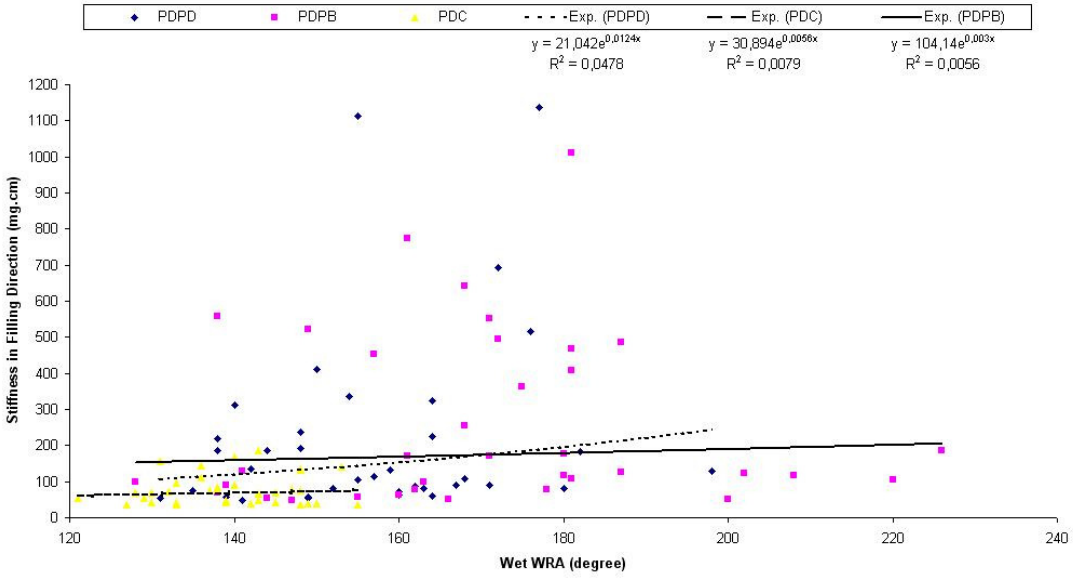

Figure 4.24 : Interaction between wet WRA and stiffness in filling direction.

Total WRA results have weak positive correlation with stiffness (see Figures 4.25 and 4.26).

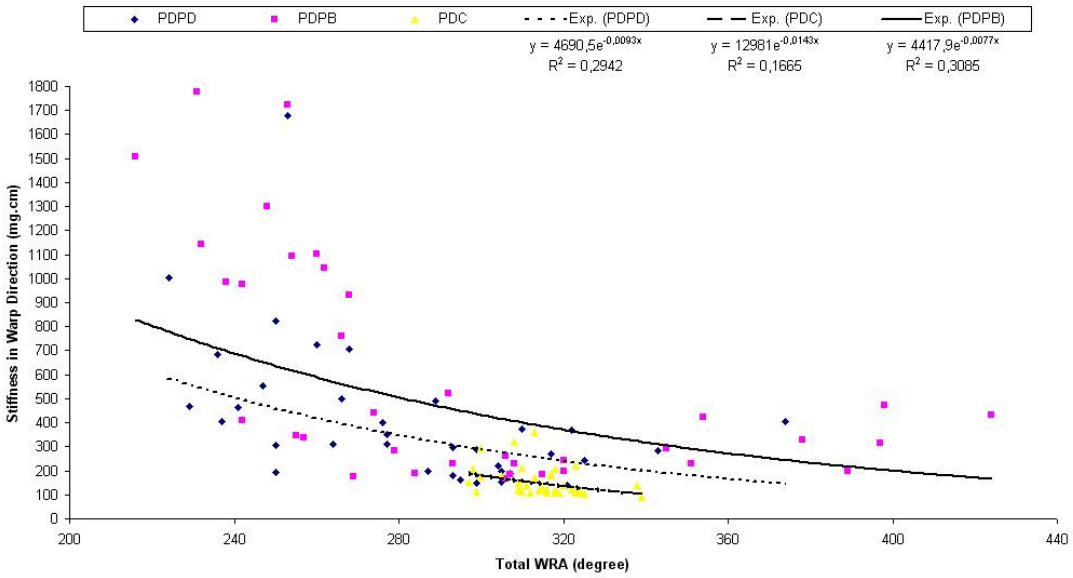

Figure 4.25 : Interaction between total WRA and stiffness in warp direction.

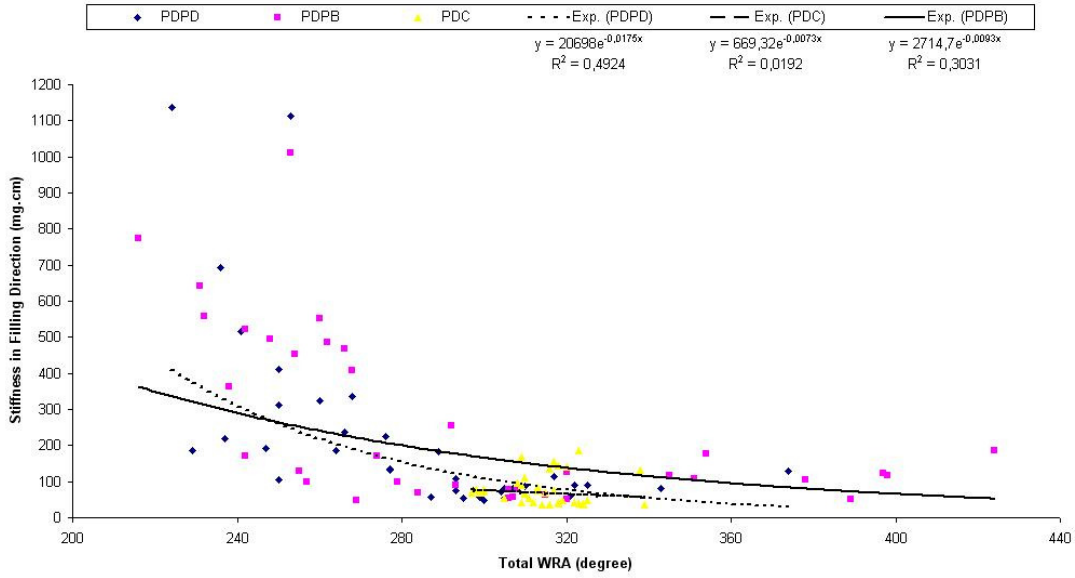

Figure 4.26 : Interaction between total WRA and stiffness in filling direction.

4.2.2.5 Smoothness

Table 4.17: Coded ID and smoothness values for ionic crosslinked samples.

Coded ID	Smoothness
111	1.8
112	2.6
113	2.4
114	2.9
115	1.7
116	1.7
121	1.9
122	2.2
123	2.0
124	2.2
125	2.1
126	2.2
131	2.0
132	2.1
133	2.2
134	2.4
135	2.4
136	2.2
141	1.9
142	2.1
143	2.0
144	2.3
145	2.0
146	2.1
151	1.8
152	1.9
153	1.8
154	2.0
155	1.9
156	1.9
161	1.7
162	1.7
163	1.8
164	1.7
165	1.6
166	1.7
211	2.1
212	2.0

Table 4.17 (continued): Coded ID and smoothness values for ionic crosslinked samples.

Coded ID	Smoothness
213	2.1
214	2.1
215	2.1
216	1.9
221	1.9
222	1.9
223	2.8
224	2.1
225	2.1
226	2.2
231	2.2
232	2.6
233	2.8
234	2.3
235	2.0
236	2.6
241	2.1
242	1.8
243	2.3
244	2.1
245	2.0
246	2.4
251	2.1
252	2.6
253	2.9
254	2.0
255	1.9
256	1.9
261	2.4
262	1.9
263	1.9
264	1.9
265	2.0
266	2.0
311	2.3
312	2.4
313	2.3
314	2.1
315	2.3
316	2.1
321	2.6
322	2.3
323	2.1
324	2.9
325	2.6
326	2.2
331	1.8
332	2.2
333	2.3
334	2.4
335	2.4
336	2.7
341	2.2
342	2.3
343	2.4
344	1.9
345	2.2
346	2.6
351	3.0
352	2.7
353	2.9
354	2.1
355	1.9
356	2.1
361	1.9
362	2.4
363	2.4
364	2.2
365	2.3
366	3.2

The crosslinked samples are tested for smoothness. Smoothness values for ionic crosslinked samples are given in Table 4.17.

The effects of the Na salt of CAA and CG on smoothness for PDPD, PDPB and PDC treated and crosslinked samples are shown in Figures 4.27 to 4.29. Smoothness value for DMDHEU treated sample is 4.0 and that for untreated sample is 1.4 respectively.

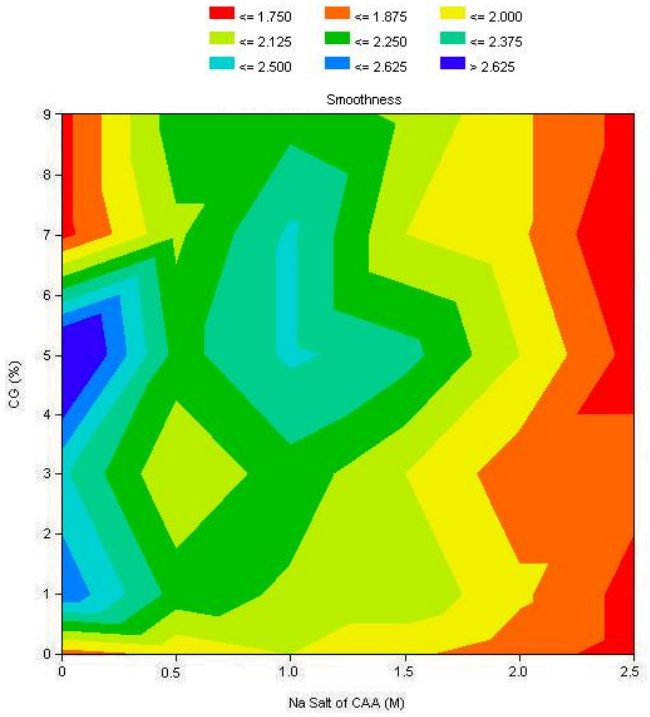

Figure 4.27 : The effects of Na salt of CAA and CG on smoothness for PDPD treated samples.

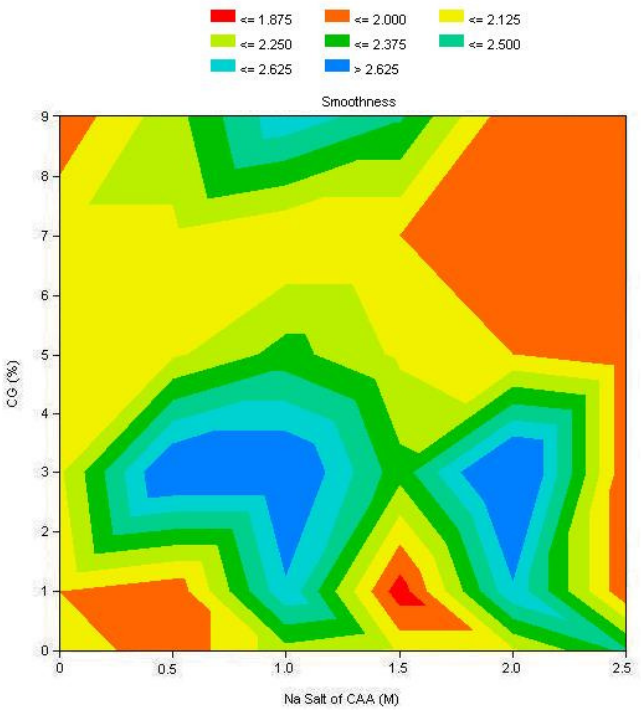

Figure 4.28 : The effects of Na salt of CAA and CG on smoothness for PDPB treated samples.

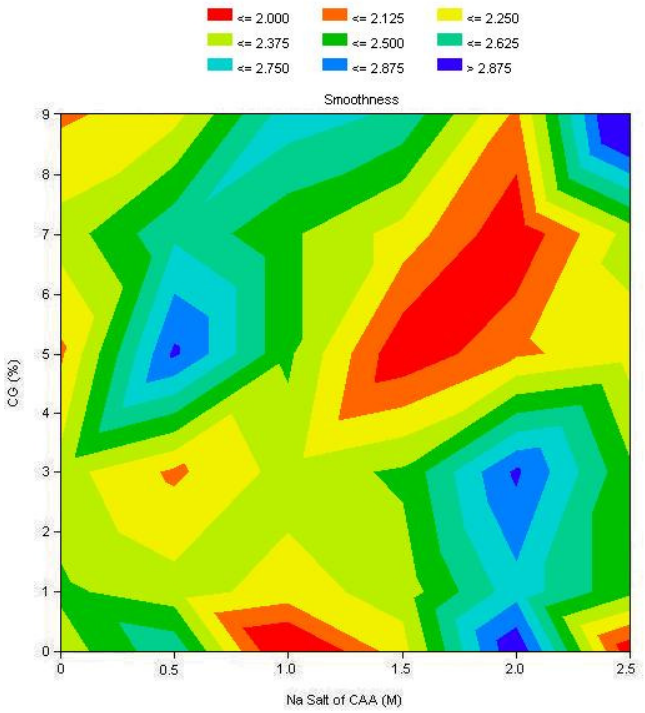

Figure 4.29 : The effects of Na salt of CAA and CG on smoothness for PDC treated samples.

The Prob > F results of the ANOVA analysis are shown in Table 4.18. It is apparent from data on Table 4.18 that the effect of Na salt of CAA and CG on smoothness is very insignificant.

Table 4.18: Prob > F values for smoothness responses of PDPD, PDPB and PDC trials.

Response	Prob > F for trial		
	PDPD	PDPB	PDC
Smoothness	0.0058	0.7529	0.8487

When smoothness is taken into consideration, we can say that all three procedures offered in this study increased fabric smoothness but only PDPD treatment had a significant effect on smoothness (see Figure 4.27) especially in 1M Na salt of CAA and 5-7% CG levels. For PDPD treated and ionic crosslinked samples, increase in molarity of Na salt of CAA decreased fabric smoothness significantly as shown in Figure 4.27. For PDPB treated and ionic crosslinked samples it is apparent from Figure 4.28 that higher smoothness values are reached at 3% CG level. PDC treatment resulted in a rather spread response in terms of molarity of Na salt of CAA and CG% (see Figure 4.29).

4.2.2.6 CIE whiteness index and dyeability

The ionic crosslinked samples are tested for CIE whiteness index and then dyed with an acid and a basic dye in order to determine the effect of ionic crosslinking on resulting dyeability of cotton fabric. Saturated dye liquors are used to investigate the dyeability limits of the crosslinked samples.

The interaction of the Na salt of CAA and CG on CIE whiteness index and on L*, C* and h* values of acid and basic dyed samples are shown in Figures 4.30 to 4.62. CIE whiteness index values for ionic crosslinked samples and L*, C*, and h* values for samples dyed with an acid dye are given in Table 4.19.

Table 4.19: Coded ID, CIE whiteness index values for ionic crosslinked samples and L*, C*, h* values for samples dyed with acid dye.

Coded ID	CIE whiteness index	L*	C*	h*
111	80.6	64.77	26.64	347.21
112	81.4	64.48	27.19	346.42
113	80.46	63.15	2766	347.1
114	79.8	64.01	27.44	348.51
115	79.78	63.01	28.12	348.9
116	79.14	57.03	32.85	350.97
121	80.69	70.21	23.96	349.74
122	79.71	69.15	24.87	348.86
123	79.87	68.55	25.76	348.58
124	80.21	68.29	25.3	348.25
125	79.85	67.96	25.65	348.84
126	78.26	67.77	25.52	350.89
131	77.65	71.73	22.91	352.35
132	78.03	70.51	23.35	351.49
133	77.75	71.03	23.21	350.9
134	78.54	71.06	23.02	351.64
135	78.64	70.97	23.35	351.33
136	78.23	71.01	23.21	351.66
141	78.12	75.65	19.36	357.72
142	79.23	75.09	20.3	356.99
143	77.82	74.02	21.02	355.73
144	78.77	74.13	21.52	356.12
145	77.4	74.02	21.56	356.47
146	77.26	73.3	21.5	354.69
151	77.2	76.33	18.59	359.1
152	77.29	76.36	17.47	357.93
153	76.53	77.35	17.47	2.19
154	77.27	77.32	17.21	0.96
155	77.67	77.33	17.31	2.36
156	77.76	76.87	18.49	1.67
161	77.72	79.11	17.95	12.63
162	78.66	80.41	16.39	9.88
163	74.9	78.06	15.88	9.79
164	75.84	77.91	17.24	11.05
165	77.84	80.31	16.32	10.27
166	73.55	78.39	15.84	10.39
211	79.82	65.06	27.14	349.86
212	79.62	65.19	26.81	347.42
213	80.03	64.02	27.86	349.26
214	80.58	63.97	27.54	348.82
215	80.09	63.01	27.65	349.07
216	78.33	58.65	30.99	349.64
221	80.06	70.92	23.51	350.91
222	80.17	70.67	23.67	351.11
223	78.57	70.35	23.49	351.03
224	79.6	69.68	24.29	351.35
225	79.17	69.71	24.25	351.5
226	77.62	68.28	24.33	356.2
231	79.63	74.22	21.1	356.24
232	79.36	74.56	20.57	354.93
233	78.51	77.67	18.13	359.34
234	79.26	76.49	18.85	358.71
235	79.61	76	18.96	358.02
236	79.01	75.74	19.44	359.56
241	79.37	77.29	18.65	359.66
242	78.9	77.59	17.83	359.28
243	77.59	78.19	16.93	1.06
244	79.47	78.3	16.75	1.59
245	78.26	77.31	17.56	1.99
246	78.16	78.71	16.59	5.02
251	77.37	80.26	15.43	8.21
252	76.85	80.59	13.54	10.76
253	76.03	80.59	14.89	13.64
254	76.31	81.34	13.4	12.11
255	75.35	80.61	14.58	14.42
256	74.61	80.28	13.15	15.08
261	76.87	80.4	14.63	16.02
262	76.75	80.37	14.42	11.82
263	75.88	80.13	14.69	13.58
264	75.19	79.54	15.5	12.99
265	76.26	79.42	15.08	10.59

Table 4.19 (continued): Coded ID, CIE whiteness index values for ionic crosslinked samples and L*, C*, h* values for samples dyed with acid dye.

Coded ID	CIE whiteness index	L*	C*	h*
266	74.71	79.45	15.45	13.67
311	78.34	69.71	22.69	349.74
312	81.21	68.37	23.85	348.07
313	80.92	64.32	26.66	350.06
314	80.24	64.52	26.81	351.87
315	80.07	64.39	26.81	352.36
316	77.01	54.4	31.87	351.53
321	69.01	77.07	19.42	358.81
322	74.99	77.4	19.62	1.83
323	75.39	77.01	19.87	5.04
324	76.24	76.34	20.35	4.01
325	75.5	75.95	21.06	8.06
326	74.8	73.72	22.31	9.58
331	69.75	79.23	19.19	9.19
332	79.33	79.37	19.15	7.76
333	78.54	78.73	19.77	10.47
334	79.03	78.4	20.35	9.74
335	78.29	77.82	20.66	12.6
336	78.39	77.33	21.54	14.04
341	77.5	78.83	20.03	9.97
342	77.9	79.31	19.55	9.24
343	79.65	78.91	18.34	8.55
344	77.33	79.21	19.51	9.61
345	78.13	78.49	19.62	12.25
346	78.19	77.54	20.93	15.54
351	80.61	79.96	18.1	13.66
352	79.02	80.34	18.2	9.56
353	79.21	79.61	18.35	9.21
354	79.68	79.33	19.23	10.94
355	78.55	79.02	19.01	10.9
356	74.26	79.43	19.47	13.76
361	77.18	78.94	19.37	9.9
362	77.73	79.9	17.26	9.41
363	78.64	79.96	18.08	9.18
364	77.45	79.47	18.68	9.49
365	78.26	78.61	19.39	8.93
366	78.03	78.91	19.56	11.54

L*, C*, and h* values for samples dyed with a basic dye are given in Table 4.20. Note that sample 166 tore out into pieces while washing off due to high chemical content, so we were unable measure its L*, C* and h* values.

Note that CIE whiteness index value for DMDHEU treated samples and untreated samples are 60.20 and 84.61 respectively. L*, C* and h* values of acid dyed untreated sample are 64.95, 26.84, 351.57 and those for basic dyed sample are 77.33, 7.83, 218.31 respectively.

Table 4.20: Coded ID and L*, C*, h* values for samples dyed with basic dye.

Coded ID	L*	C*	h*
111	78.83	7.42	213.86
112	78.43	9.38	214.53
113	78.69	9.3	214.43
114	78.54	6.98	214.27
115	77.14	7.6	210.61
116	65.25	7.34	203.89
121	73.31	15.33	214.65
122	70.76	17.84	216.8
123	72.46	16.38	215.82
124	73.13	14.47	216.38
125	73.11	16.08	213.66
126	67.05	16.12	212.86
131	61.54	22.06	221.51
132	62.4	21.45	221.53
133	61.3	22	222.01
134	62.78	21.29	221.2
135	61.13	22.3	222.2
136	63.86	19.76	219.16
141	55.22	21.69	224.41
142	56.28	20.15	224.31
143	52.33	25.1	223.72
144	55.34	24.14	223.29
145	53.94	23.99	224.37
146	54.61	22.26	223.84
151	43.9	23.15	227.14
152	45.13	22.71	226.62
153	46.05	20.48	227.87
154	46.77	21.25	227.76
155	44.28	23.34	228.05
156	48.36	22.86	225.93
161	40.24	22.76	229.89
162	42.61	21.32	230.31
163	42.18	21.53	228.24
164	34.2	16.52	224.33
165	38.38	13.88	221.58
166	-	-	-
211	77.72	8.42	216.45
212	77.69	7.37	218.07
213	77.47	7.49	217.73
214	75.2	7.78	215.33
215	76.19	7.54	214.25
216	68.79	7.78	206.05
221	71.96	16.35	216.56
222	71.05	16.86	217.2
223	70.56	16.99	217.42
224	66.66	21.55	218.6
225	65.38	23.63	217.68
226	66.69	15.58	214.43
231	62.99	21.38	221.05
232	62.17	20.96	222.41
233	54.72	22.61	224.62
234	58.93	20.73	223.72
235	56.72	22.25	223.46
236	57.08	21.42	223.35
241	54	23.27	223.25
242	55.74	19.99	225.01
243	50.7	24.57	224.62
244	51.66	21.52	226.55
245	50.2	24.34	223.86
246	49.55	22.3	224.62
251	37.39	26.49	229.97
252	43.07	21.18	227.05
253	40.64	20.71	229.34
254	42.68	19.41	227.62
255	34.96	14.53	224.75
256	35.38	21.38	230.05
261	38.62	21.45	229.57
262	41.18	19.94	228.41
263	38.38	20.96	228.45
264	38.11	19.76	230.33
265	40.27	20.51	229.52
266	36.59	20.11	231.09

Table 4.20 (continued): Coded ID and L*, C*, h* values for samples dyed with basic dye.

Coded ID	L*	C*	h*
311	77.87	9.22	214.61
312	79.25	8.41	215.55
313	77.16	8.14	213.55
314	76.31	8.15	212.26
315	76.55	6.87	208.73
316	66.86	7.01	204.64
321	66.83	21.55	219.65
322	65.11	22.87	219.84
323	65.72	21.88	218.21
324	65.9	22.11	218.13
325	66.54	19.74	215.18
326	61.53	17.78	213.63
331	56.83	24.87	222.34
332	62.08	17.63	224.14
333	62.49	18.55	221.33
334	61.29	21.03	220.63
335	61.15	20.89	221.39
336	58.8	21.83	220.43
341	49.52	26.73	225.74
342	53.42	21.77	225.28
343	52.95	23.06	224.29
344	56.11	21.33	223.15
345	55.03	24.52	222.04
346	53.57	23.52	223.66
351	50.46	23.01	225.75
352	54.99	21.42	225.22
353	53.99	22.42	224.7
354	54.54	22.32	223.74
355	55.03	24.42	222.1
356	53.11	25.14	222.02
361	51.29	23.04	225.68
362	50.7	24.53	226.05
363	53.44	24.64	223.11
364	53.64	24.88	223.21
365	53.15	23.77	223.38
366	52.41	23.16	224.33

The Prob > F results of the ANOVA analysis are shown in Table 4.21. It is apparent from data on Table 4.21 that the effect of Na salt of CAA and CG on CIE whiteness index and dyeability of samples are very significant. The only exception for that is the CIE whiteness index value of PDC treated sample.

Table 4.21: Prob > F values for CIE whiteness index and L*, C* and h* responses of PDPD, PDPB and PDC trials.

Response	Prob > F for trials		
	PDPD	PDPB	PDC
CIE whiteness index	<0.0001	<0.0001	<0.8209
Acid L*	<0.0001	<0.0001	<0.0001
Acid C*	<0.0001	<0.0001	<0.0001
Acid h*	<0.0001	<0.0001	<0.0001
Basic L*	<0.0001	<0.0001	<0.0001
Basic C*	<0.0001	<0.0005	<0.0001
Basic h*	<0.0001	<0.0001	<0.0001

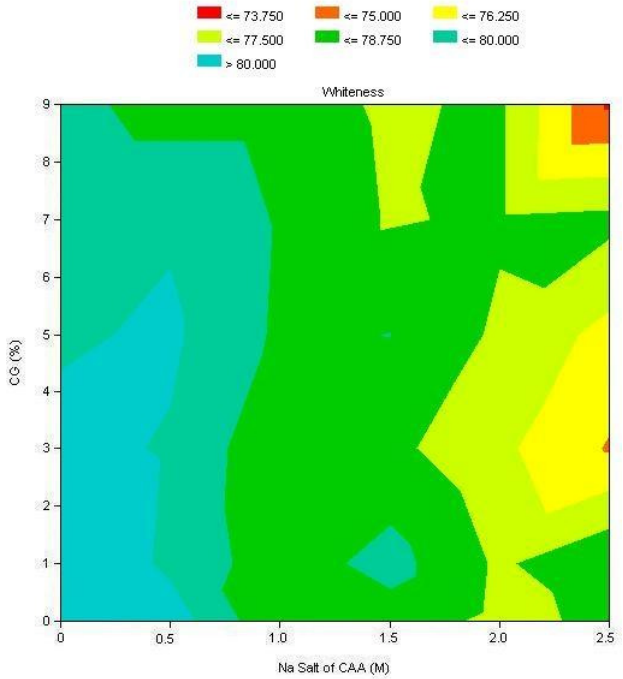

Figure 4.30 : The effects of Na salt of CAA and CG on CIE whiteness index for PDPD treated samples.

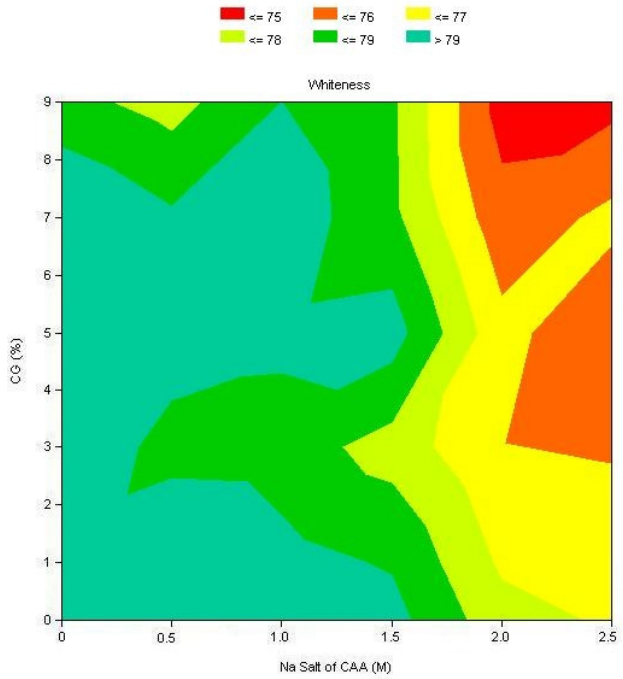

Figure 4.31 : The effects of Na salt of CAA and CG on CIE whiteness index for PDPB treated samples.

For PDPD and PDPB trials (see Figures 4.30 and 4.31), CIE whiteness index decreases with increasing Na salt of CAA level as expected, but the decreas is very

limited. Up to 1M Na salt of CAA level, which imparted the highest WRA values, the decrease is only down to 79 which is acceptable and still superior to the whiteness of DMDHEU treated fabric. For PDC the trend is vice versa as seen in Figure 4.32; CIE whiteness index decreased at around 0.5M Na salt of CAA and then increased to the level of CIE whiteness index of untreated cotton fabric. Just as for CAA, increasing CG% decreases CIE whiteness index for PDPB and PDPD (see Figures 4.30 and 4.31), but increases CIE whiteness index for PDC (see Figure 4.32). For all the carboxymethylation methods studied, CIE whiteness index decreases only to a limited extend and it is superior to that of durable press finished cotton.

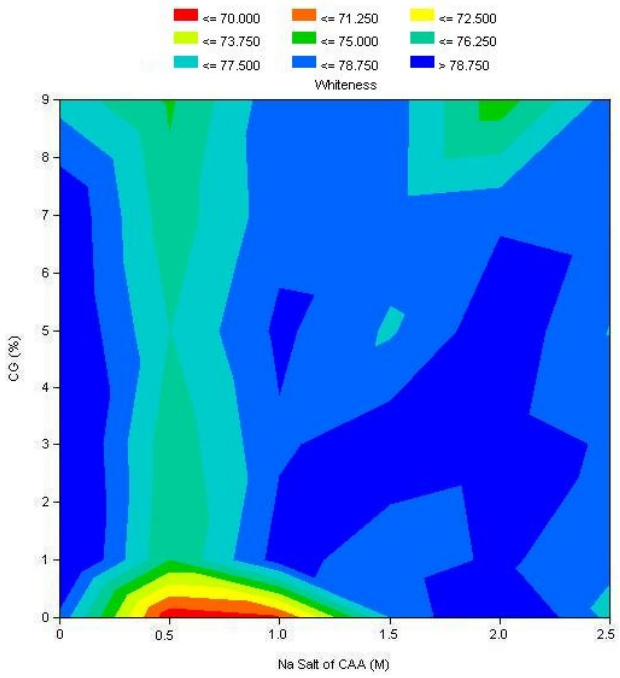

Figure 4.32 : The effects of Na salt of CAA and CG on CIE whiteness index for PDC treated samples.

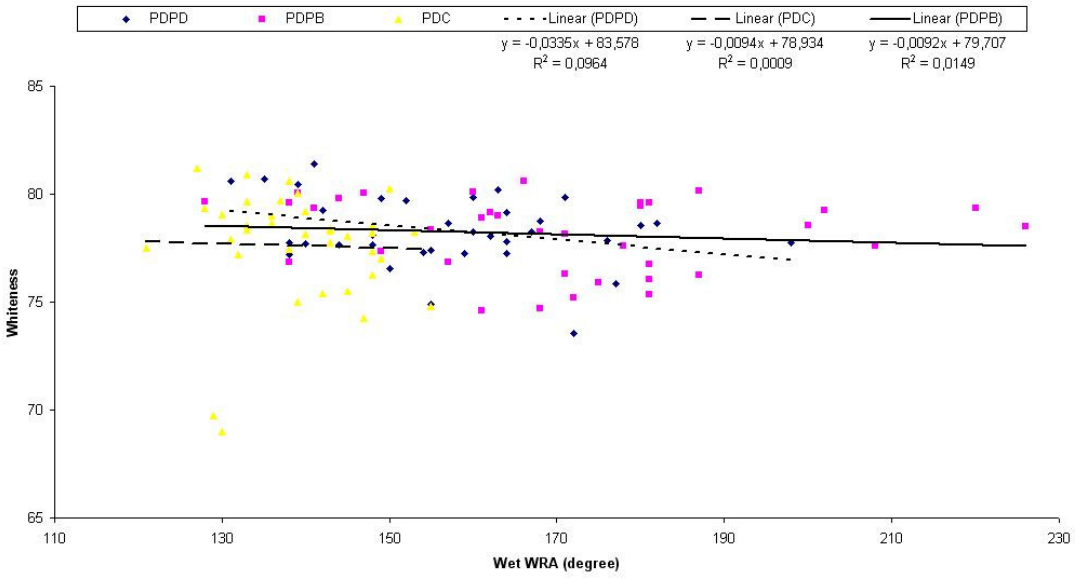

Figure 4.33 : Interaction between wet WRA and CIE whiteness index.

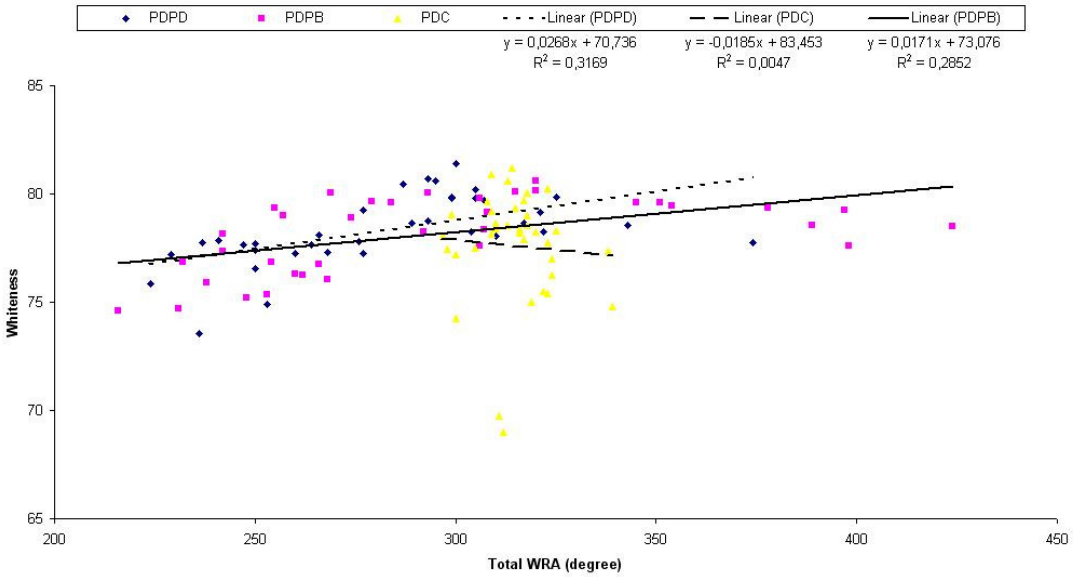

Figure 4.34 : Interaction between total WRA and CIE whiteness index.

CIE whiteness index slightly decreases with increasing wet WRA as shown in Figure 4.33. Increase in total WRA slightly increased CIE whiteness index for PDC and PDPD treated samples, but it slightly decreased CIE whiteness index for PDC samples as shown in Figure 4.34.

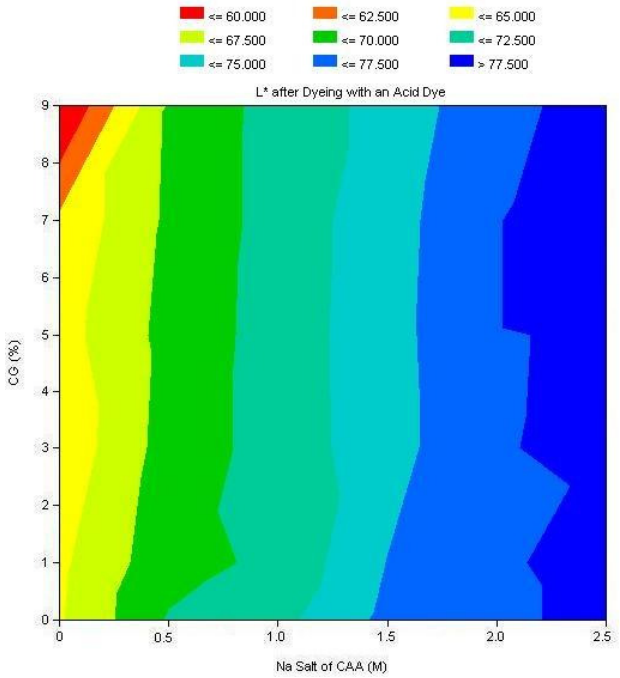

Figure 4.35 : The effects of Na salt of CAA and CG on L* for PDPD treated and acid dyed samples.

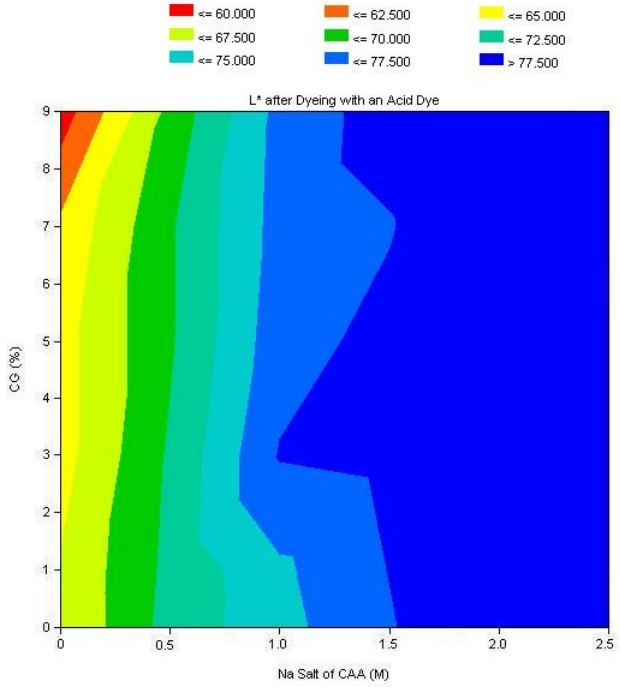

Figure 4.36 : The effects of Na salt of CAA and CG on L* for PDPB treated and acid dyed samples.

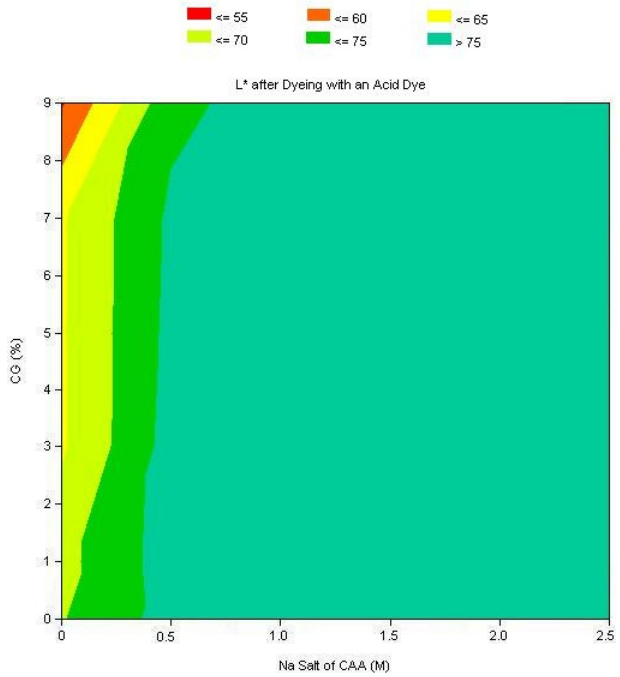

Figure 4.37 : The effects of Na salt of CAA and CG on L* for PDC treated and acid dyed samples.

Na salt of CAA and L* values for samples colored with acid dye (see Figures 4.35 to 4.37) are directly proportional with very high R^2 values (see Figure 4.38) which means that increase in number of anionic sites decreases the ability of acid dye to bond with cotton fabric. As the concentration of Na salt of CAA increases, it is harder for acid dye to bond with cotton fabric due to high negative charge of the fabric.

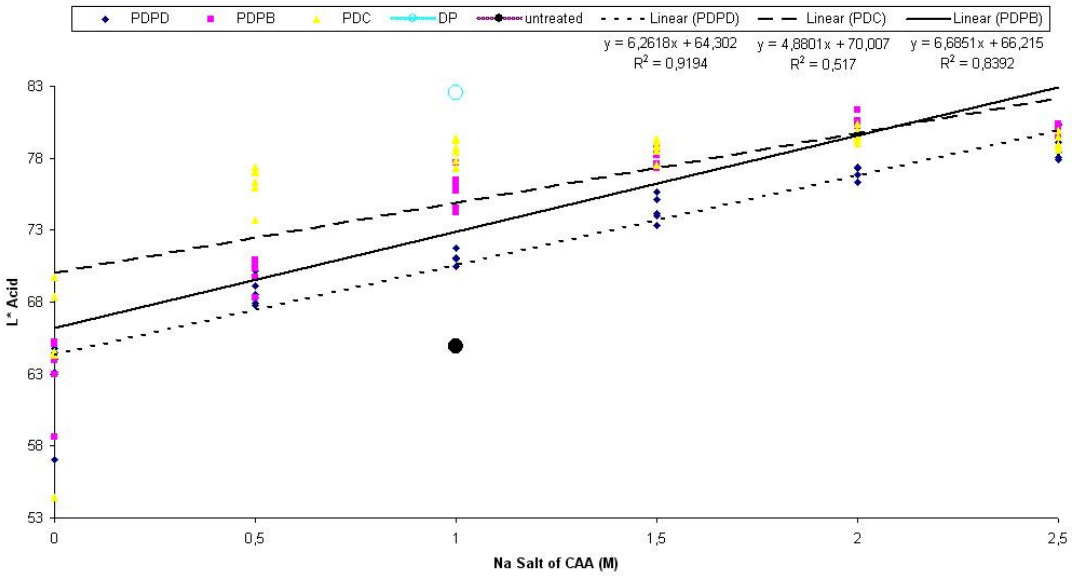

Figure 4.38 : Interaction between Na salt of CAA and L* for samples dyed with an acid dye.

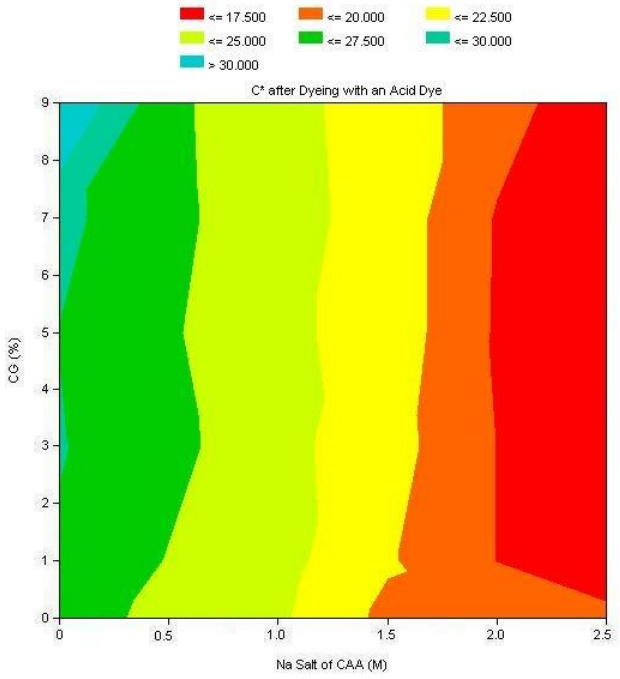

Figure 4.39 : The effects of Na salt of CAA and CG on C* for PDPD treated and acid dyed samples.

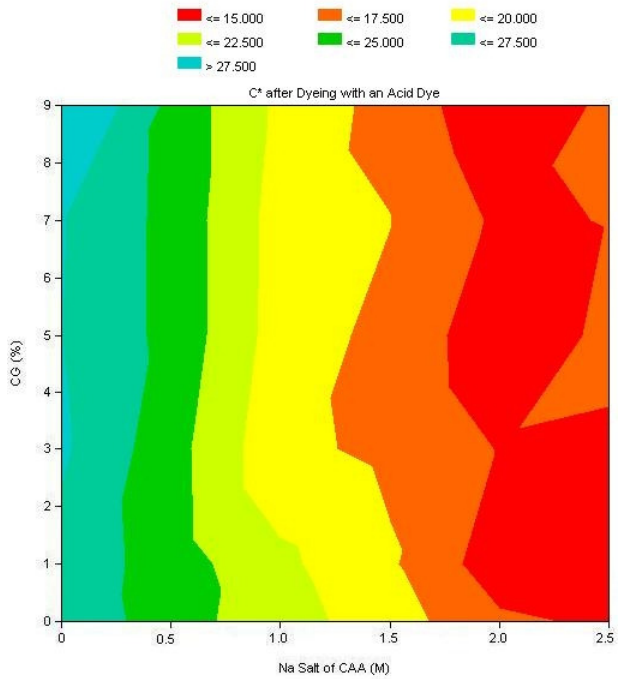

Figure 4.40 : The effects of Na salt of CAA and CG on C* for PDPB treated and acid dyed samples.

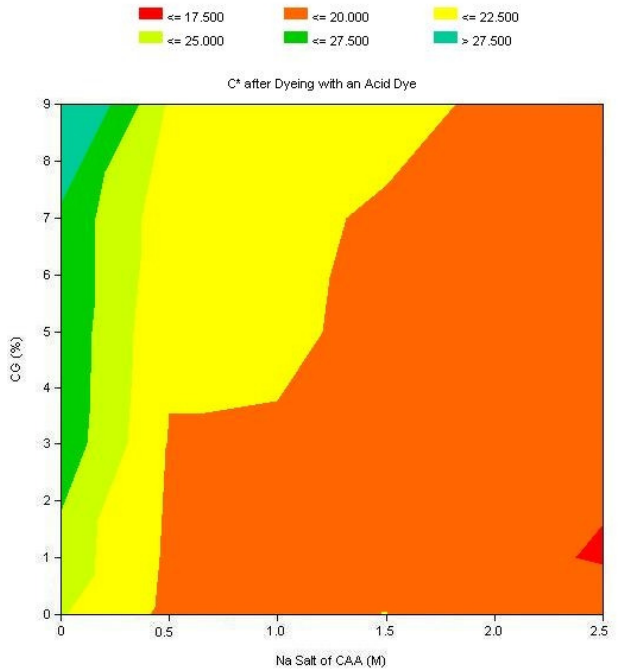

Figure 4.41 : The effects of Na salt of CAA and CG on C* for PDC treated and acid dyed samples.

C* (see Figures 4.39 to 4.41) and h* (see Figure 4.42 to 4.44) values decrease with increasing concentration of Na salt of CAA, but the trend is not as strong as that of

L*'s (see Figures 4.45 and 4.46 respectively). For PDPD and PDPB trials, both C* and h* sharply decrease after 2M Na salt of CAA level, but for PDC treatment the critical level is even lower which is arounf 0.5M.

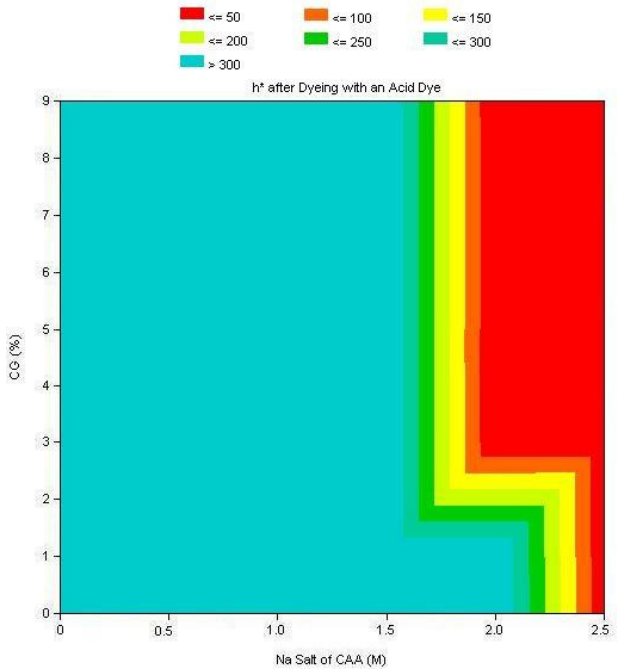

Figure 4.42 : The effects of Na salt of CAA and CG on h* for PDPD treated and acid dyed samples.

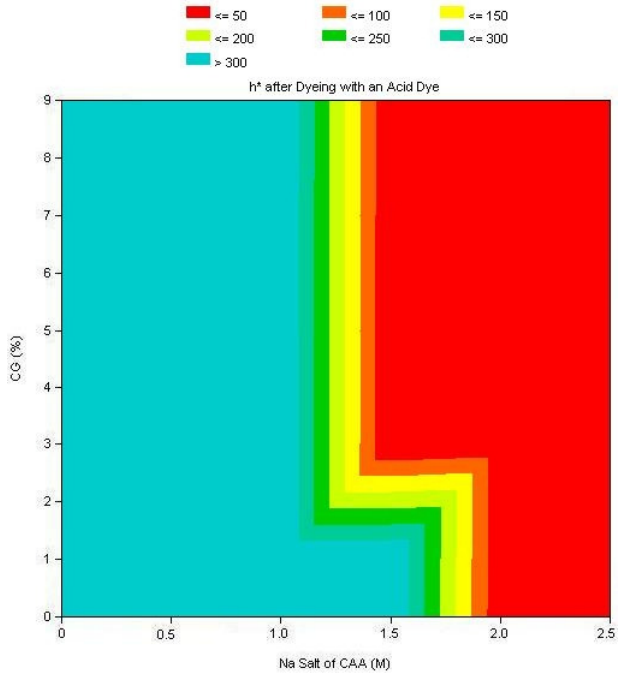

Figure 4.43 : The effects of Na salt of CAA and CG on h* for PDPB treated and acid dyed samples.

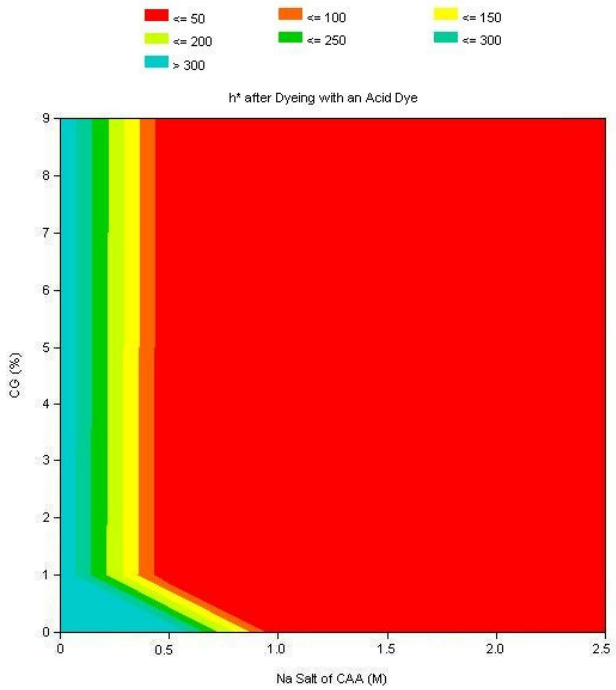

Figure 4.44 : The effects of Na salt of CAA and CG on h* for PDC treated and acid dyed samples.

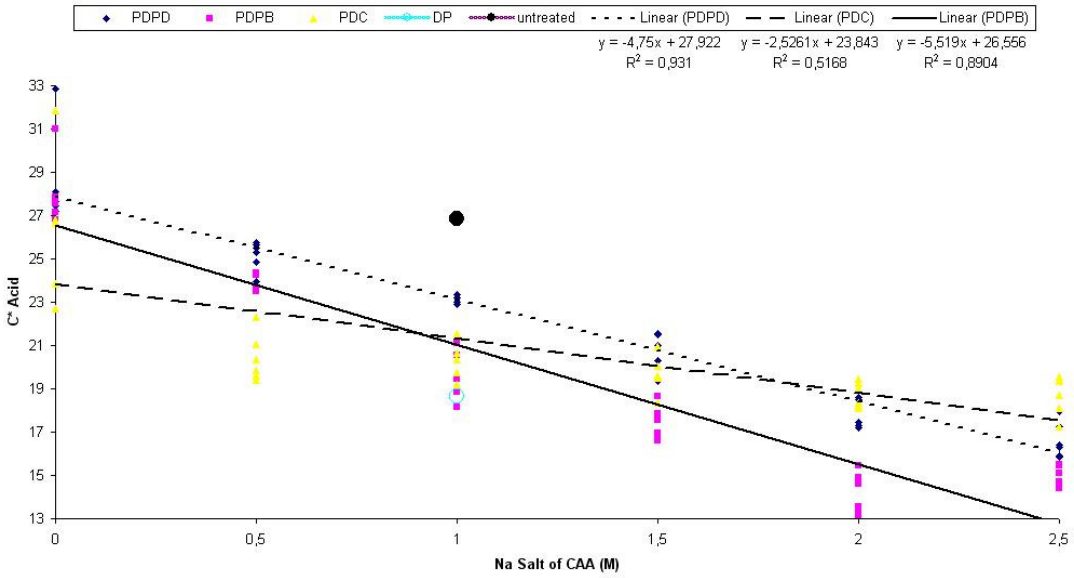

Figure 4.45 : Interaction between Na salt of CAA and C* for samples dyed with an acid dye.

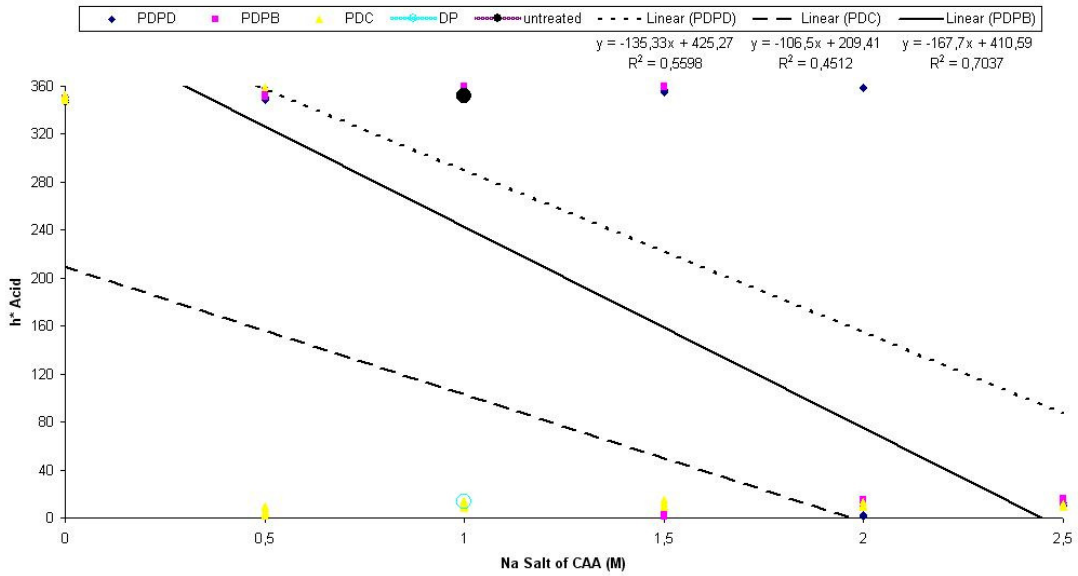

Figure 4.46 : Interaction between Na salt of CAA and h* for samples dyed with an acid dye.

As seen in Figures 4.35 to 4.37 and 4.39 to 4.44, variations in CG% value also has very little effect on L*, C* and h* values of acid dyed samples which means that cationic glycerin does not have available cationic sites for the acid dye to bond with. It is obvious that most of the cationic glycerin is crosslinked with anionic sites on the fabric which is also a measure of effectiveness of using cationic glycerin in ionic crosslinking of cotton fabric.

Na salt of CAA and L* values for cotton fabric samples colored with basic dye (see Figures 4.47 to 4.49) are inversely proportional with very high R^2 values (see Figure 4.50) which means that increase in number of anionic sites increased the ability of basic dye to bond with cotton fabric, as expected. The rather circular contour plot diagrams for all three methods show that CG% has an effect on dyeability of ionic crosslinked cotton with basic dye but it is less significant when compared with that of Na salt of CAA. PDPB treated samples offered lower L* values when compared with PDPD and PDC treated samples which means that the dyeability of PDPB treated samples to darker shades is higher than those of PDPD and PDC treated samples.

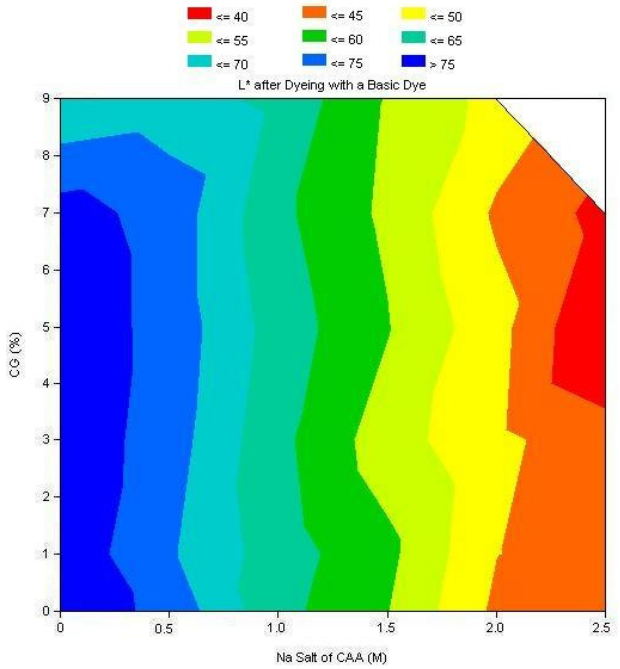

Figure 4.47 : The effects of Na salt of CAA and CG on L* for PDPD treated and basic dyed samples.

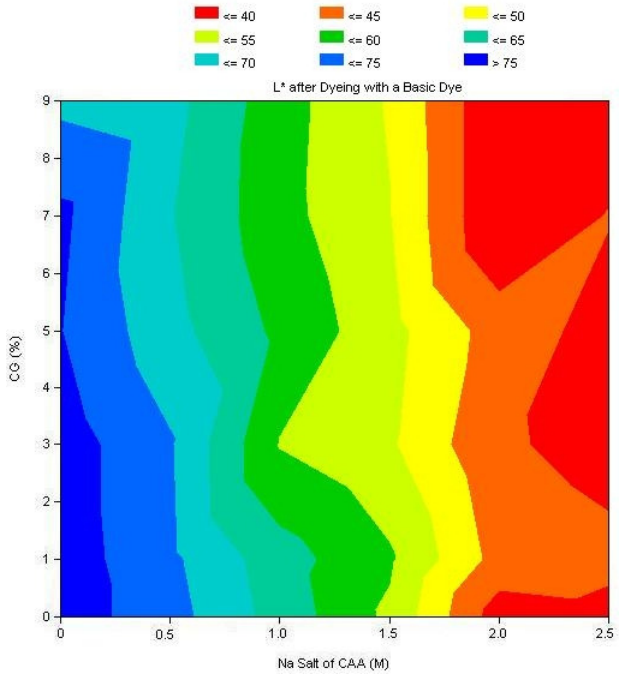

Figure 4.48 : The effects of Na salt of CAA and CG on L* for PDPB treated and basic dyed samples.

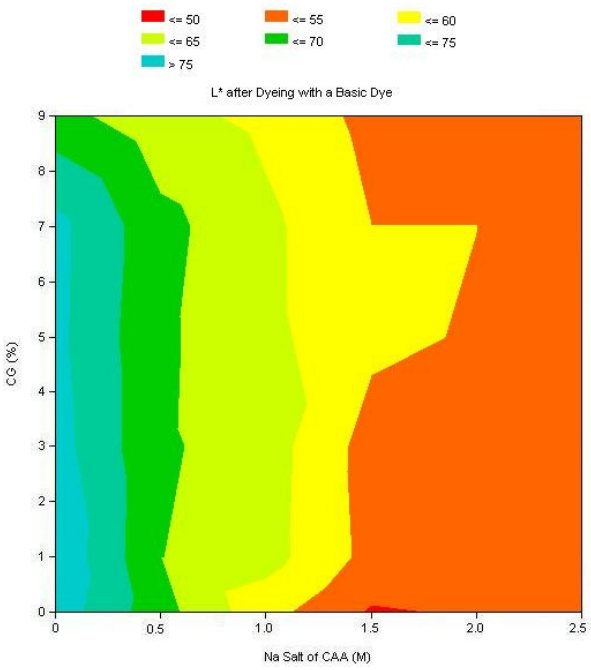

Figure 4.49 : The effects of Na salt of CAA and CG on L* for PDC treated and basic dyed samples.

Increase in CG% value has very little effect on L*, C* and h* values of basic dyed samples (see Figures 4.47 to 4.49 and 4.51 to 4.56) but for PDPB treatment with 1M Na salt of CAA and 3% CG or with 0.5M Na salt of CAA and 7% CG, the highest C* values may be reached.

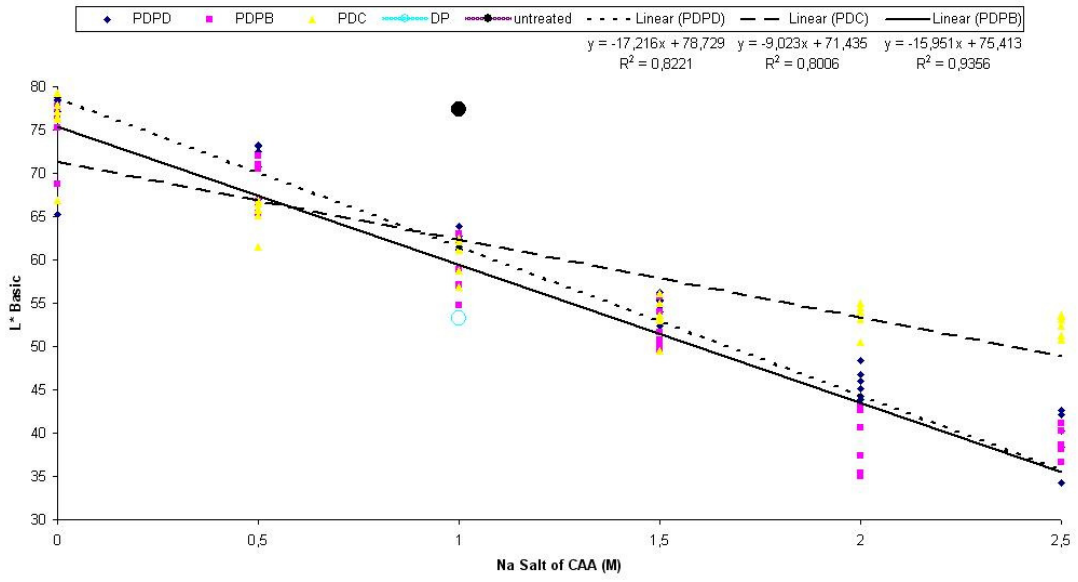

Figure 4.50 : Interaction between Na salt of CAA and L* for samples dyed with a basic dye.

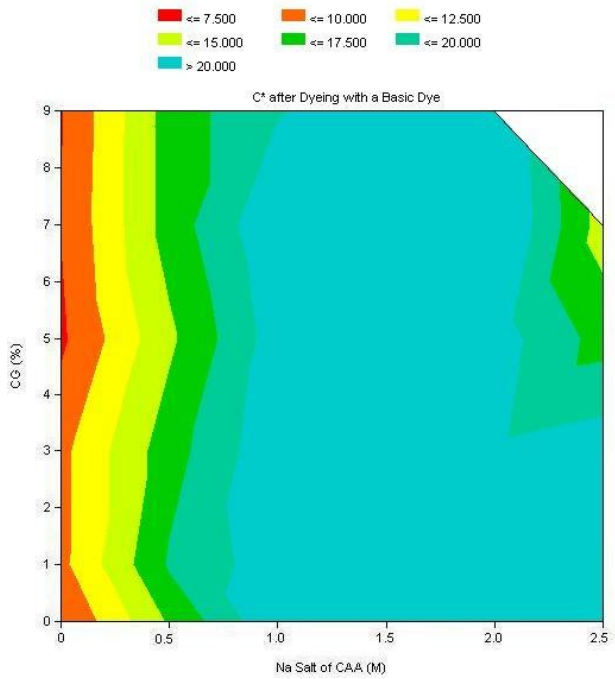

Figure 4.51 : The effects of Na salt of CAA and CG on C* for PDPD treated and basic dyed samples.

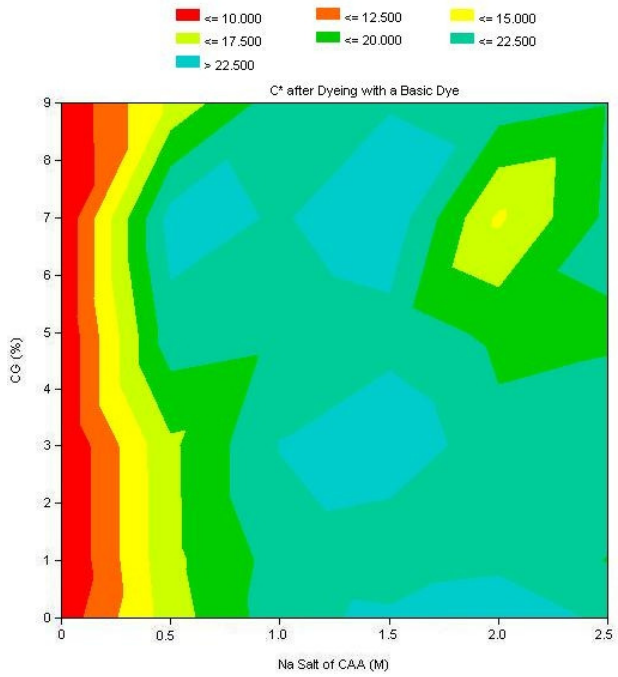

Figure 4.52 : The effects of Na salt of CAA and CG on C* for PDPB treated and basic dyed samples.

C* (see Figures 4.51 to 4.53) and h* (see Figures 4.54 to 4.56) values of basic dyed samples increase with increasing concentration of Na salt of CAA showing that the

saturation and tone of color increases which means that cotton fabric can be dyed to darker shades.

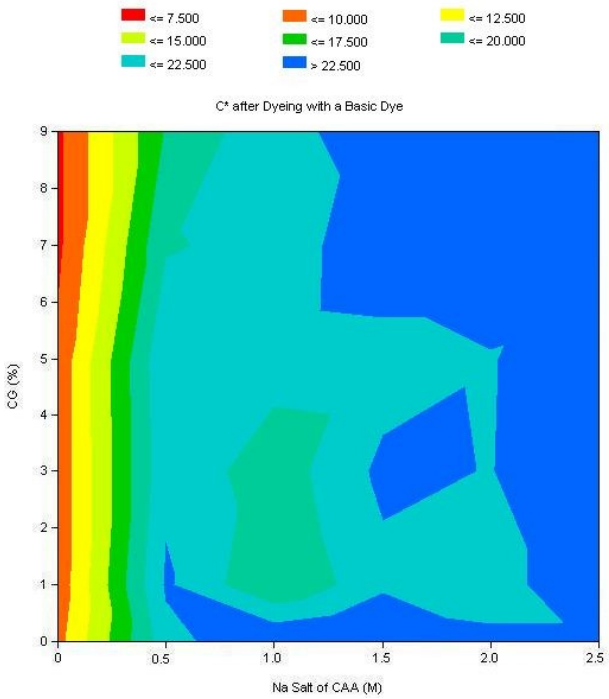

Figure 4.53 : The effects of Na salt of CAA and CG on C* for PDC treated and basic dyed samples.

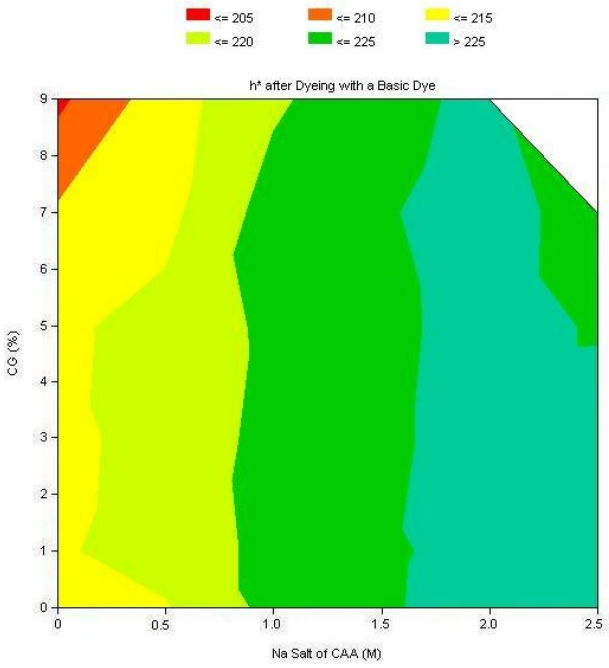

Figure 4.54 : The effects of Na salt of CAA and CG on h* for PDPD treated and basic dyed samples.

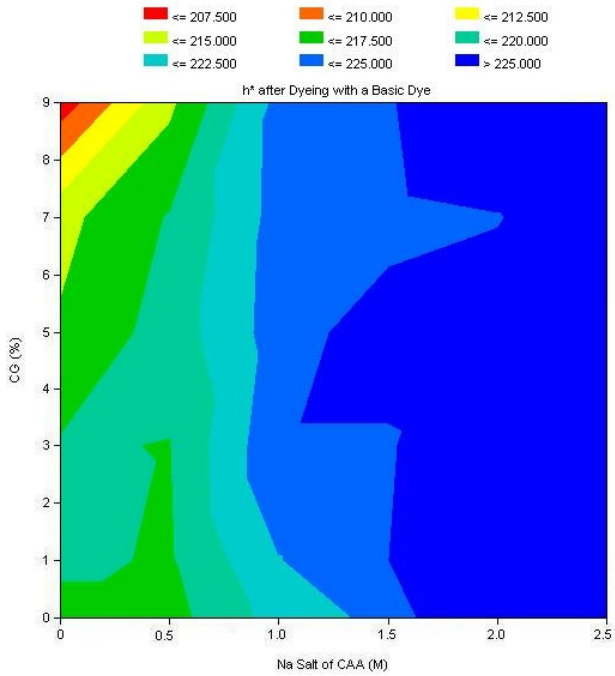

Figure 4.55 : The effects of Na salt of CAA and CG on h* for PDPB treated and basic dyed samples.

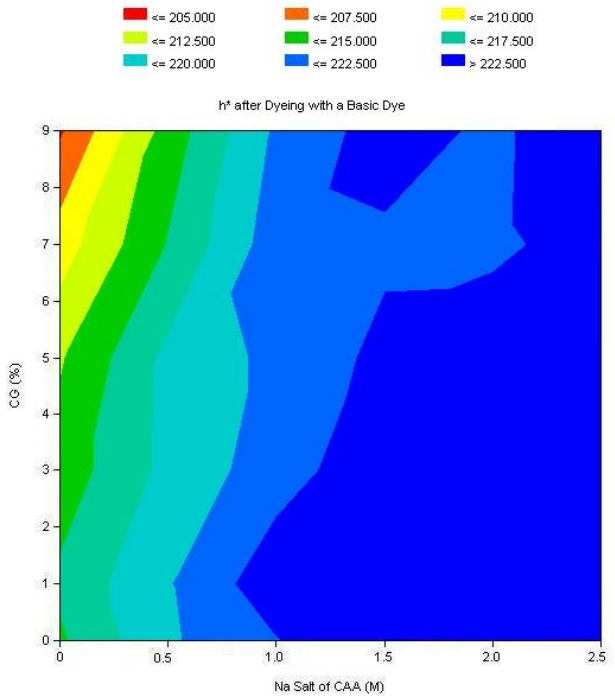

Figure 4.56 : The effects of Na salt of CAA and CG on h* for PDC treated and basic dyed samples.

Using 1M of Na salt of CAA looks to be enough to reach very high h* values for all three carboxymethylation methods followed. It is also apparent from Figures 4.53 to

4.55 that as CG% increases, h* values decrease. This was expected as the dye competes with cationic glycerin in bonding with cotton fabric.

4.2.2.7 Breaking strength, elongation and energy to peak load

The crosslinked samples are tested for breaking strength, elongation and energy to peak load. Average breaking strength, elongation and energy to peak load values of ionic crosslinked samples in warp direction are given in Table 4.22.

Table 4.22: Coded ID, average breaking strength, elongation and energy to peak load values of ionic crosslinked samples in warp direction.

Coded ID	Average breaking strength (Kgf)	Elongation (%)	Energy to peak load (Kg*mm)
111	30.07	10.77	14.11
112	30.36	10.60	13.86
113	23.47	9.47	12.39
114	29.60	10.53	13.80
115	28.78	10.80	14.13
116	27.11	10.37	13.59
121	28.94	11.87	15.57
122	30.92	12.27	16.08
123	26.47	11.17	14.63
124	28.04	11.43	15.01
125	24.83	10.97	14.37
126	27.98	11.83	15.51
131	32.05	15.97	21.00
132	27.85	14.27	18.73
133	33.43	15.17	19.90
134	32.54	14.03	18.42
135	33.98	12.90	16.92
136	32.26	11.70	15.32
141	25.34	17.20	22.57
142	25.43	15.13	19.88
143	28.22	15.03	19.70
144	27.53	14.37	18.90
145	30.30	14.80	19.45
146	30.32	15.40	20.23
151	25.93	20.90	27.46
152	30.19	23.53	30.84
153	32.33	23.20	30.43
154	29.44	10.10	26.34
155	27.71	19.40	25.48
156	31.07	18.33	24.04
161	18.15	22.87	30.00
162	30.29	22.43	29.44
163	30.15	31.33	41.11
164	31.08	30.53	40.04
165	30.15	24.27	31.86
166	32.31	27.07	35.54
211	28.62	10.50	13.73
212	29.35	10.47	13.69
213	31.00	10.43	13.68
214	30.38	9.83	12.90
215	31.46	10.53	13.81
216	28.29	10.47	13.68
221	30.73	11.53	15.13
222	29.13	11.30	14.82
223	29.59	11.83	15.49
224	29.56	11.17	14.62
225	29.02	11.50	15.08
226	30.19	11.63	15.25
231	28.88	13.47	17.68
232	31.09	13.27	17.42
233	29.61	15.73	20.70
234	29.02	13.43	17.63
235	31.70	14.73	19.38
236	32.77	15.30	20.07

Table 4.22 (continued): Coded ID, average breaking strength, elongation and energy to peak load values of ionic crosslinked samples in warp direction.

Coded ID	Average breaking strength (Kgf)	Elongation (%)	Energy to peak load (Kg*mm)
241	28.41	17.07	22.37
242	32.38	17.53	22.98
243	33.65	17.37	22.76
244	32.14	17.60	23.07
245	30.89	19.07	25.01
246	27.33	17.40	22.85
251	33.13	23.83	31.27
252	32.79	23.23	30.47
253	36.41	24.83	32.60
254	32.39	23.47	30.80
255	36.65	26.87	35.21
256	36.10	25.73	33.82
261	30.96	26.47	34.74
262	32.99	24.33	31.93
263	35.65	25.90	34.02
264	34.61	24.27	31.82
265	35.25	23.43	30.71
266	36.54	25,43	33.39
311	24.75	7.87	10.32
312	20.63	6.93	9.12
313	25.85	7.60	10.00
314	25.66	7.73	10.17
315	26.73	8.20	10.77
316	26.87	7.93	10.41
321	22.05	7.83	10.30
322	19.20	7.23	9.50
323	24.60	8.43	11.11
324	24.52	7.87	10.36
325	23.12	7.40	9.75
326	23.20	7.90	10.39
331	21.49	10.23	13.41
332	23.27	9.67	12.66
333	21.14	8.57	11.27
334	21.84	8.40	11.04
335	20.86	7.83	10.33
336	25.40	9.33	12.25
341	23.79	12.60	16.55
342	18.97	11.10	14.55
343	22.96	14.30	18.74
344	23.87	10.93	14.33
345	19.55	9.40	12.29
346	22.80	9.73	12.75
351	23.49	14.57	19.08
352	22.97	12.60	16.54
353	24.17	9.93	13.03
354	21.40	11.53	15.15
355	18.31	10.40	13.64
356	19.43	12.13	15.92
361	24.78	14.57	19.13
362	23.22	12.10	15.87
363	24.18	11.03	14.45
364	20.89	11.30	14.82
365	19.18	9.57	12.53
366	19.43	10.67	13.99

Average breaking strength, elongation and energy to peak load values of ionic crosslinked samples in filling direction are given in Table 4.23.

Table 4.23: Coded ID, average breaking strength, elongation and energy to peak load values of ionic crosslinked samples in filling direction.

Coded ID	Average breaking strength (Kgf)	elongation (%)	Energy to peak load (Kg*mm)
111	19.30	21.40	107.38
112	18.21	20.40	97.78
113	16.45	20.65	89.30
114	19.07	22.70	113.60
115	16.62	21.95	96.40
116	20.11	23.45	119.62
121	19.04	22.15	110.41
122	19.37	24.25	118.35
123	19.73	24.25	121.83
124	17.61	21.45	69.35
125	13.60	20.65	72.16
126	17.43	21.65	94.21
131	18.55	28.55	128.32
132	21.42	26.50	142.17
133	19.65	27.80	136.41
134	17.74	26.25	114.88
135	20.56	26.25	132.87
136	21.46	26.75	142.72
141	19.36	27.25	128.74
142	19.56	25.75	122.58
143	15.31	24.25	90.13
144	18.79	25.25	119.48
145	21.05	26.50	141.21
146	19.07	27.00	123.44
151	16.60	29.60	117.48
152	17.86	30.85	128.93
153	23.17	32.10	178.38
154	22.74	31.10	174.16
155	15.49	25.00	99.48
156	20.81	29.05	150.34
161	27.70	22.20	165.33
162	20.25	28.50	143.05
163	23.54	39.70	224.26
164	20.59	33.65	169.19
165	19.24	32.35	150.69
166	22.19	38.20	202.02
211	21.83	23.75	133.55
212	20.52	23.95	125.65
213	21.82	23.50	130.17
214	18.30	24.00	111.95
215	19.75	23.20	117.59
216	21.08	24.50	129.83
221	18.63	24.00	109.21
222	20.47	24.25	128.15
223	21.38	24.25	134.26
224	20.05	22.45	118.52
225	18.71	21.90	106.98
226	21.60	25.50	141.61
231	21.28	24.25	135.55
232	21.62	24.00	135.62
233	20.19	30.05	147.66
234	23.33	26.75	157.50
235	17.59	23.50	110.60
236	19.63	24.75	122.11
241	17.56	25.00	109.83
242	21.87	26.00	150.01
243	20.47	26.25	135.96
244	20.77	27.75	140.06
245	22.91	32.60	180.46
246	20.75	29.85	149.28
251	16.20	30.80	128.57
252	20.20	30.10	151.05
253	25.93	35.90	225.20
254	23.55	34.60	207.57
255	23.99	39.20	226.11
256	22.30	33.85	191.18
261	24.03	34.35	205.02
262	20.33	31.10	155.41
263	23.21	34.60	189.82
264	25.60	34.90	217.22
265	22.20	33.10	175.15

Table 4.23 (continued): Coded ID, average breaking strength, elongation and energy to peak load values of ionic crosslinked samples in filling direction.

Coded ID	Average breaking strength (Kgf)	elongation (%)	Energy to peak load (Kg*mm)
266	25.03	35.65	217.08
311	18.09	17.40	78.27
312	13.72	15.80	57.00
313	16.50	16.65	70.15
314	14.03	15.30	53.75
315	15.21	15.60	60.98
316	15.86	16.85	66.38
321	17.56	16.85	76.92
322	15.30	16.85	66.13
323	14.74	17.65	62.67
324	15.76	16.85	67.77
325	16.58	17.90	75.13
326	14.34	16.35	57.67
331	12.69	18.65	58.47
332	16.44	19.15	75.99
333	13.69	18.40	61.09
334	15.85	17.65	69.25
335	16.08	17.15	71.51
336	17.08	19.15	81.77
341	17.79	22.15	95.71
342	11.86	17.40	52.45
343	16.88	21.65	89.21
344	15.76	19.90	77.14
345	15.67	18.40	73.30
346	11.14	17.15	45.59
351	13.66	20.65	69.31
352	13.83	19.90	66.54
353	16.44	20.15	82.00
354	14.68	18.90	68.86
355	10.16	17.90	44.60
356	14.91	19.40	69.64
361	16.15	22.95	91.78
362	14.35	20.40	71.12
363	18.09	21.15	94.91
364	16.56	20.90	84.00
365	10.88	18.40	50.18
366	14.56	19.65	69.83

As mentioned before, breaking strength, elongation and energy to peak load values for DMDHEU treated samples are 5.65 Kgf, 6.13%, 7.52 Kg.mm in warp direction and 4.42 Kgf, 12.30%, 14.69 Kg.mm in filling direction, and those for untreated sample are 23.86 Kgf, 10.3%, 87.62Kg.mm in warp direction and 17.23 Kgf, 17.90%, 76.83 Kg.mm in filling direction respectively.

The Prob > F results of the ANOVA analysis are shown in Table 4.24. It is apparent from data on Table 4.24 that the effects of Na salt of CAA and CG on breaking strength, elongation and energy to peak load of samples in warp direction are very significant, but those in filling direction are less significant or even insignificant. The main reason for that may be the tension always being in warp direction during treating our samples. We believe the tension exerted during drying and curing in the oven helped our samples gain extra strength related qualities.

Table 4.24: Prob > F values for breaking strength, elongation and energy to peak load responses of PDPD, PDPB and PDC trials.

Response	Prob > F for trials		
	PDPD	PDPB	PDC
Breaking strength (warp)	0.0367	<0.0001	<0.0001
Breaking strength (filling)	<0.0551	<0.0116	<0.3818
Elongation (warp)	<0.0001	<0.0001	<0.0001
Elongation (filling)	<0.0001	<0.0001	<0.0001
Energy to peak load (warp)	<0.0001	<0.0001	<0.0001
Energy to peak load (filling)	<0.0001	<0.0001	<0.0928

The effects of the Na salt of CAA and CG on breaking strength, elongation and energy to peak load for PDPD, PDPB and PDC treated and crosslinked samples are shown in Figures 4.57 to 4.98.

As shown in Figure 4.57, breaking strength in warp direction for PDPD samples is not directly related with increase in CG% or Na salt of CAA. It is higher at a Na salt of CAA level of 1M regardless of the percentage of CG% applied except 1%CG level. This level of CG results in a decrease in breaking strength but only to a limited extend. Contrart to that PDPB samples have higher breaking strength in warp direction when higher amount of CG and Na salt of CAA are used (see Figure 4.58).

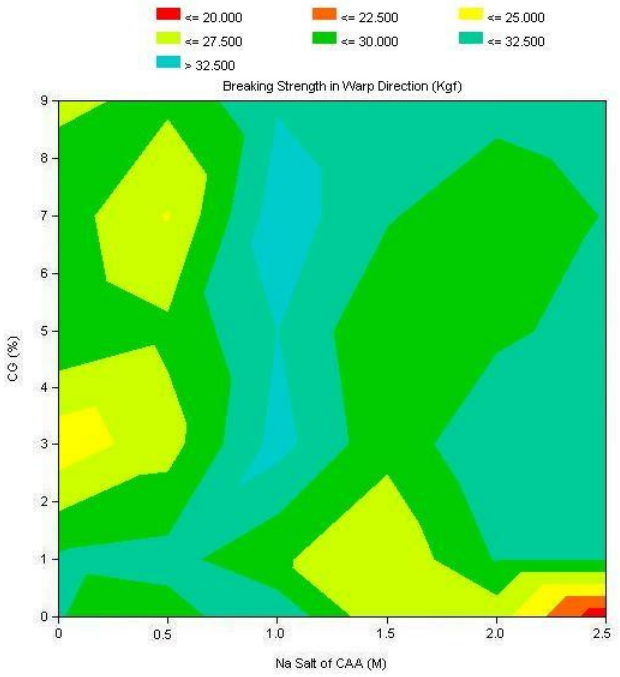

Figure 4.57 : The effects of Na salt of CAA and CG on breaking strength in warp direction for PDPD treated samples.

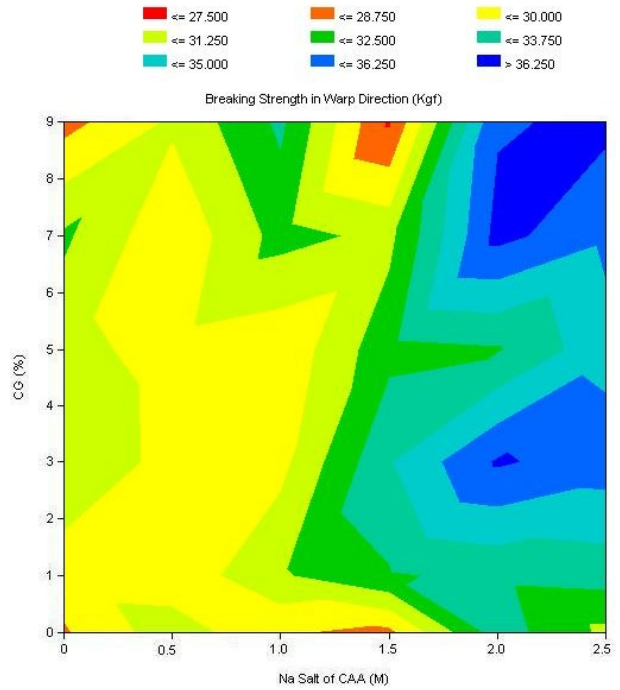

Figure 4.58 : The effects of Na salt of CAA and CG on breaking strength in warp direction for PDPB treated samples.

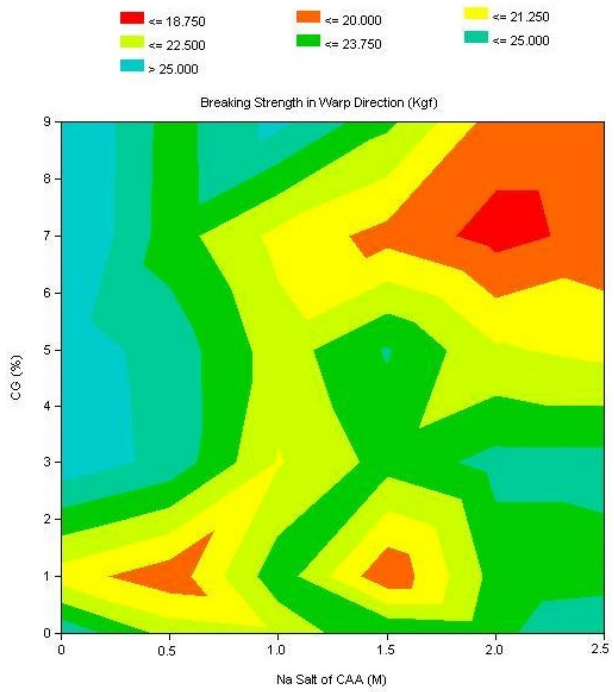

Figure 4.59 : The effects of Na salt of CAA and CG on breaking strength in warp direction for PDC treated samples.

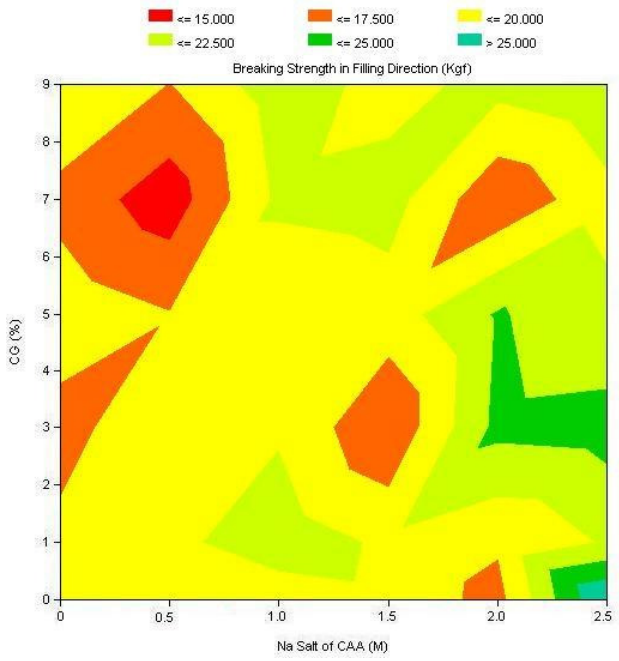

Figure 4.60 : The effects of Na salt of CAA and CG on breaking strength in filling direction for PDPD treated samples.

The effect of increase in molarity of Na salt of CAA on breaking strength in warp direction for PDPB samples are more significant than that of CG but the highest

breaking strength values in warp direction are reached in the highest levels of CG and Na salt of CAA. As shown in Figure 4.59, breaking strength in warp direction for PDC samples decrease with increasing amounts of CG and Na salt of CAA.

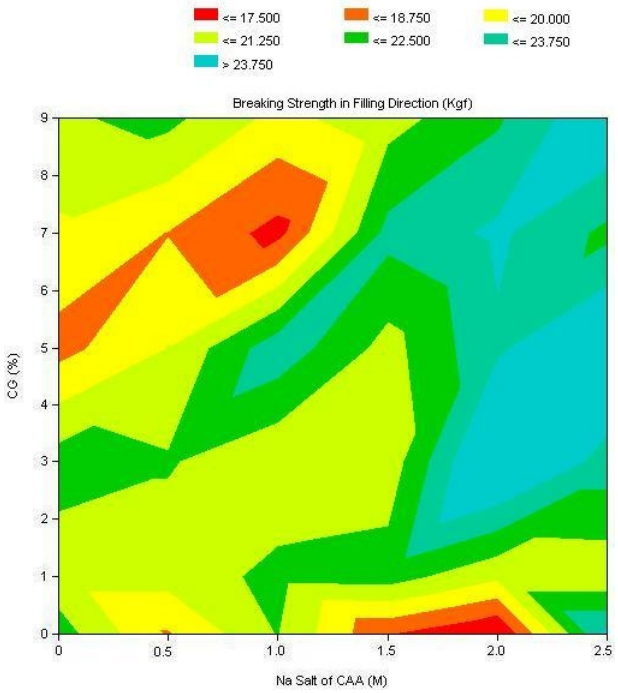

Figure 4.61 : The effects of Na salt of CAA and CG on breaking strength in filling direction for PDPB treated samples.

As shown in Figure 4.60, breaking strength in filling direction for PDPD samples is not directly related with increase in CG% or Na salt of CAA. It is higher when concentrations of one of both Na salt of CAA and CG are high but the trend is not significant. Contract to that PDPB samples have higher breaking strength in warp direction when molarity of Na salt of CAA and CG% used are higher than 1.5M and 1% respectively (see Figure 4.61). As shown in Figure 4.62, breaking strength values in filling direction for PDC sample are insignificant.

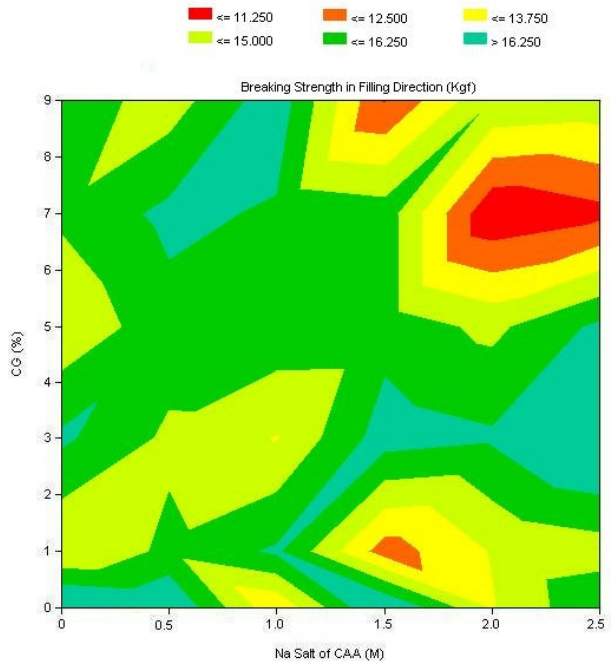

Figure 4.62 : The effects of Na salt of CAA and CG on breaking strength in filling direction for PDC treated samples.

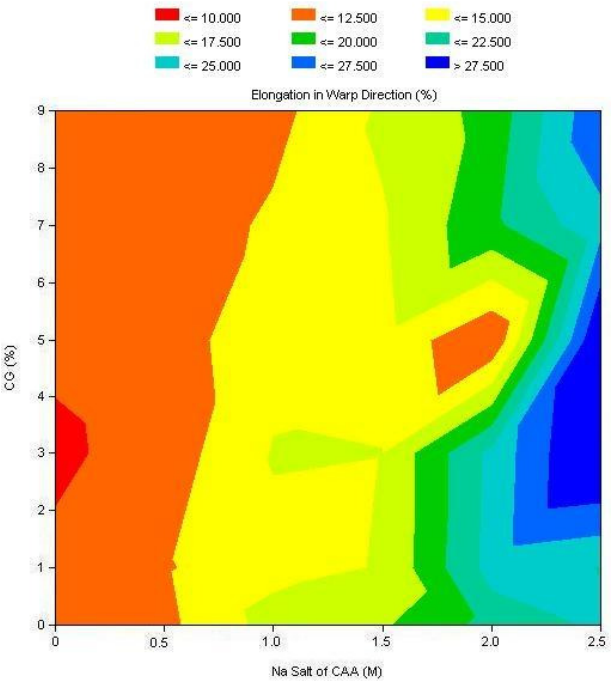

Figure 4.63 : The effects of Na salt of CAA and CG on elongation in warp direction for PDPD treated samples.

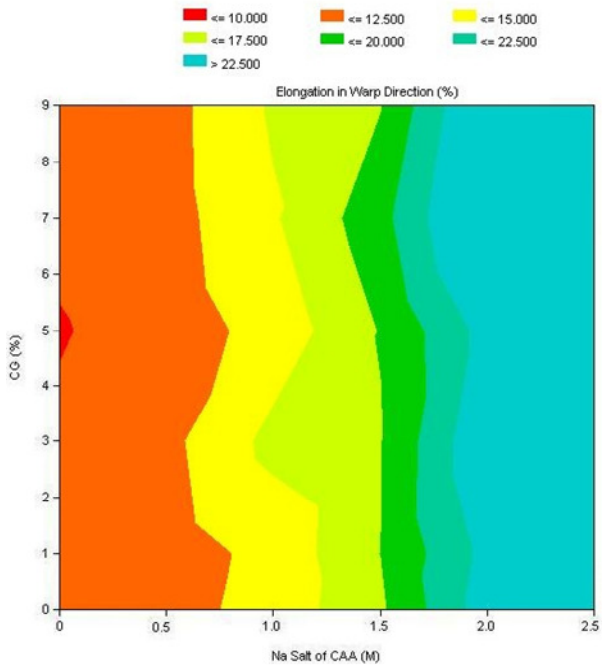

Figure 4.64 : The effects of Na salt of CAA and CG on elongation in warp direction for PDPB treated samples.

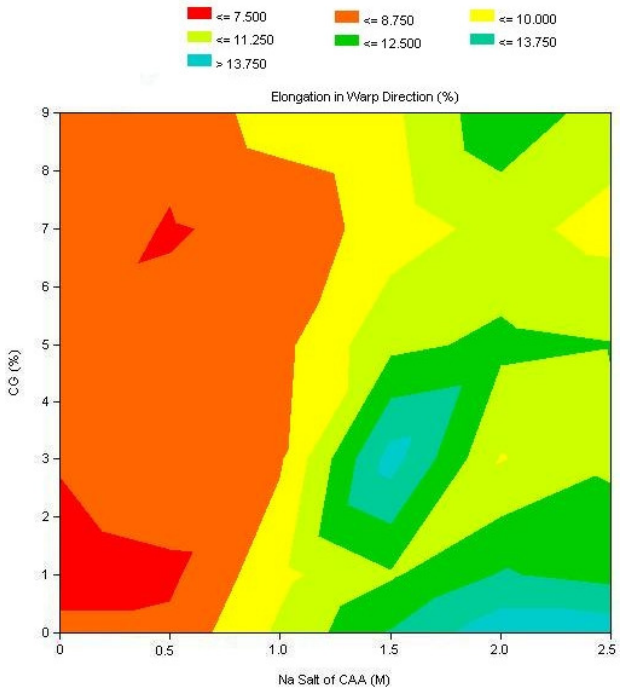

Figure 4.65 : The effects of Na salt of CAA and CG on elongation in warp direction for PDC treated samples.

Elongation in warp direction for PDPD, PDPB and PDC are mainly determined by the amount of Na salt of CAA applied as shown in Figure 4.63, 4.64 and 4.65 respectively.

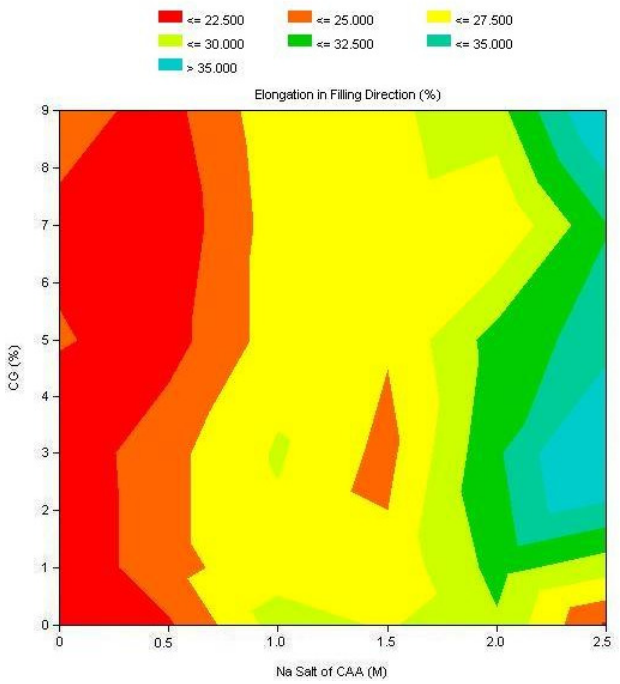

Figure 4.66 : The effects of Na salt of CAA and CG on elongation in filling direction for PDPD treated samples.

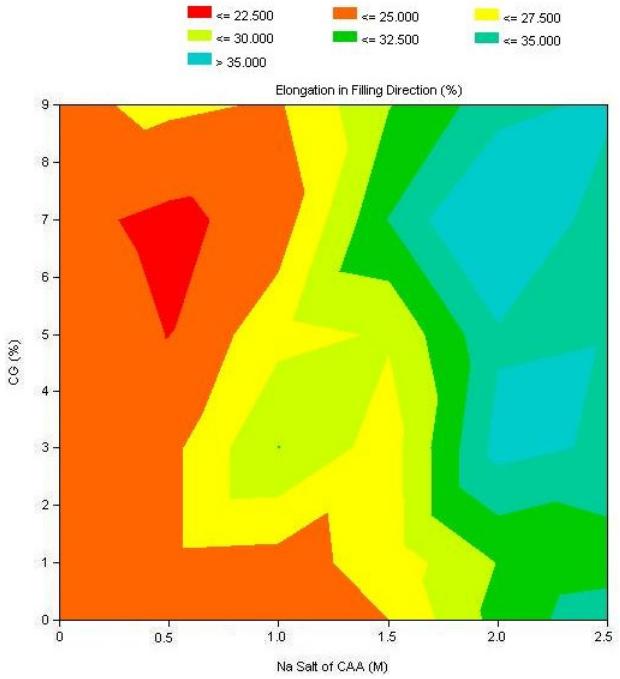

Figure 4.67 : The effects of Na Salt of CAA and CG on elongation in filling direction for PDPB treated samples.

The trend is more significant for PDPD and PDPB treated samples (see Figure 4.63 and 4.64). The highest elongation values are reached at high Na salt of CAA levels regardless of the amount of CG applied except for PDC treated sample that had a high elongation at 3% CG level with 1.5M Na salt of CAA as shown in Figure 4.65.

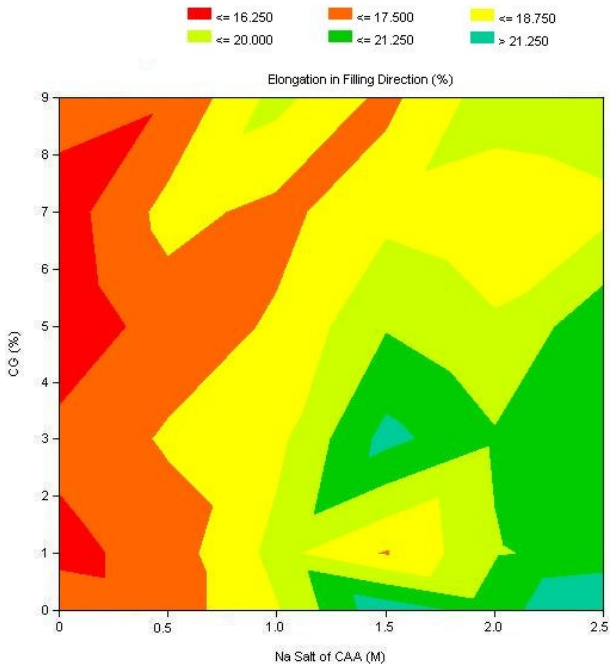

Figure 4.68 : The effects of Na salt of CAA and CG on elongation in filling direction for PDC treated samples.

The amount of Na salt of CAA had significant effect on elongation in filling direction for PDPD, PDPB and PDC as shown in Figure 4.66, 4.67 and 4.68 respectively. When CG% is higher than 5% for PDPD treatment, elongation slightly decreases (see Figure 4.66). As shown In Figure 4.67, highest elongation results with PDPB treatment are reached at higher concentrations of Na salt of CAA and CG but the chemical levels giving better WRA performance result (1M Na salt of CAA and 3% CG) offers a local maximum of arounf 30% which is very high. The effect of CG% on elongation is weak except for PDPB treated samples (see Figure 4.67). PDC had the same peak at 3% CG level with 1.5M Na salt of CAA as shown in Figure 4.68.

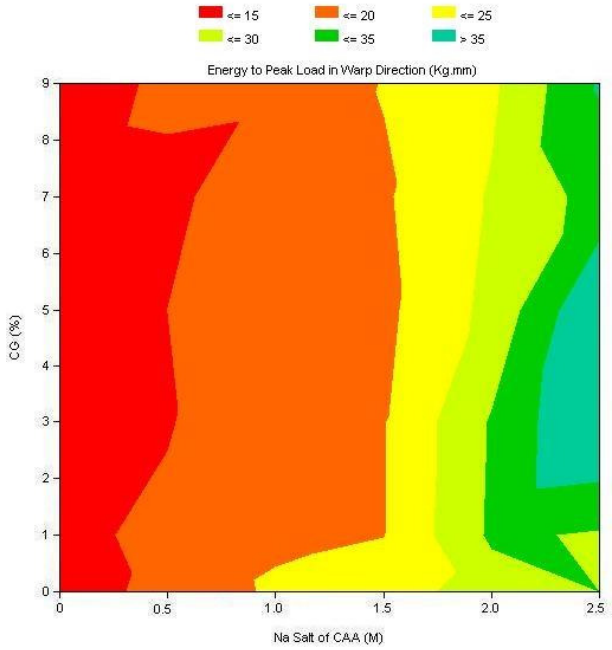

Figure 4.69 : The effects of Na salt of CAA and CG on energy to peak load in warp direction for PDPD treated samples.

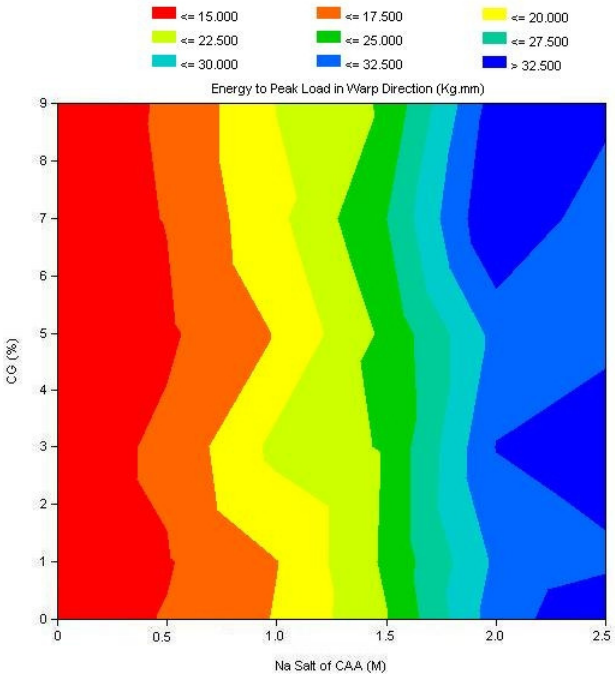

Figure 4.70 : The effects of Na salt of CAA and CG on energy to peak load in warp direction for PDPB treated samples.

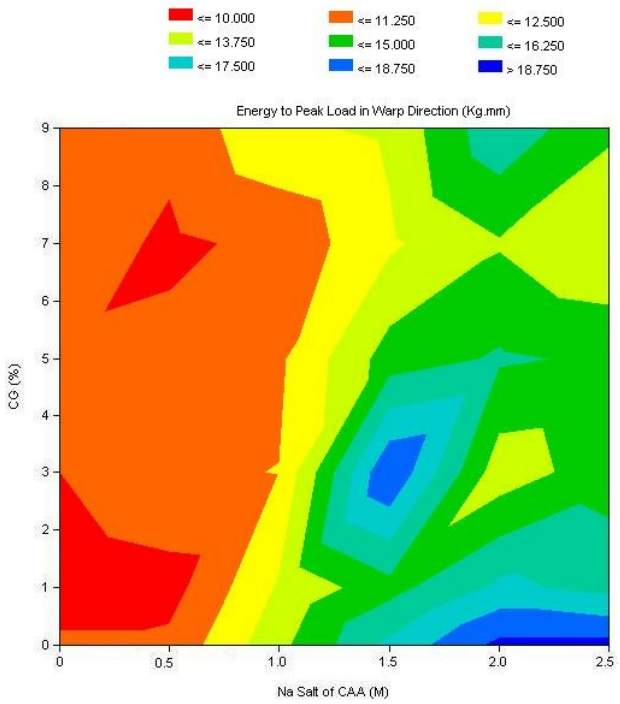

Figure 4.71 : The effects of Na salt of CAA and CG on energy to peak load in warp direction for PDC treated samples.

Energy to peak load in warp direction for PDPD, PDPB and PDC treated samples followed a similar trend with elongation in warp direction for PDPD, PDPB and PDC. Energy to peak load values increased as molarity of Na salt of CAA increased as shown in Figure 4.69, 4.70 and 4.71. The effect of Na salt of CAA is more significant for PDPD and PDPB treated samples (see Figure 4.69 and 4.70). One again, PDC treated sample that had a peak value at 3% CG level with 1.5M Na salt of CAA as shown in Figure 4.71.

Energy to peak load in filling direction for PDPD, PDPB and PDC treated samples followed a similar trend with breaking strength in filling for PDPD, PDPB and PDC treated samples (see Figure 4.72, 4.73 and 4.74 respectively). As shown in Figure 4.72, breaking strength in filling direction for PDPD was mostly increased by increase in molarity of Na salt of CC used. Contrart to that PDPB samples have higher breaking strength in warp direction when molarity of Na salt of CAA is higher than 1M which shows that CG has an effect on resulting energy to peak load values (see Figure 4.73). As shown in Figure 4.74, breaking strength values in filling direction for PDC sample are insignificant.

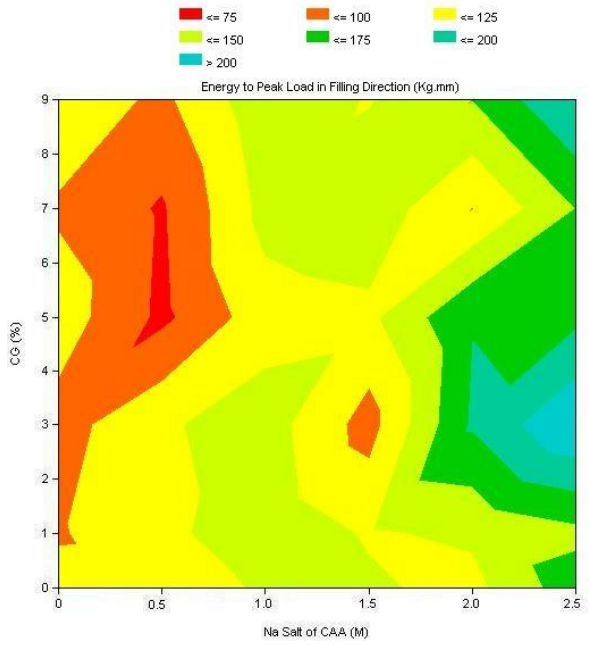

Figure 4.72 : The effects of Na salt of CAA and CG on energy to peak load in filling direction for PDPD treated samples.

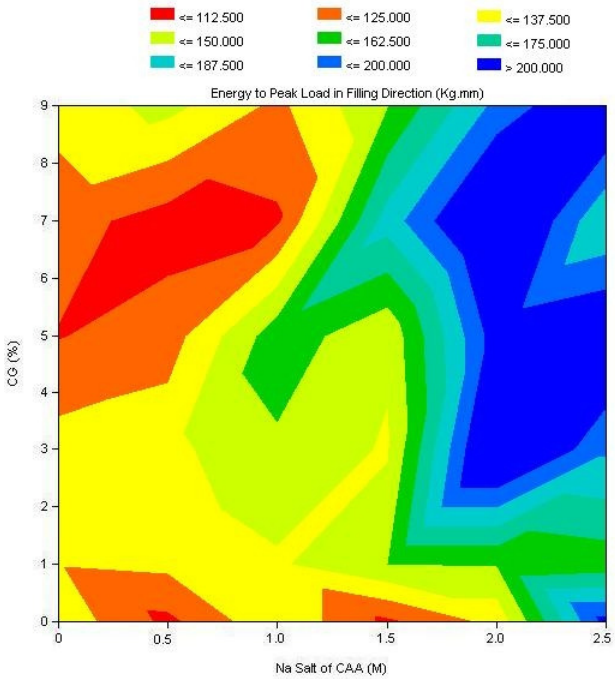

Figure 4.73 : The effects of Na salt of CAA and CG on energy to peak load in filling direction for PDPB treated samples.

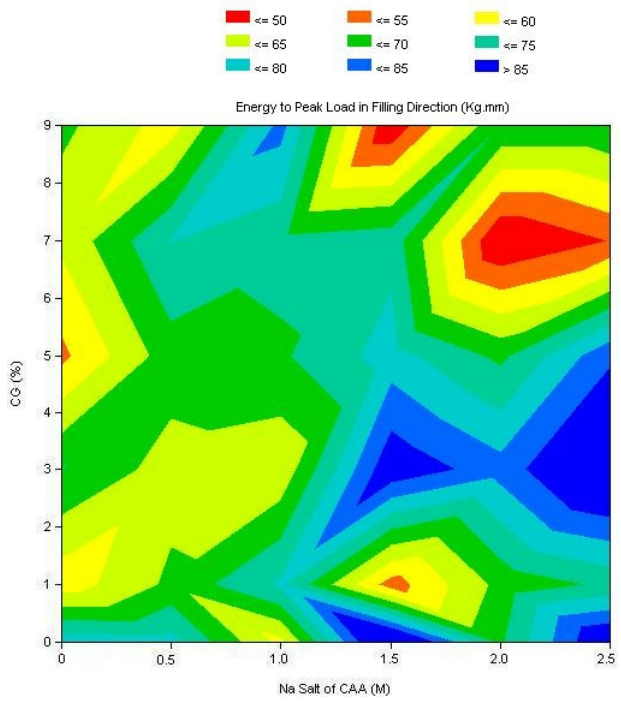

Figure 4.74 : The effects of Na salt of CAA and CG on energy to peak load in filling direction for PDC treated samples.

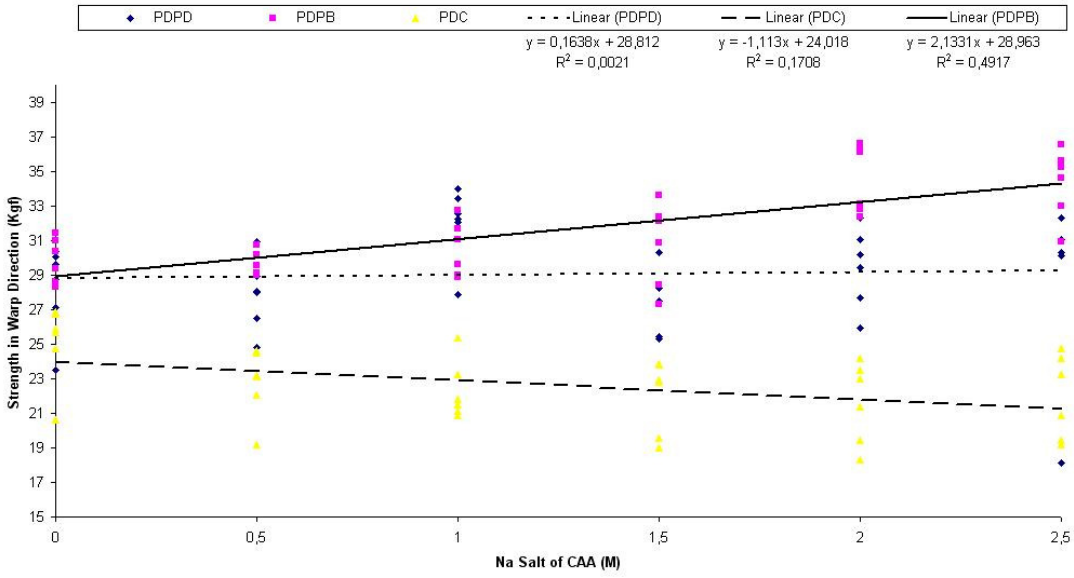

Figure 4.75 : Interaction between Na salt of CAA and breaking strength in warp direction.

As shown in Figure 4.75, the breaking strength values in warp direction are positively but weakly correlated with Na salt of CAA.

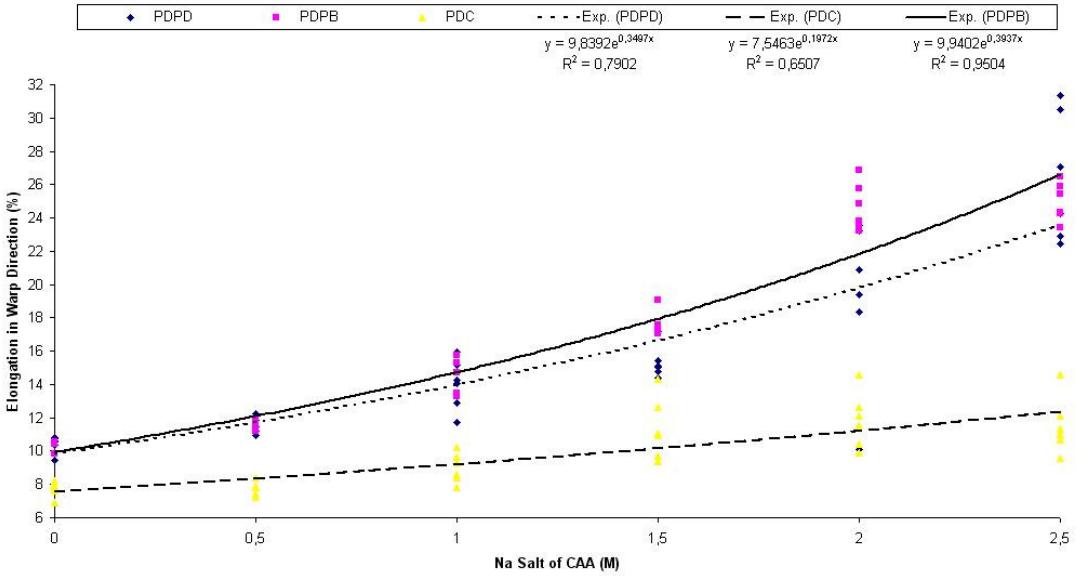

Figure 4.76 : Interaction between Na salt of CAA and elongation in warp direction.

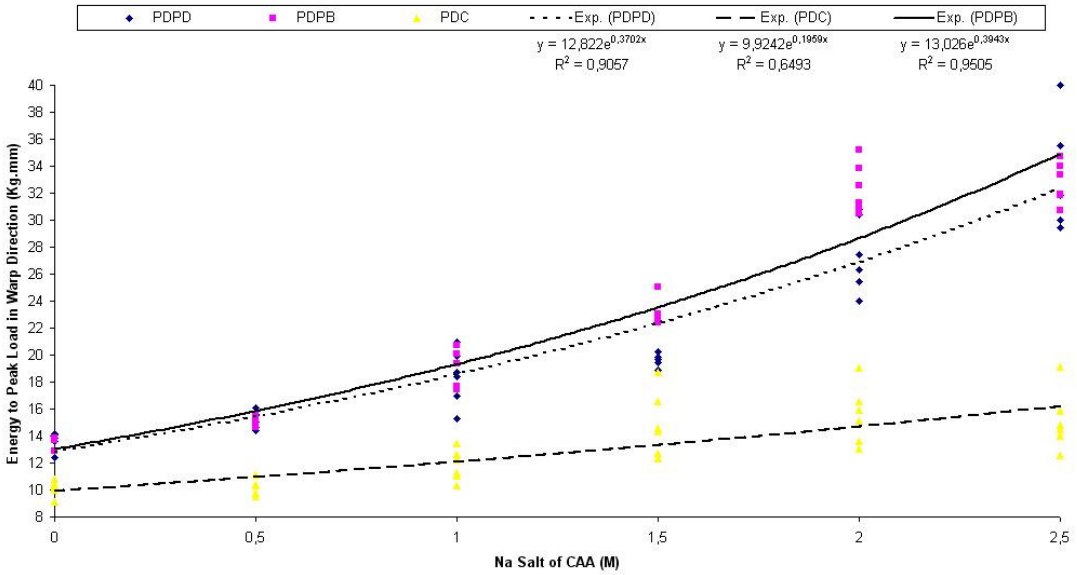

Figure 4.77 : Interaction between Na salt of CAA and energy to peak load in warp direction.

Elongation values are very highly correlated (R^2 values are 0.9504, 0.7902, and 0.6507 for PDPB, PDPD, and PDC respectively) and following the same trend, R^2 values of energy to peak load for PDPB, PDPD, and PDC are 0.9505, 0.9057, and 0.6493 respectively (see Figures 4.76 and 4.77).

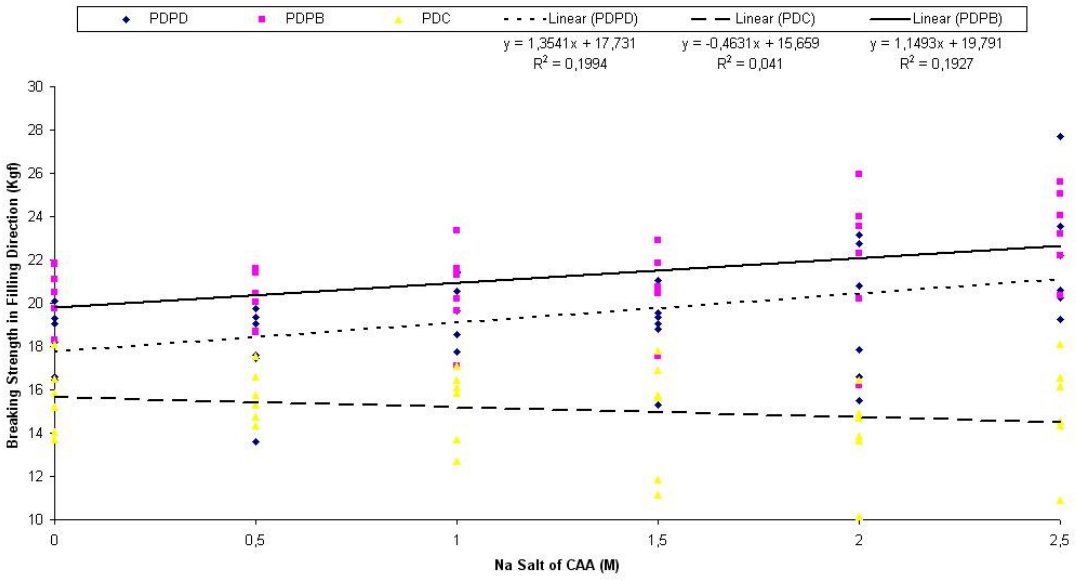

Figure 4.78 : Interaction between Na salt of CAA and breaking strength in filling direction.

The breaking strength values in filling direction are positively but very weakly correlated with Na salt of CAA as shown in Figure 4.78.

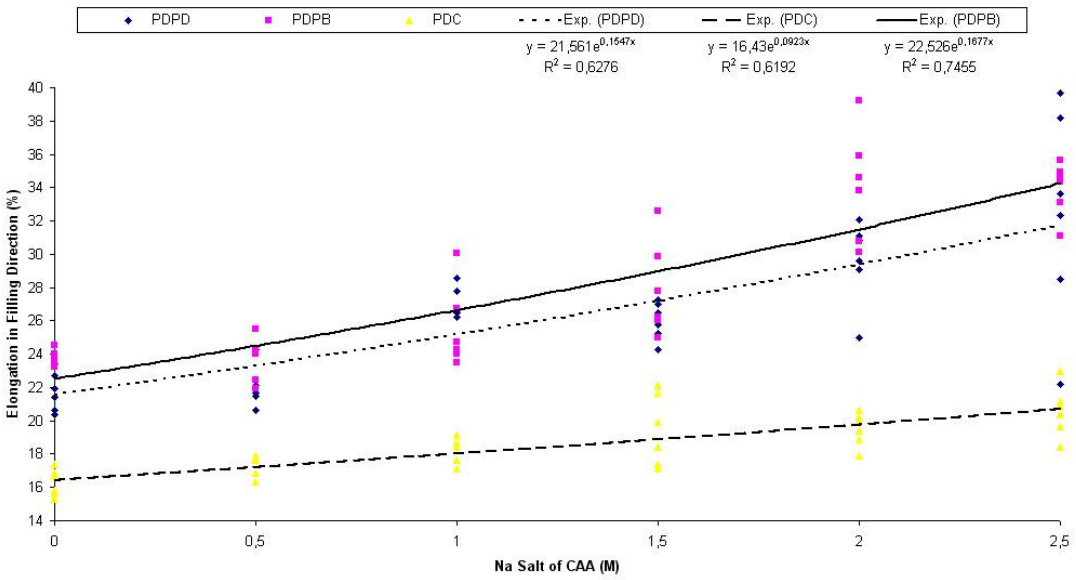

Figure 4.79 : Interaction between Na salt of CAA and elongation in filling direction.

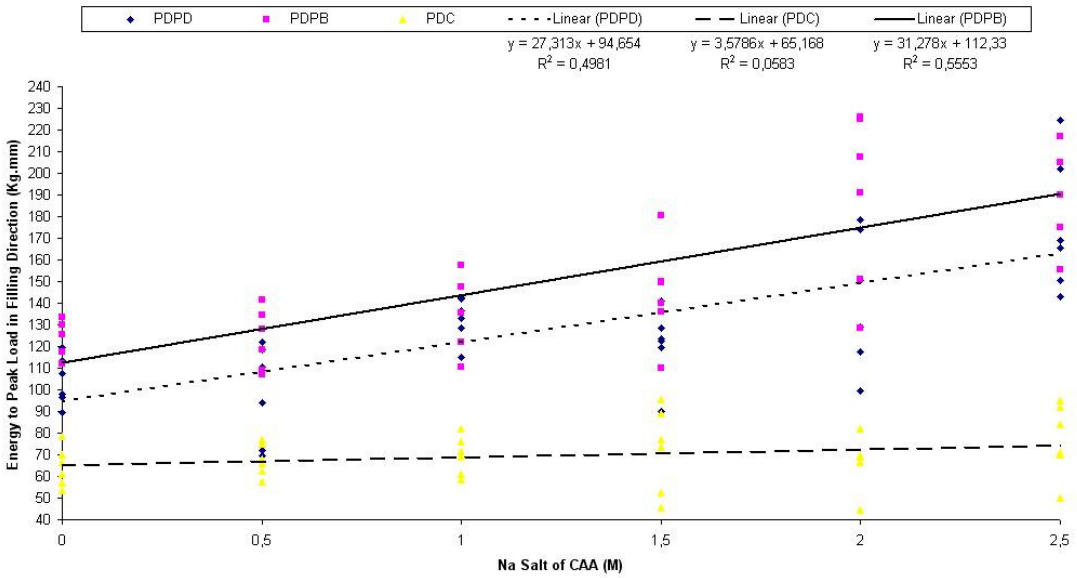

Figure 4.80 : Interaction between Na salt of CAA and energy to peak load in filling direction.

Elongation values are highly correlated (R^2 values are 0.7455, 0.6276, and 0.6192 for PDPB, PDPD, and PDC respectively) and being weaker but following the same trend, energy to peak load R^2 values for PDPB, PDPD, and PDC are 0.5553, 0.4981, and 0.0583 respectively (see Figures 4.79 and 4.80). CG% has almost no effect on breaking strength or elongation or energy to peak load in warp and filling directions as seen in Figures 4.57 to 4.74.

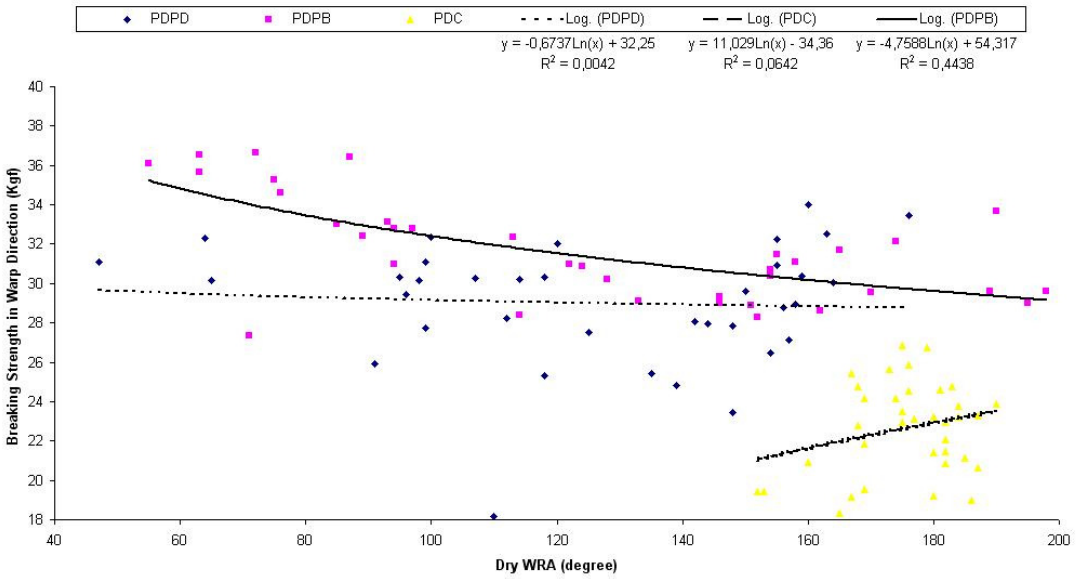

Figure 4.81 : Interaction between dry WRA and breaking strength in warp direction.

Increase in dry WRA decreases breaking strength in warp direction especially for PDPB samples and correlation is very weak for PDPD and PDC samples as shown in Figure 4.81.

Dry WRA and elongation in warp direction are highly correlated and elongation and energy to peak load decrease with increasing dry WRA, especially for PDPB and PDPD trials as shown in Figures 4.82 and 4.83.

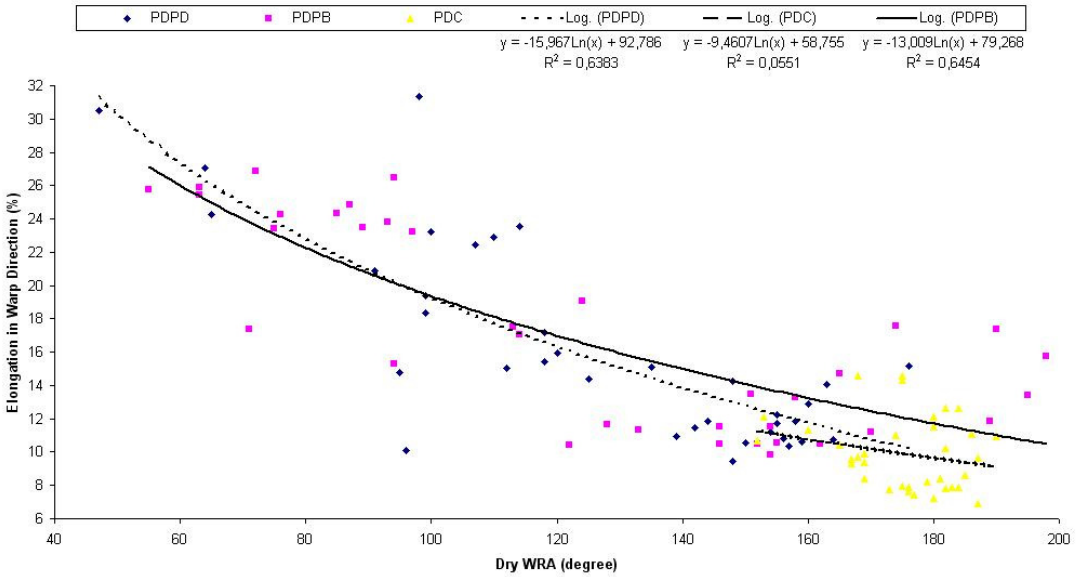

Figure 4.82 : Interaction between dry WRA and elongation in warp direction.

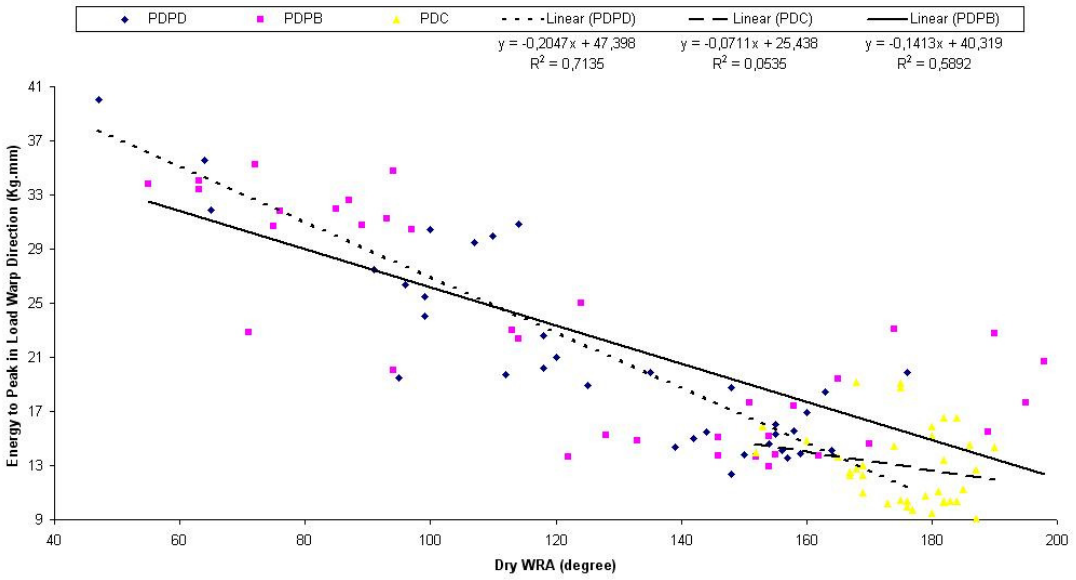

Figure 4.83 : Interaction between dry WRA and energy to peak load in warp direction.

As shown in Figure 4.84, increase in dry WRA has a very little effect on breaking strength in filling direction.

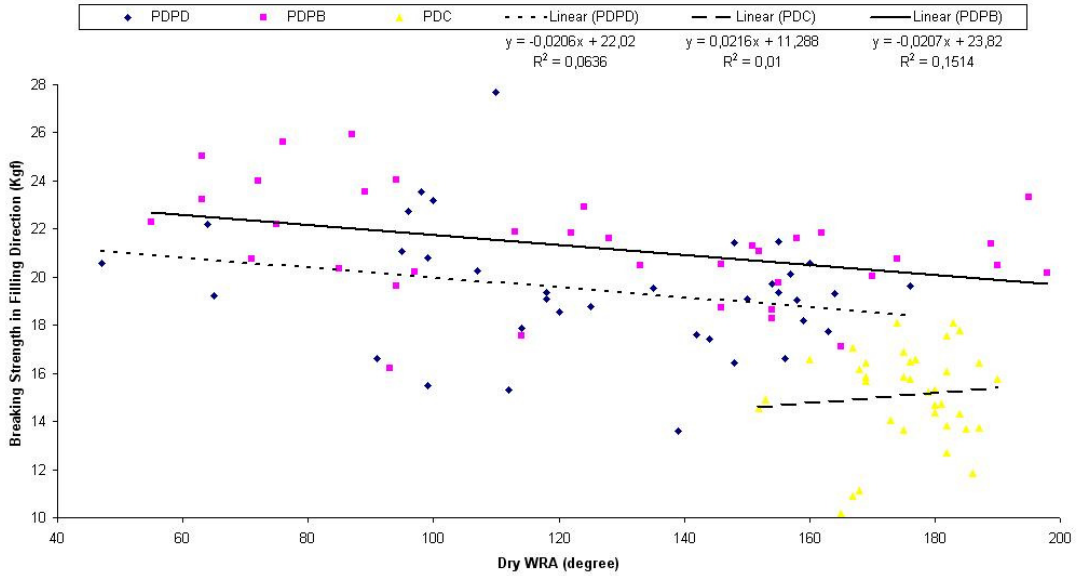

Figure 4.84 : Interaction between dry WRA and breaking strength in filling direction.

But increase in dry WRA decreases elongation and energy to peak load in filling direction especially for PDPB and PDPD samples as shown in Figures 4.85 and 4.86.

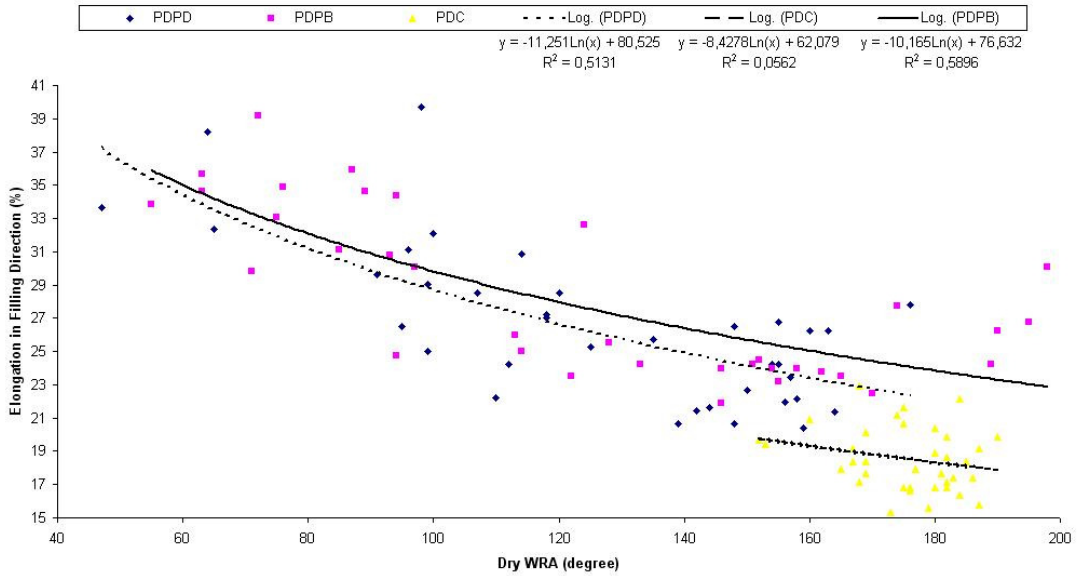

Figure 4.85 : Interaction between dry WRA and elongation in filling direction.

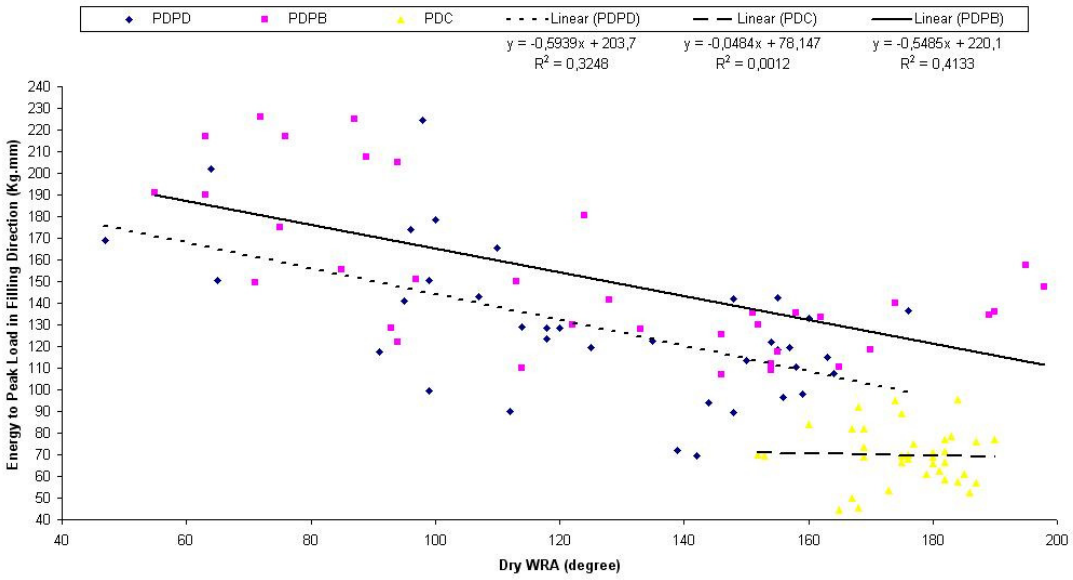

Figure 4.86 : Interaction between dry WRA and energy to peak load in filling direction.

As shown in Figure 4.87, increase in wet WRA increases breaking strength in warp direction, but only to a limited extend. The effect of increase in wet WRA on breaking strength values is higher for PDPD samples than for PDPB and PDC.

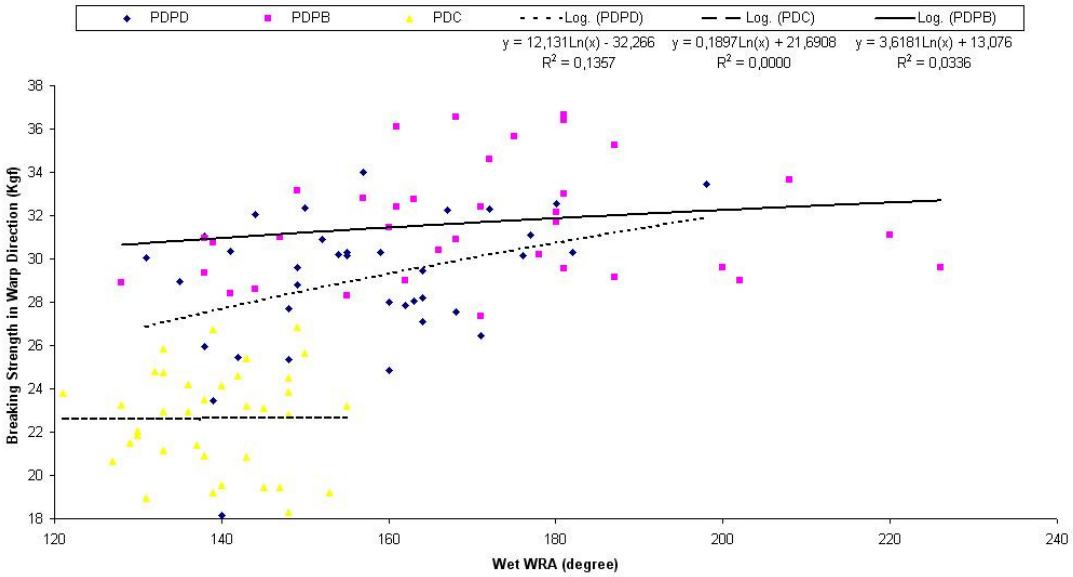

Figure 4.87 : Interaction between wet WRA and breaking strength in warp direction.

As shown in Figure 4.88, increase in wet WRA increases elongation in warp direction for PDPD and PDPB treated samples, but it decreases the elongation in warp direction for PDC treated samples.

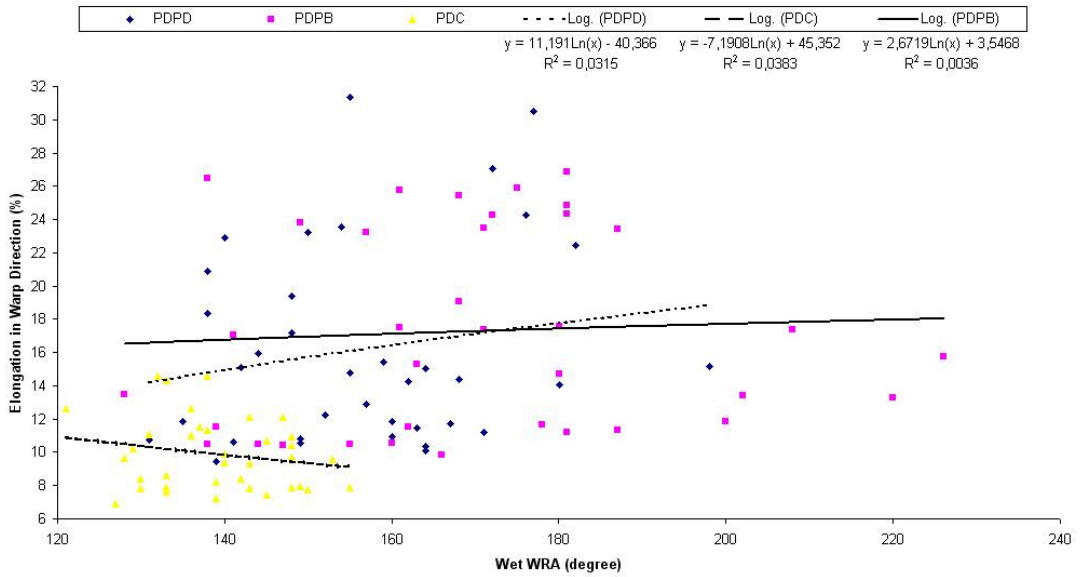

Figure 4.88 : Interaction between wet WRA and elongation in warp direction.

With increasing wet WRA, energy to peak load values increase for PDPD, almost stay constant for PDPB and decrease for PDC treated samples as expected (see Figure 4.89).

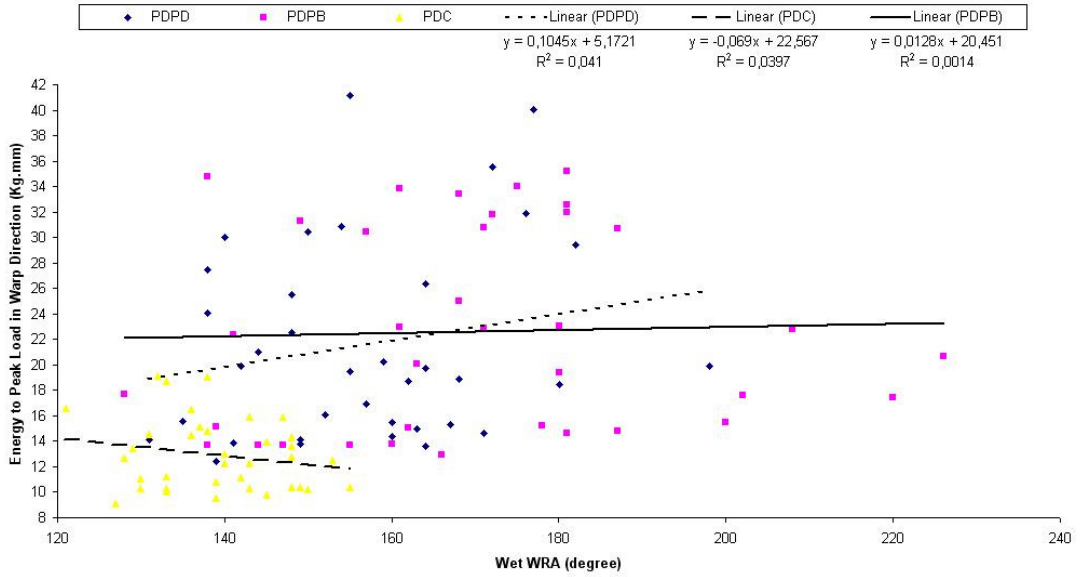

Figure 4.89 : Interaction between wet WRA and energy to peak load in warp direction.

In filling direction, increase in wet WRA results in a slight increase in breaking strength and elongation (and thus in energy to peak load) for PDPB and PDPD treated samples while for PDC treated samples, it results in a decrease (see Figures 4.90, 4.91 and 4.92).

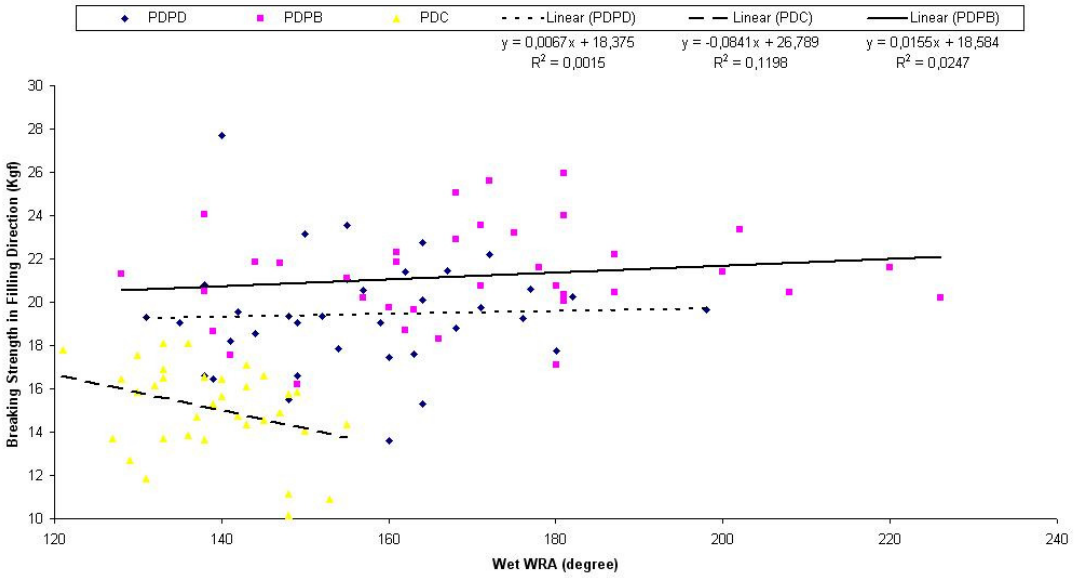

Figure 4.90 : Interaction between wet WRA and breaking strength in filling direction.

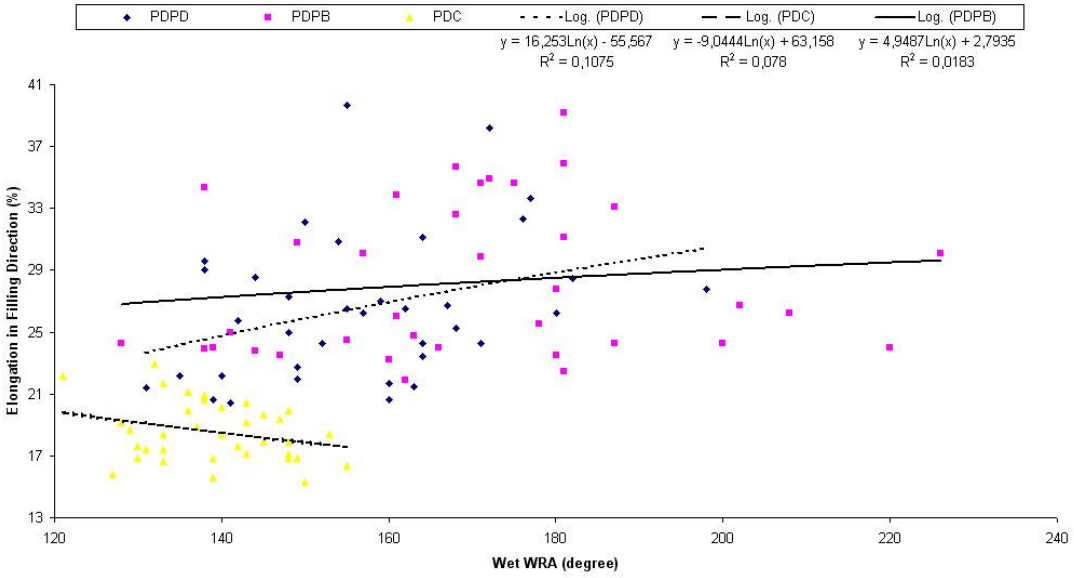

Figure 4.91 : Interaction between wet WRA and elongation in filling direction.

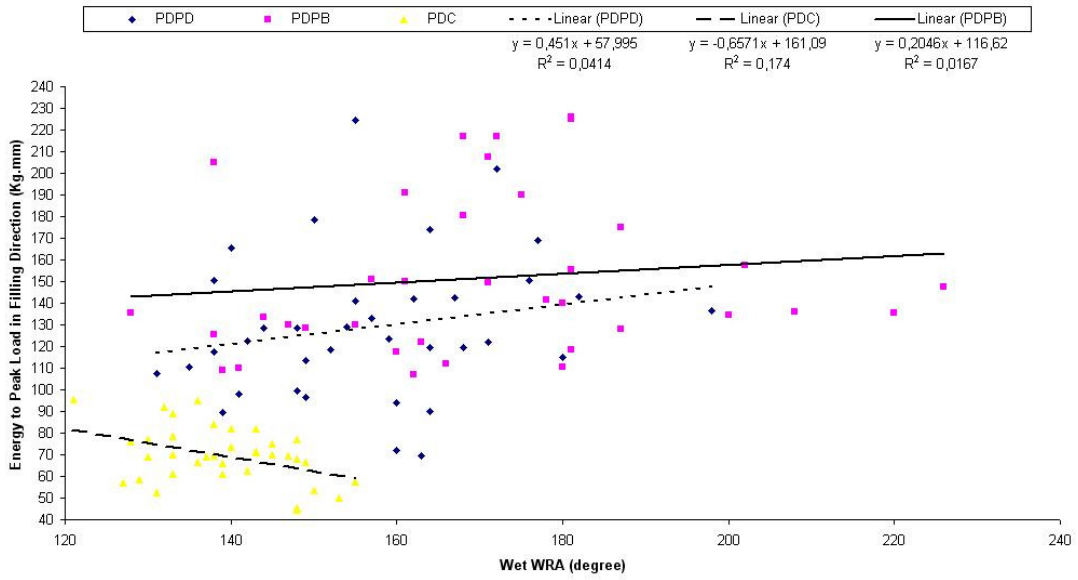

Figure 4.92 : Interaction between wet WRA and energy to peak load in filling direction.

As shown in Figure 4.93, increase in total WRA increases breaking strength in warp direction for PDC and PDPD treated samples, but it decreases breaking strength in warp direction for PDPB.

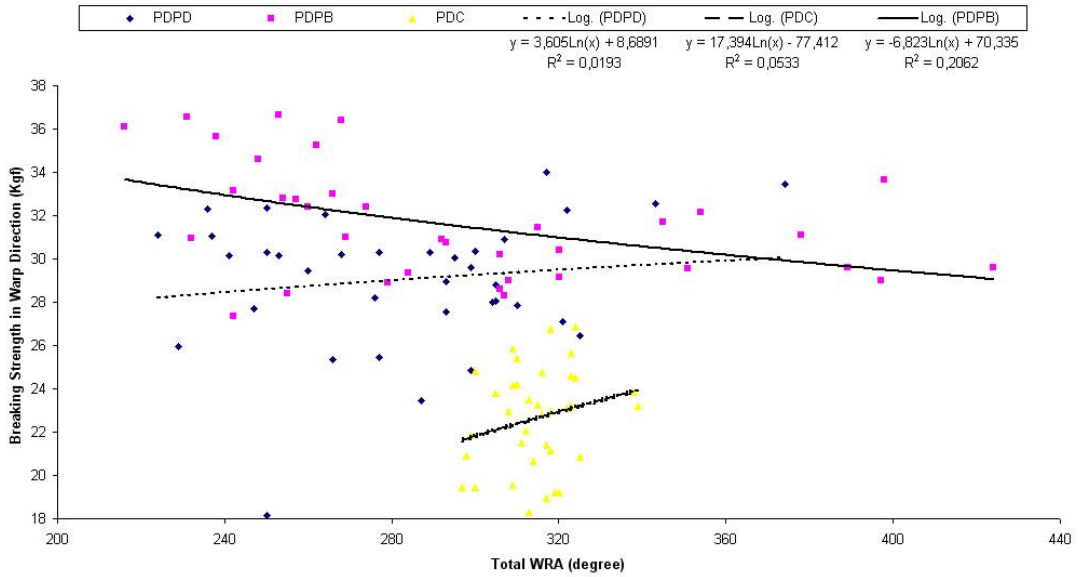

Figure 4.93 : Interaction between total WRA and breaking strength in warp direction.

Increase in total WRA decreases elongation and energy to peak load in warp direction for all 3 carboxymethylation methods studied (see Figure 4.94 and 4.95).

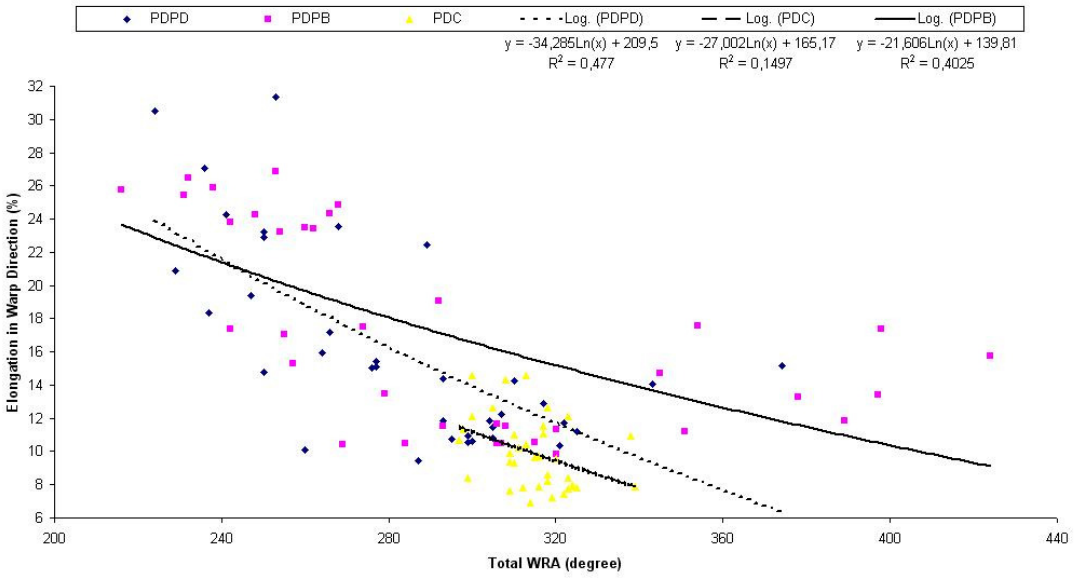

Figure 4.94 : Interaction between total WRA and elongation in warp direction.

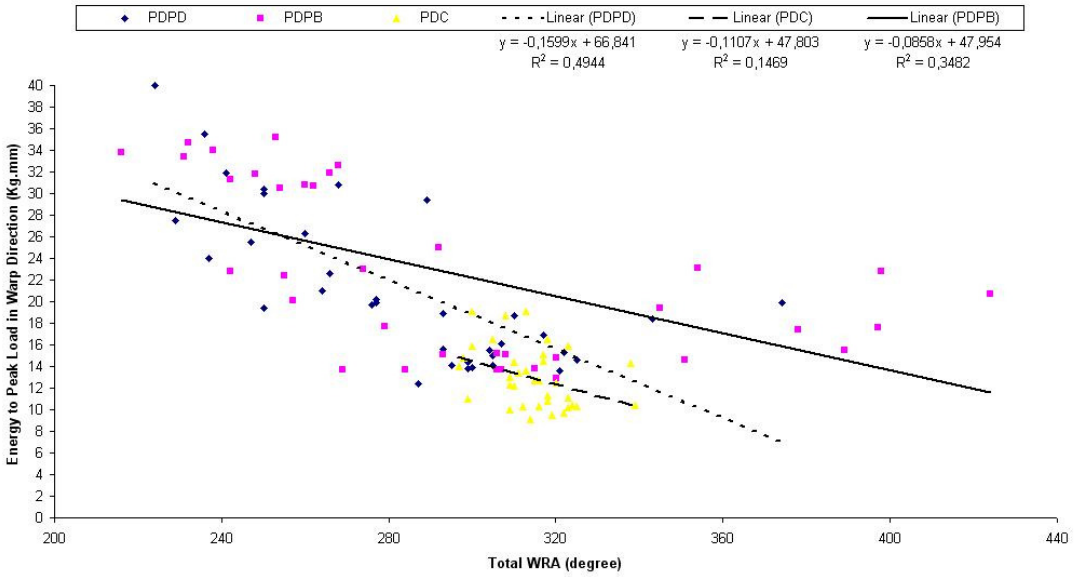

Figure 4.95 : Interaction between total WRA and energy to peak load in warp direction.

In filling direction, increasing total WRA resulted in slight decreases in breaking strength and stronger decreases in elongation and energy to peak load values for all 3 carboxymethylation methods studied (Figures 4.96, 4.97 and 4.98 respectively).

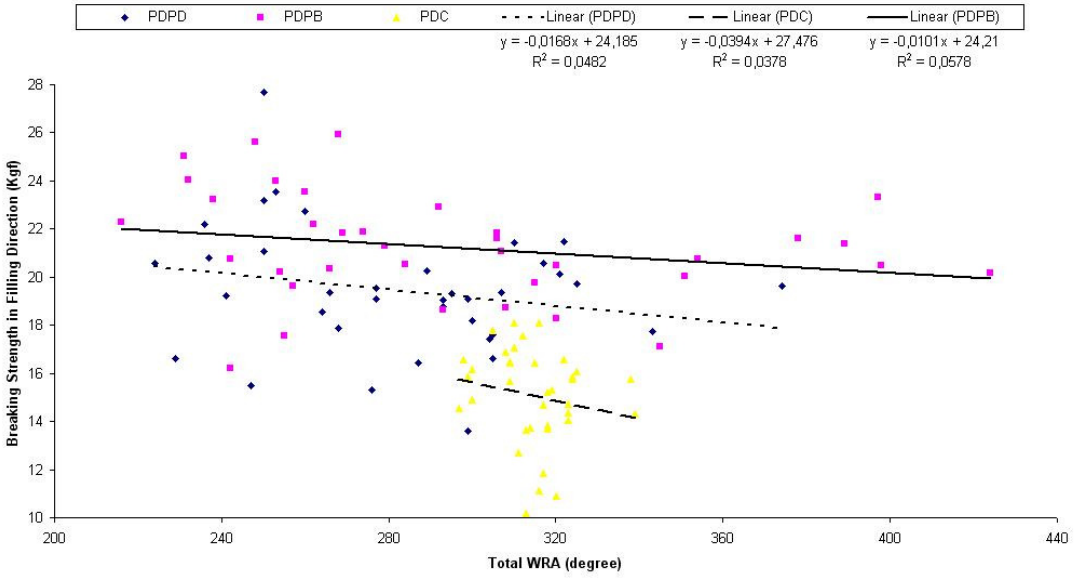

Figure 4.96 : Interaction between total WRA and breaking strength in filling direction.

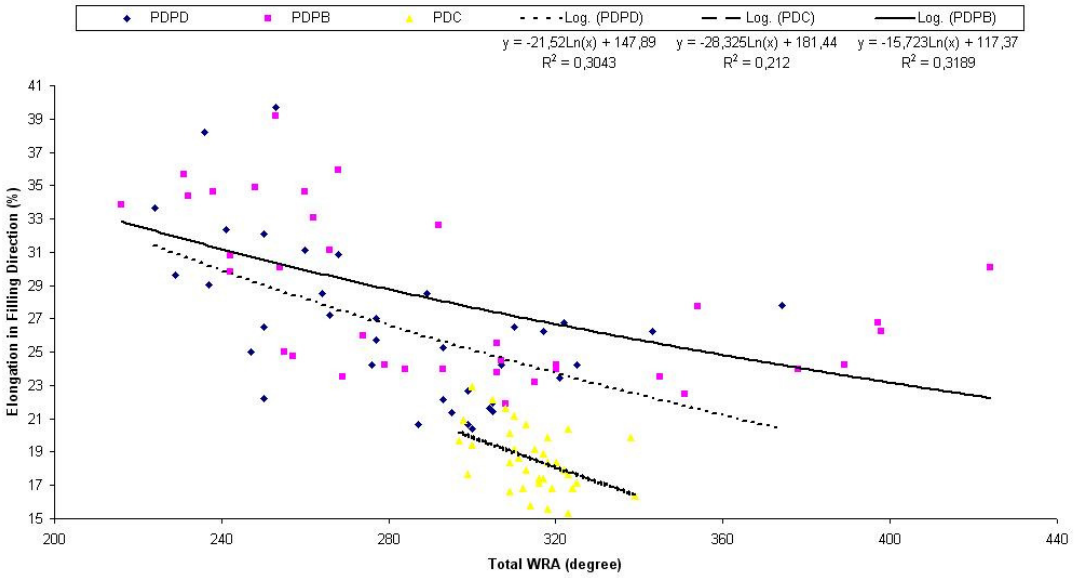

Figure 4.97 : Interaction between total WRA and elongation in filling direction.

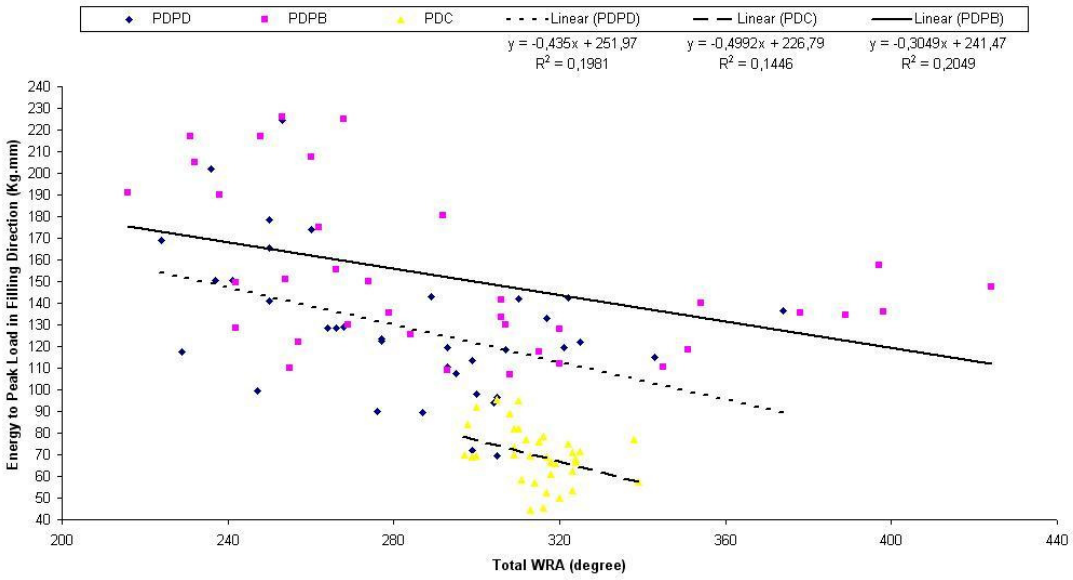

Figure 4.98 : Interaction between total WRA and energy to peak load in filling direction.

4.2.3 Results of central composite designed experiments

The dry, wet and total WRA values of samples for optimization by using central composite design are given in Table 4.25.

Table 4.25: Coded and actual design factor levels for optimization.

Coded ID	Na salt of CAA (M)	CG (%)	Dry WRA (°)	Wet WRA (°)	Total WRA (°)
22	0.5	1	133	187	320
24	0.5	5	170	181	351
42	1.5	1	113	161	274
44	1.5	5	174	180	354
23	0.5	3	189	200	389
43	1.5	3	190	208	398
32	1	1	158	220	378
34	1	5	195	202	397
33	1	3	198	226	424
33	1	3	198	226	424

4.2.3.1 Estimated optimized recipes and estimated response values

The estimated chemical levels to reach highest WRA results and estimated maximum WRA results are given in Table 4.26. R^2 estimates the proportion of the variation in the response around the mean that can be attributed to terms in the model rather than to random error. It is also the square of the correlation between the actual and predicted (estimated) response. An R^2 of 1 shows a perfect fit. In our study, high R^2

values (0.93 for Optimum Total, 0.96 for Optimum Dry and 0.90 for Optimum Wet) showed that the estimated model fitted well with the actual data.

The face centered models that predict dry WRA and wet WRA in terms of actual values at different factor levels within the scope of the experiments are shown in Equation 4.1 and Equation 4.2. This model was used for prediction of dry and wet WRA throughout the entire experimental volume evaluated.

Table 4.26: Estimated response values for optimum PDPB recipes.

Sample ID	Na salt of CAA (M)	Cationic glycerin (%)	Dry WRA (°)	Wet WRA (°)	Total WRA (°)
Optimum Total (OT)	0.9831557	3.3869385	-	-	435.40565
Optimum Dry	0.9941366	3.675301	207.67037	-	-
Optimum Wet	0.9709301	2.9448885	-	229.46068	-

$$\text{Dry WRA } (^{o}) = 37.51786 + 138.71429\, X_1 + 55.07143\, X_2 - 80.85714\, X_1^2 - 8.30357\, X_2^2 + 6\, X_1\, X_2 \quad \textbf{(4.1)}$$

$$\text{Wet WRA } (^{o}) = 91.97619 + 204.63095\, X_1 + 25.90476\, X_2 - 114.85714\, X_1^2 - 5.42857\, X_2^2 + 6.25\, X_1\, X_2 \quad \textbf{(4.2)}$$

where X_1= Na salt of CAA(M); X_2= cationic glycerin (%).

The Prob > F results of the ANOVA analysis are shown in Table 4.27. As shown in Table 4.27, Prob > F values are significant.

Table 4.27: Prob > F values for dry and wet WRA responses of optimization trials.

Response	Prob > F for trial
	PDPB
Dry WRA	0.007
Wet WRA	0.0407

4.2.3.2 Actual optimized recipes and their response values

We conducted experiments by using chemical levels that are approximately equal to estimated chemical levels. These actual chemical levels and the measured responses are also given in Table 4.28.

Table 4.28: Actual chemical and response values for optimum PDPB recipes.

Sample ID	Na salt of CAA (M)	Cationic glycerin (%)	Dry WRA (^{o})	Wet WRA (^{o})	Total WRA (^{o})
Optimum Total (OT)	0.983	3.39	202	226	428
Optimum Dry	0.994	3.68	203	208	411
Optimum Wet	0.971	2.95	193	228	421

4.3 Comparison of the Response Values of Chosen Optimized Recipe Treated Fabric with Those of Traditionally (DMDHEU) Treated Fabric

Breaking strength, elongation, energy to peak load and CIE whiteness index values for untreated, DMDHEU treated samples, and ionic crosslinked sample OT, which has optimum total WRA, are given in Table 4.29. It is apparent from these results that cotton fabric gained strength and elongation after ionic crosslinking while DMDHEU treated samples had drastically lost strength and elongation. The CIE whiteness index of sample OT was measured as 77.59 before CG treatment. The CIE whiteness index of DMDHEU treated sample decreased significantly, as expected.

Table 4.29: Breaking strength, elongation, energy to peak load and CIE whiteness index values for untreated, DMDHEU treated and OT samples.

Sample ID	Breaking strength (Kgf)	Elongation (%)	Energy to peak load (Kg.mm)	CIE whiteness index
Untreated (bleached)	23.86	10.3	87.62	84.61
DMDHEU	5.65	6.13	7.52	60.20
OT	31.22	17.65	167.26	80.84

4.4 Comparison of the Yarn Strength and SEM Images of Selected PDPB Treated Samples with Those of Traditionally (DMDHEU) Treated Fabric

We broke untreated, DMDHEU treated and selected ionic crosslinked yarn samples that are prepared by only using PDPB carboxymethylation. Details on crosslinking treatment of these samples and their tensile strength and elongation values are given in Table 4.30. It is apparent from these results that cotton yarn gained strength and elongation after ionic crosslinking while DMDHEU treated samples had drastically lost strength (-57.6%) and elongation (-46.0%) as expected. The highest tensile strength (376.40 gf) is gained by cotton samples which are treated with 2M CAA+3% CG while the highest elongation (%32.3) is gained after treatment with 2M CAA+7% CG. Increase in CG% slightly decreases tensile strength which means that, as for WRA, there is a level for strength after which additional number of crosslinks does not help to enhance the demanded quality.

Table 4.30: Tensile strength values for untreated, DMDHEU treated and selected ionic crosslinked yarn samples.

Sample ID	Crosslinking procedure	Tensile strength (gf)	Elongation (%)
Untreated (bleached)	Not crosslinked	248.32	8.7
DMDHEU	DMDHEU	105.24	4.7
231	1M Na Salt of CAA	327.64	20.5
233	1 M Na Salt of CAA + 3% CG	296.15	16.5
235	1 M Na Salt of CAA + 7% CG	226.61	12.6
251	2M Na Salt of CAA	301.32	12.6
253	2 M Na Salt of CAA + 3% CG	376.40	20.4
255	2 M Na Salt of CAA + 7% CG	326.36	32.3

The SEM images of these samples are given in Figures 4.101 to 4.108 respectively. For comparisons, SEM images of tensile breaks of raw cotton (see Figure 4.99) and that of resin-treated cotton (see Figure 4.100) from Hearle, Lomas and Cooke are given as well [40].

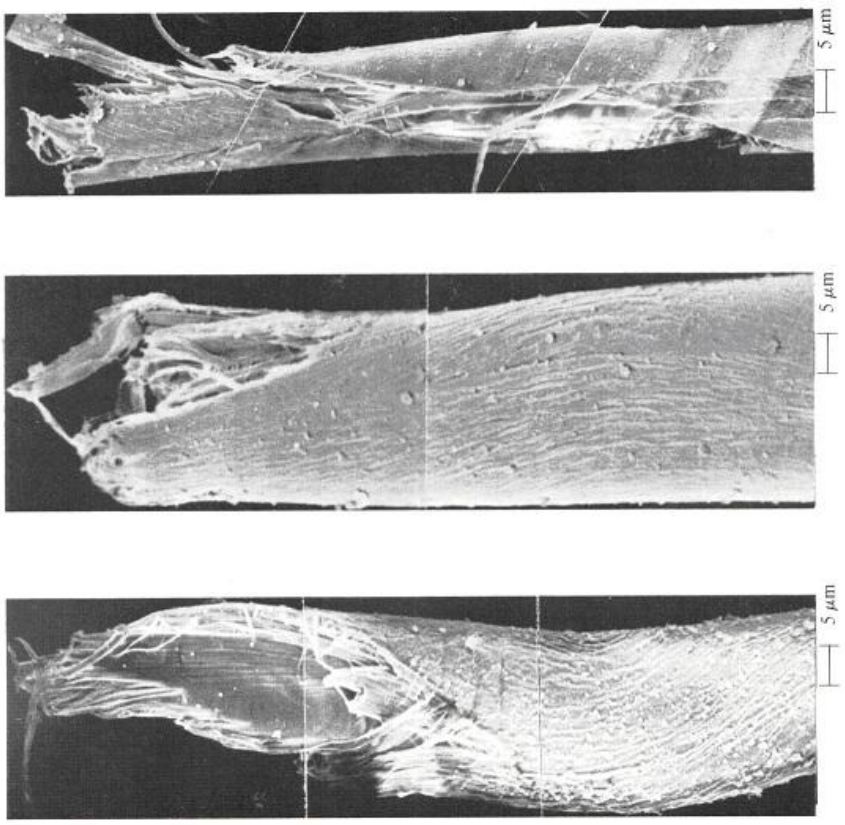

Figure 4.99 : Tensile breaks of raw cotton [40].

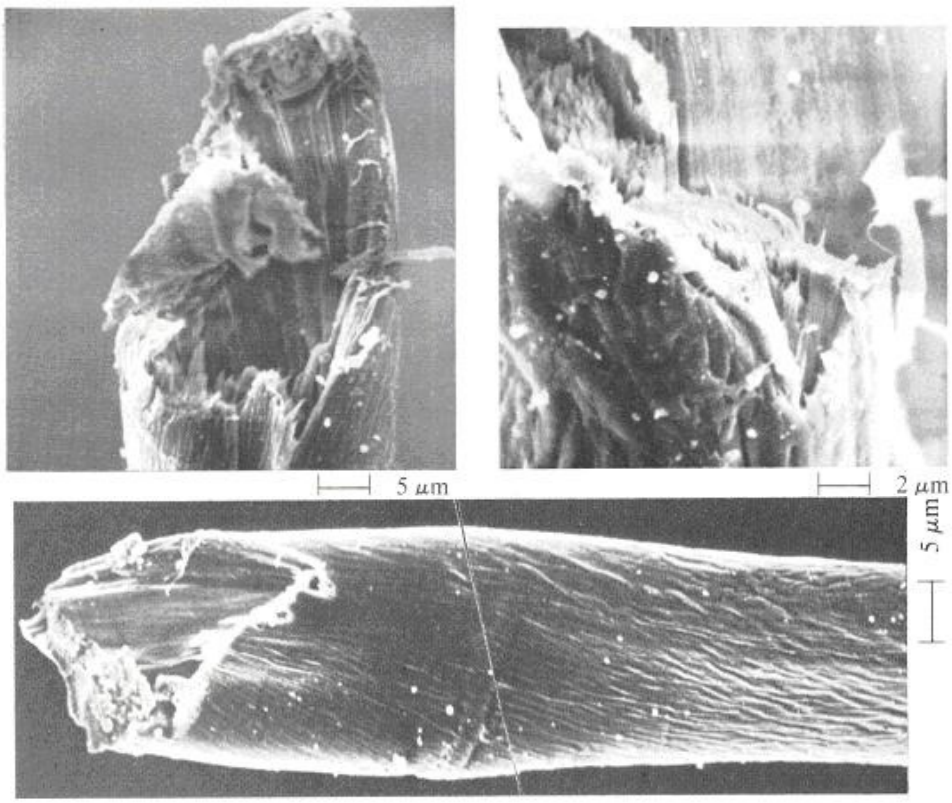

Figure 4.100 : Tensile breaks of resin treated cotton [40].

As seen in Figure 4.99, tensile break of raw cotton shows an axial split which runs round the fiber and then tears back along the fiber. As expected, our untreated fiber tore the same way, as seen in Figure 4.101.

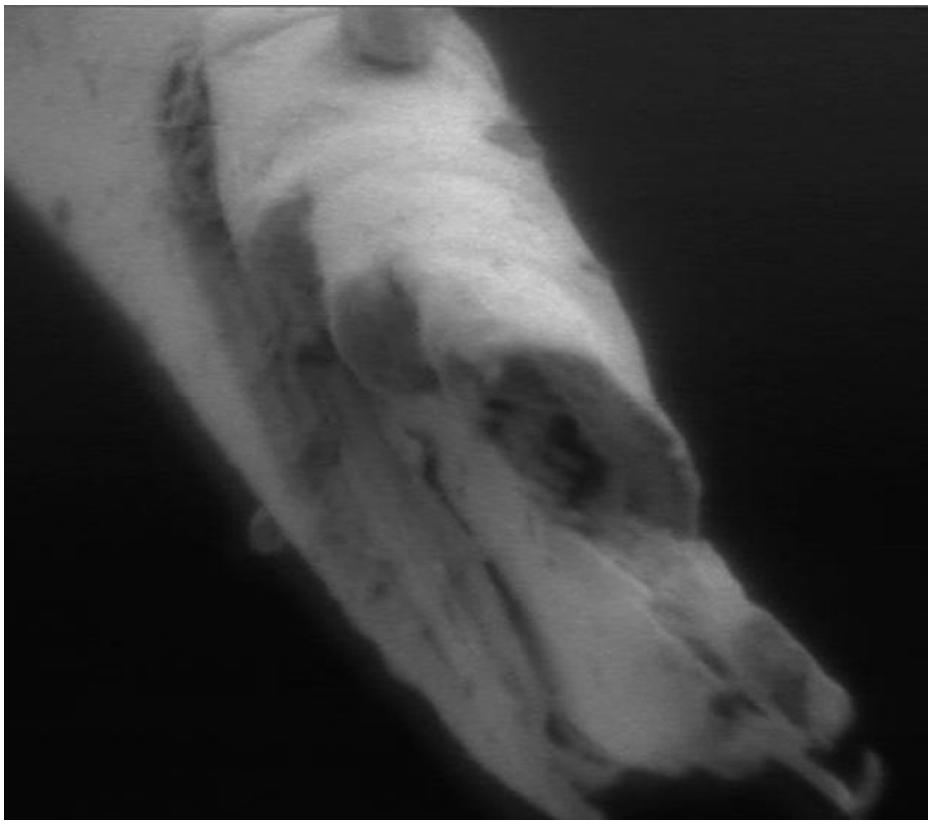

Figure 4.101 : Tensile break of bleached cotton.

Hearle, Lomas and Cooke states that when cotton fiber is chemically crosslinked by resin treatment, the cellulose fibrils hold more firmly together, axial splitting is hindered and distorted forms of granular breaks across the fiber or breaks that run in a single transverse fracture round the fiber are observed (see Figure 4.100). They also state that type of break depends on the degree of chemical attraction between the fibrils and granular breaks across the fiber shows strong interaction while axial split between fibrils show weak interaction [40]. Tensile breaks of DMDHEU treated cotton as shown in Figure 4.102 show very similar images to resin-treated cotton which is shown in Figure 4.100.

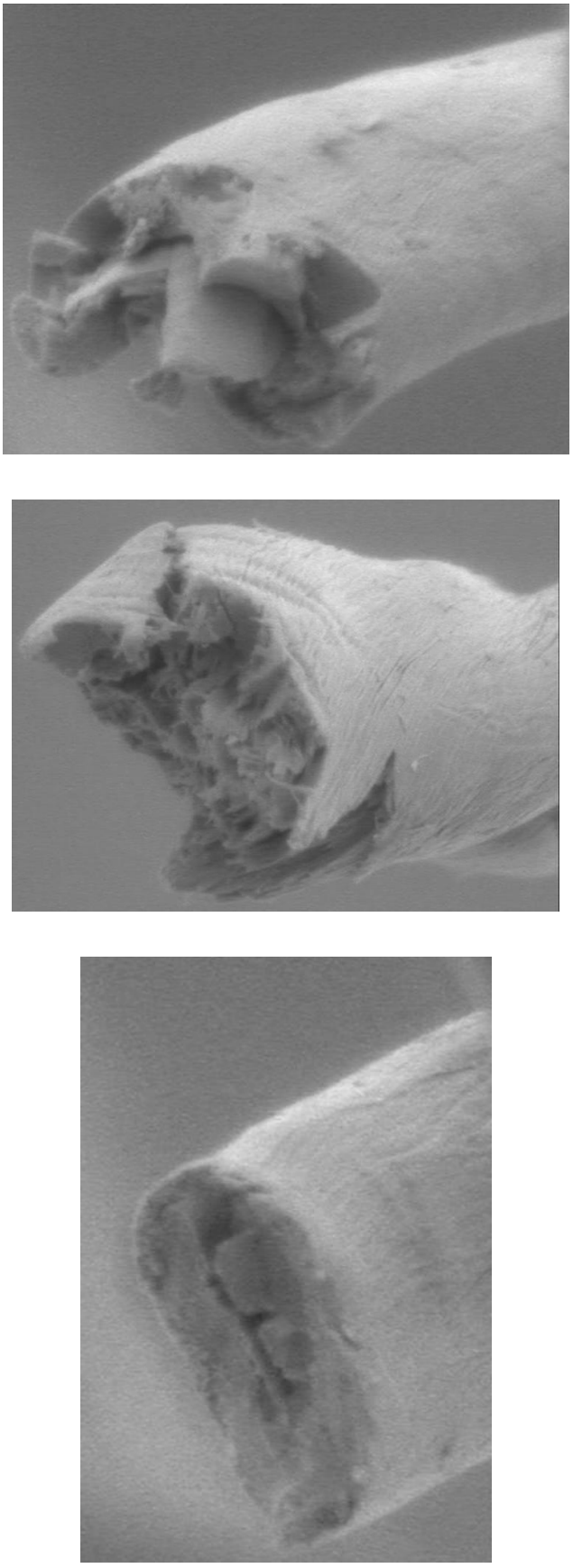

Figure 4.102 : Tensile breaks of DMDHEU treated cotton.

The fractures are granular which indicate that the fibrils hold together and do not slide when stress is exerted on them. This may be the explanation to the question why DMDHEU treatment cause loss in strength.

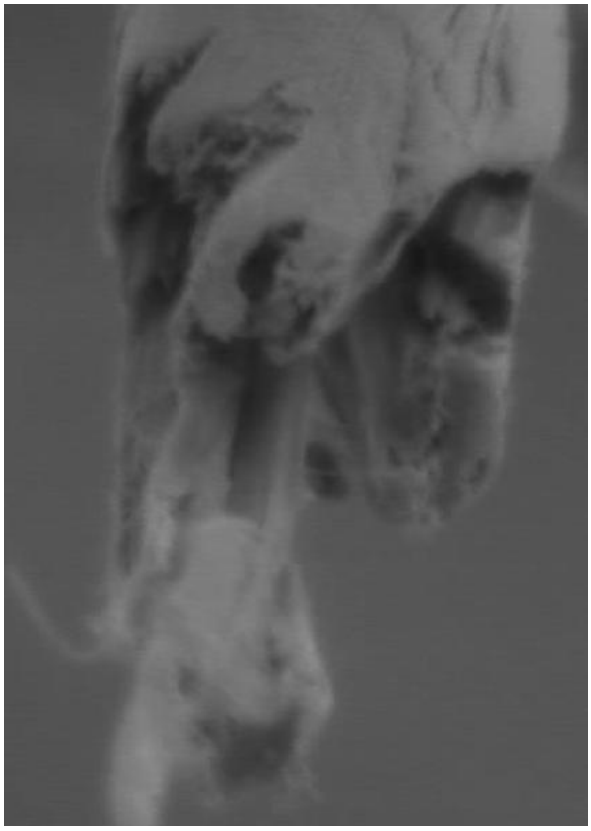

Figure 4.103 : Tensile break of sample 231.

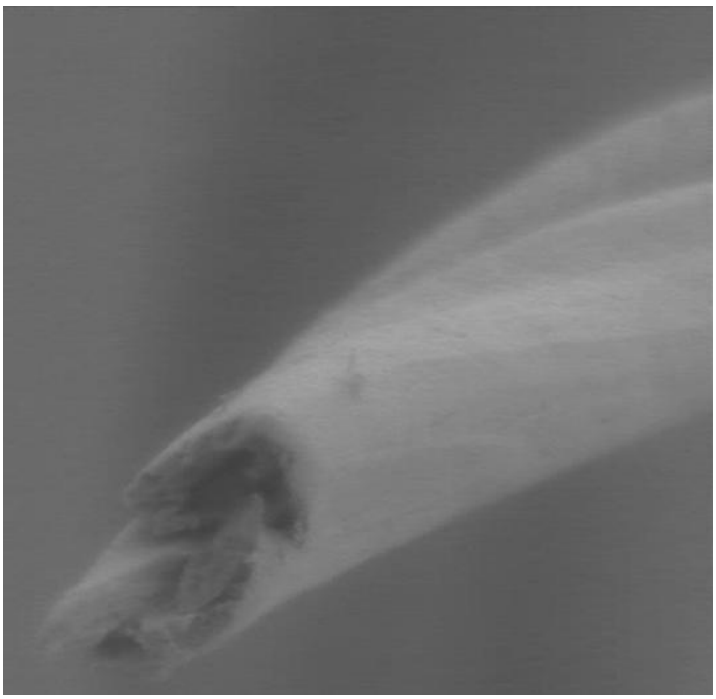

Figure 4.104 : Tensile break of sample 233.

As seen in Figure 4.103 for sample 231 and in Figure 4.106 for sample 251 there are axial splits showing that the interaction between fibrils are weak. This is rather expected as these two samples had no CG treatment and thus they are not crosslinked at all.

Figure 4.105 : Tensile break of sample 235.

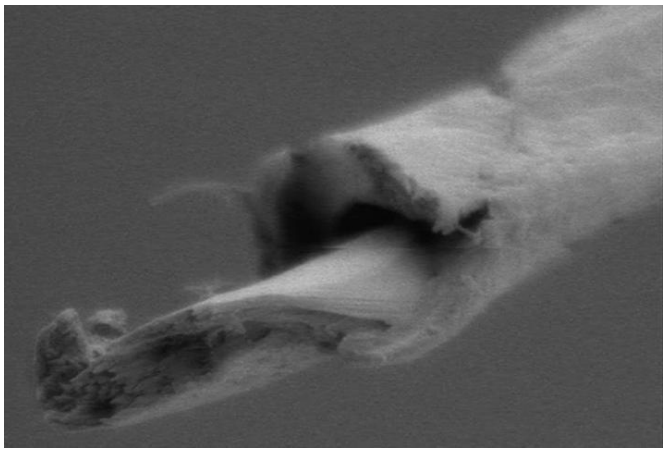

Figure 4.106 : Tensile break of sample 251.

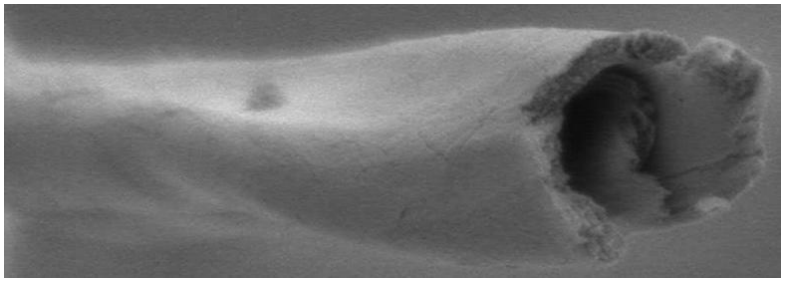

Figure 4.107 : Tensile break of sample 253.

Samples 233, 235 and 253 had similar splits; all three images represent granular break indicating that the interaction between fibrils are very high (see Figures 4.104, 4.105 and 4.107 respectively).

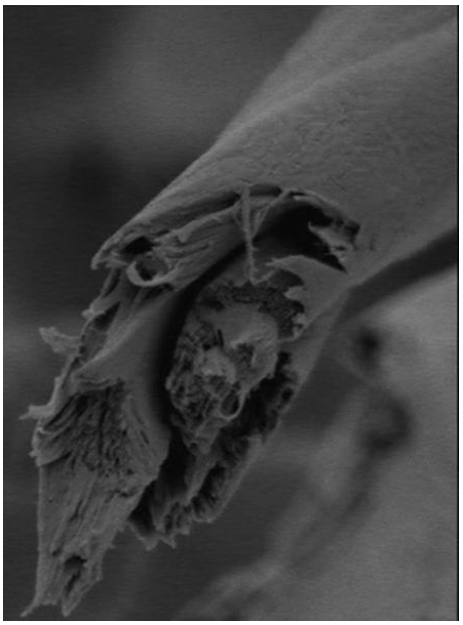

Figure 4.108 : Tensile break of sample 255.

Sample 255 had a combination of granular and short axial splits as shown in Figure 4.108. The levels of chemicals used in treatment were very high (2 M CAA+7% CG) but the split was rather spread than being a sharp break. We believe the high number of available carboxyl sites and high content of CG caused the ionic crosslinks support the fabric by breaking and reforming as does hydrogen bonds in cotton and caused a rather axial split. High elongation value may be a direct result of this phenomenon.

4.5 Reproducibility of Ionic Crosslinking

We prepared 10 fabrics that we treated following the exactly same procedure (which is PDPB with 0.5M Na salt of CAA and 3% CG) to see if our experiments and their results are reproducible. The carboxymethylation content values are as given in Table 4.31. The average carboxymethylation content value is 23.003mmoles/100g cotton with a standard deviation of 0.5302 which is very low.

Table 4.31: CM contents (mmoles/100g cotton) for 10 fabrics.

	Blank	1	2	3	4	5	6	7	8	9	10
Weight (g)		0.2407	0.2462	0.2457	0.2458	0.2438	0.2314	0.2424	0.2434	0.2445	0.2402
Volume of titrant (mL)	25	23.9	23.9	23.9	23.85	23.9	23.9	23.9	23.85	23.85	23.9
CM content (mmoles/100g cotton)		22.85	22.34	22.39	23.39	22.56	23.77	22.69	23.62	23.52	22.90

Table 4.32: WRA, nitrogen content and stiffness values for 10 fabrics.

Coded ID	Average WRA			Nitrogen content (%)	Stiffness in warp direction (mg.cm)	Stiffness in filling direction (mg.cm)
	Dry (°)	Wet (°)	Total (°)			
1	185	223	408	0.16088	365.29	77.91
2	184	208	392	0.1688	374.97	72.63
3	191	201	393	0.15502	318.48	88.35
4	186	205	391	0.16146	352.09	89.00
5	180	210	390	0.16511	328.20	92.17
6	186	218	404	0.16577	320.16	79.93
7	183	205	387	0.17719	304.72	80.55
8	190	202	392	0.16014	326.71	79.61
9	187	205	393	0.1658	334.95	86.67
10	183	209	393	0.16456	302.28	75.49
Average	185.50	208.60	394.30	0.16	332.79	82.23
Standard deviation	3.31	6.98	6.50	0.01	24.39	6.44

Table 4.33: Average breaking strength, elongation and energy to peak load results for 10 fabrics in warp direction.

Coded ID	Average breaking strength, elongation and energy to peak load in warp direction		
	Breaking strength (Kgf)	Elongation (mm)	Energy to peak load (Kg*mm)
1	30.27	9.90	13.02
2	29.72	9.57	12.57
3	29.22	8.90	11.68
4	33.39	11.97	15.68
5	34.76	9.73	12.79
6	29.56	8.87	11.68
7	30.76	8.57	11.24
8	30.68	10.93	14.31
9	23.85	9.23	12.12
10	36.81	9.53	12.57
Average	30.90	9.72	12.77
Standard deviation	3.53	1.03	1.34

Table 4.34: Average breaking strength, elongation and energy to peak load results for 10 fabrics in filling direction.

Coded ID	Average breaking strength, elongation and energy to peak load in filling direction		
	Breaking strength (Kgf)	Elongation (mm)	Energy to peak load (Kg*mm)
1	19.50	26.20	122.83
2	21.06	28.30	144.91
3	16.48	26.00	98.49
4	18.72	25.70	115.44
5	22.45	26.80	145.12
6	20.82	28.20	133.67
7	16.32	25.30	97.67
8	19.47	26.00	123.59
9	23.12	25.00	145.49
10	16.81	24.00	96.97
Average	19.48	26.15	122.42
Standard deviation	2.43	1.34	19.90

Other average and standard deviation values for dry, wet and total WRA, L*, C*, and h* values, nitrogen content, stiffness, and breaking strength, elongation, energy to peak load in warp and filling directions are as given in Tables 4.32 to 4.36 respectively. It is apparent from the results that there are variations but these are very low.

Table 4.35: CIE whiteness index, L*, C*, h* and nitrogen content results for 10 fabrics after coloration with acid dye.

Coded ID	CIE whiteness index	Acid dyed			
		C*	h*	L*	Nitrogen content (%)
1	77.68	29.57	345.93	60.54	0.23027
2	77.45	29.72	346.1	60.56	0.25064
3	78.72	29.76	345.61	59.82	0.18722
4	78.43	29.35	345.88	60.48	0.18826
5	77.9	29.12	346.1	61.25	0.23131
6	78.47	29.68	347.18	61.14	0.22047
7	78.2	29.62	346.98	61.4	0.22661
8	78.03	28.87	346.71	61.81	0.24953
9	78.15	29.16	346.43	61.07	0.20832
10	77.74	29.4	346.06	61.01	0.22912
Average	78.08	29.43	346.30	60.91	0.22
Standard deviation	0.40	0.30	0.51	0.57	0.02

Table 4.36: CIE whiteness index, L*, C*, h* and nitrogen content results for 10 fabrics after coloration with basic dye.

Coded ID	CIE whiteness index	Basic dyed			
		C*	h*	L*	Nitrogen content (%)
1	77.68	3.42	239.61	75.77	0.26001
2	77.45	3.51	245.84	75.11	0.24139
3	78.72	3.43	239.93	76.25	0.2255
4	78.43	3.54	241.3	75.55	0.1794
5	77.9	3.39	244.57	75.75	0.27147
6	78.47	3.43	243.07	75.75	0.16638
7	78.2	3.32	239.74	76.41	0.25845
8	78.03	3.7	241.98	75.43	0.26204
9	78.15	3.46	243.2	75.58	0.24318
10	77.74	3.38	242.83	76.23	0.25255
Average	78.08	3.46	242.21	75.78	0.24
Standard deviation	0.40	0.11	2.10	0.41	0.04

5. CONCLUSION

Today's textile industry is searching for an alternative to conventional durable press finishes that can give the same advantages as formaldehyde based finishes without causing strength loss, formaldehyde release and decrease in whiteness. Ionic crosslinking of cellulose has the potential to fulfill these requirements as there is no formaldehyde release. The best method for forming ionic crosslinks is making the cotton fabric anionic by carboxymethylation and then treating it with cationic glycerin. Our results showed that using cationic glycerin as the cationic agent brings better fabric properties in terms of strength and CIE whiteness index, and worse fabric properties in terms of both WRA and fabric smoothness ratings after induced wrinkling compared to conventional method. Although WRA and fabric smoothness rating results of ionic crosslinking are worse than DMDHEU, we increased the dry WRA of bleached fabric samples by 75 degrees, wet WRA by 101 degrees, total WRA by 173 degrees and fabric smoothness rating by 1.4 via optimization of ionic crosslinking process. So we reached an optimum dry WRA of 203 degrees, an optimum wet WRA of 228 degrees, an optimum total WRA of 428 degrees and a fabric smoothness rating of 2.8 with significant increase in breaking strength and satisfactory CIE whiteness index results. On the other hand, DMDHEU treated fabric had dry WRA of 280 degrees, wet WRA of 275 degrees, total WRA of 555 degrees and fabric smoothness rating of 4. The cotton fabric that was treated to give highest total WRA increased strength by 31%, elongation by 71% and energy to peak load by 91% while DMDHEU fabric was shown to decrease strength by 76%, elongation by 40% and energy to peak load by 91%. One possible explanation of this situation is that unlike covalent bonds formed by treatment of fabric with N-methylol based resins in conventional durable press finishing, the ionic crosslinks increase the flexibility of the polymer chains. The flexible polymer chains have mobility to line up and become firmer under an applied force. This lining up of the polymer chains provides resistance against much higher forces. As a result ionic crosslinked fabric has a higher elongation at breaking load than untreated and DMDHEU treated fabrics. Having a higher breaking strength and elongation, energy to peak load is

significantly increased. While imparting wrinkle recovery and strength, CIE whiteness index of cotton fabric decreased down to only 80.84 (4.5% decrease) while whiteness of DMDHEU treated fabric decreased down to 60.20 (29% decrease). The stiffness of cotton fabric after ionic crosslinking did not increase too much which means that ionic crosslinking does not decrease the level of comfort when the treated fabric is used in garment form. Additionally, the dyeability of the fabric is also investigated. It is clearly shown that chroma, lightness and hue values of ionic crosslinked fabrics are better than those of bleached cotton fabric after dyeing with basic dyestuff.

6. FUTURE WORK

This work indicates that ionic crosslinking resulted in an increase in WRA performance of cotton fabric but the highest WRA level reached is less than that imparted by DMDHEU treatment. Ionic crosslinking treatment offered significant increase in breaking strength and acceptable CIE whiteness index values as well as increased dyeability with basic dyes but in order to commercialize this procedure as a commercial alternative to DMDHEU treatment, the resulting WRA performance needs to be further increased. Special surfactants may be involved in the process in order to increase the penetration of chemicals into the fabric and thus the uniform distribution of ionic crosslinks. Glycerin was used in the synthesis of cationic agent because it was cheaper, available, and cationic glycerin imparted the highest WRA with acceptable stiffness and increased breaking strength when compared to cationic agents synthesized by using other alcohols. Alternatively, a more hydrophobic agent may be used which will impart the same WRA performance; the hydrophilic nature of this agent may result in a more durable finish on the fabric. Competitive chemistry may be used in order to predict the possible effects of alternative agents and to avoid conducting a mass of trials; the effects of crosslinking agents having longer chains may be presumed and an in depth investigation of the mechanism may be conducted in order to better understand the mechanism of ionic crosslinking.

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