

EFFECT OF CATALYTIC SYSTEMS ON THE MECHANICAL PROPERTIES LOSS OF SOME EGYPTIAN CROSS LINKED COTTON FABRICS

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Abstract

Severe tensile strength loss has been the major disadvantage of durable press finished 100% cotton fabrics. The objective of this study is to evaluate the contribution to the overall strength loss by acid degradation and by crosslinking of cellulose, and to investigate the relationship between the strength loss due to crosslinking and the molecular structure of the crosslinking agent in order to develop a fundamental understanding of the mechanism of tensile strength loss in crosslinked cotton fabric. Based on the understanding of the mechanism, it will be possible to reach the final objective of optimizing the strength reaction and improving the performance of durable press finished cotton fabrics and garments.

This study examined the effects of the catalyst systems on the mechanical strength of Egyptian two cotton fabrics made from Giza 89 and Giza 80 cotton varieties were crosslinked with dimethyldihydroxy ethylene urea (DMDHEU). Different variables such as time, temperature, concentration of catalysts were studied.

The obtained results could be summerized as follows:

- 1.The wrinkle recovery angle (WRA), and durable press rating (DP), of Egyptian cotton Giza 89 fabric treated with DMDHEU increased more than Giza 80 fabric with increasing the concentration of the catalytic system till 2% at 160°C in 3 minutes.
- 2.The strength loss of the cotton fabrics used increased in the presence of the catalytic system (activated or buffered) to reach the maximum loss 80% with the activated catalyst.
- 3.DMDHEU concentration is critical for optimizing the tensile strength retention of finished fabrics.
- 4.The magnitude of fabric strength loss is affected by the temperature, time, concentration of the catalyst, and both of cation and anion used as the catalyst.
- 5.Activated catalyst, which includes an organic acid caused more severe fabric strength loss due to additional cellulose degradation induced by the organic acid in the catalyst system.

INTRODUCTION

Durable press finishing is widely used in the textile industry to impart wrinkle-resistance to cotton fabric and garment. Significant loss in the mechanical strength of the durable press finished fabrics beside high expensive cost of the dyes have been the major concern in the industry. The low tensile strength retention of the crosslinked cotton fabrics reduces the durability of the fabrics and has become the major obstacle for applications of durable press finishing processes to cellulosic fabrics with relatively low strength and good dyeing efficiency.

Kang, *et al.* (1998), found that the strength loss of the cotton fabrics treated with the multifunctional carboxylic acids could be attributed to two factors, acid-catalyzed depolymerization and crosslinking of the cellulose molecules.

The majority of the durable press finishing agents used by the textile and garment industry are formaldehyde-based N-methylol compounds such as dimethyl-dihydroxyethyleneurea (DMDHEU), (Lewin, *et al.* 1983). DMDHEU is the most extensively agent for cotton by the textile industry. The abrasion and tensile properties of crosslinked cotton fabric had been reported. The catalysts used for the N-methylol crosslinking agents are metal salts of mostly inorganic acids, such as magnesium chloride, aluminium chloride, and zinc chloride. An organic acid may be included to form an activated catalyst system to accelerate the cellulose crosslinking reaction (Gupta *et al.* 1973).

The loss of mechanical strength as a result of crosslinking cotton fabrics with formaldehyde and dimethylethyleneurea (DMEU) has been reported (Grant *et al.* 1968, Meyer *et al.* 1976, and Murphy *et al.* 1971). The tensile strength loss was attributed to degradation of cellulose molecules and fiber embrittlement caused by crosslinking (Segal *et al.* 1973). A decrease in the degree of polymerization of cellulose due to crosslinking of cotton with DMEU has been reported (Segal *et al.* 1973). Severe tensile strength loss caused by the catalysts used for formaldehyde and DMEU has also been observed (Segal *et al.* 1972).

The effects of crosslinking with DMDHEU on chemical properties of mercerized and liquid-ammonia treated cotton fabrics was documented (Zeronain et al. 1989, 1990).

In this study, the effect of the catalyst systems and the crosslinking on the tensile strength of two Egyptian cotton fabrics crosslinked by DMDHEU is presented. In order to separately evaluate the effects of catalysts and that of crosslinking on the fabric strength, it was necessary to remove the DMDHEU crosslinks from cotton. An effective method for the hydrolysis of the DMDHEU-treated cotton fabric using high concentration of NaOH reported by (Abhyankar *et al.* 1998) was used.

MATERIALS AND METHODS

Materials

Two Egyptian cotton fabrics made from Giza 89 and Giza 80 cotton varieties obtained from Misr- El-Mehalla Company, during the season of 2000-2001 were used in this study desized, scoured, and bleached. DMDHEU was a commercial product consisting of buffered aqueous 45%, solid solution (Freerez 900 supplied by Freedom Chemicals). The buffered catalyst magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) was a commercial product. The activated catalysts were commercial products consisting of an aqueous solution of magnesium chloride ($MgCl_2$), zinc chloride ($ZnCl_2$), magnesium nitrate $Mg(NO_3)_2$, and magnesium acetate $Mg(Ac)_2$ were all reagent grade (aldrich).

Fabric treatment

The cotton fabric was first impregnated in a solution containing the catalyst or DMDHEU and catalyst, then padded twice to obtain an average wet pickup of 100- 102%, dried at 80°C for 3 minutes, and finally cured in a curing oven at a specified temperature for a specified period of time.

Hydrolysis of crosslinked cotton fabric

The fabric samples treated with DMDHEU were impregnated with 23% NaOH solution, and the solution was heated and kept at the boiling point for 10

minutes. The fabric was then washed with hot water followed by cool water until the pH of the rinsing water reached 6-7. After the treatment of the fabric with the NaOH solution, the number of yarns in 2.5cm of the cotton samples (standard width for tensile strength measurement) increased from an average of 74 to an average of 93. The tensile strength values measured for the hydrolyzed cotton fabric were adjusted for shrinkage using a factor of 0.796 (74/93).

Fabric performance evaluation

The performance of the untreated and treated cotton fabrics was evaluated after one home laundering washing/drying cycle. The wrinkle recovery angle (WRA), durable press rating (DP), and the tensile strength were evaluated according to AATCC test Method 66-1990, AATCC test Method 124-1992 and ASTM Method D5035-95, respectively.

RESULTS AND DISCUSSION

Effects of crosslinking by DMDHEU

Cotton fabrics were treated with a constant level of DMDHEU (8%), and different concentrations of each commercial $MgCl_2$ catalyst system (labeled buffered and activated), and then cured at 160°C for 3 minutes. The catalyst concentration, WRA, and DP rating for the cotton fabric crosslinked are presented in Table 1. The WRA, and DP ratings for the cotton fabrics were found to increase as the catalyst concentrations increased from zero to 2.0%, and then stabilized at higher catalyst concentrations. Both WRA, and DP of Giza 86 cotton fabric shows a slight increase than that of Giza 80 cotton fabric. Then, the data reveal that the minimum catalyst concentration required to obtain adequate WRA, and DP rating is 2% for both commercial catalyst systems. In addition, even though WRA for both catalyst systems are very similar for catalyst concentration above 1%, the activated catalyst system yielded a higher DP rating.

The percent tensile strength loss of cotton fabrics discussed above is presented in Figure 1, for Giza 89 and Giza 80 respectively as a function of catalyst concentration. The tensile strength loss is greater for the activated catalyst at all

concentrations used. The strength loss for the buffered catalyst system increases with the concentration and levels off for concentration above 2%, whereas the tensile strength loss continued with concentration for the activated catalytic system. The increased tensile strength loss for this activated system is believed to be due to increased acid catalyzed degradation of the cellulose caused by the presence of citric acid, similar to that found in cotton fabrics treated with polycarboxylic acids (Kang, I *et al* 1998). The tensile strength loss for Giza 89 was greater than that of Giza 80 for both activated and buffered catalysts due to the increase in cellulose degradation.

Table1. The catalyst concentration, WRA, and DP rating for Giza 89, and Giza 80 cotton fabric crosslinked with DMDHEU

Catalyst conc.(%)	WRA*				DP Rating**			
	Buffered		Activated		Buffered		Activated	
	G 80	G 89	G 80	G 89	G 89	G 86	G 80	G 89
0.00	205	211	205	213	2.0	2.2	2.0	2.3
0.25	219	223	200	228	2.5	2.8	2.5	3.0
0.5	249	255	207	258	2.8	3.3	3.0	3.5
1.0	270	269	268	270	3.0	3.5	3.5	4.1
2.0	282	288	285	298	3.3	3.7	4.0	4.5
2.5	283	285	288	293	3.3	3.8	4.0	4.5
3	283	283	287	295	3.3	3.5	4.0	4.8
4	282	288	281	299	3.3	3.3	4.0	4.6

Where:

* (WRA) is the wrinkle recovery angle for a control sample was 193°, and 192° for Giza 89, and Giza 80 respectively. ** (DP) is the drable press

The tensile strength loss has been attributed to two main factors that due to the degradation of the cellulose and that due to the presence of crosslinks. In order to separately evaluate these effects, a procedure utilizing aqueous NaOH was used

to remove the crosslinks (Abhyankar et al. 1998). The WRA for all cotton fabrics thus treated was found to be similar to that for the control samples (192^o, and 193^o), thus indicating that the crosslinks were effectively removed through application of this treatment. After eliminating the influence of the crosslinks on the tensile strength loss (reversible loss), the remaining tensile strength loss was due to the cellulose degradation (irreversible loss).

The percentage of the tensile strength loss due to cellulose degradation and that due to the crosslinking for the DMDHEU-treated cotton fabric cured using the buffered commercial catalyst is presented in Figure 2, for Giza 89 and Giza 80 respectively. The percentage of the tensile strength loss due to crosslinking decreases whereas that due to the cellulose degradation increases from 0.25 to 3.0%. Crosslinking is the predominant factor for the fabric strength loss at low catalyst concentration (below 3%). When the catalyst concentration reaches 3.0% and above, the contributions due to cellulose degradation and crosslinking level off with both contributing approximately 50% of the total strength loss.

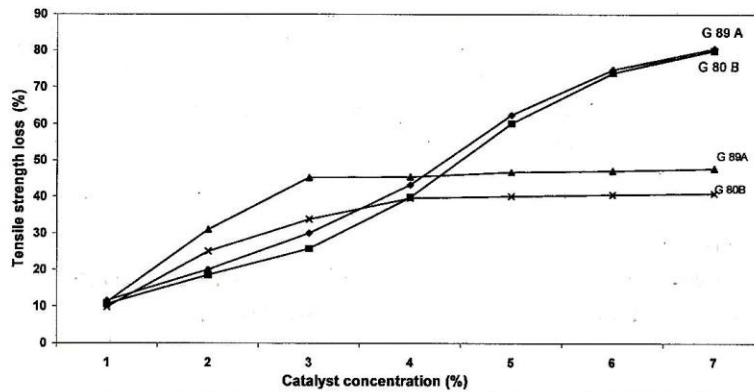


Figure 1. Tensile strength loss for Giza 89, and Giza 80 fabrics treated with DMDHEU in the presence of activated (A), and buffered (B) catalyst systems and cured at 160C for 3 minutes.

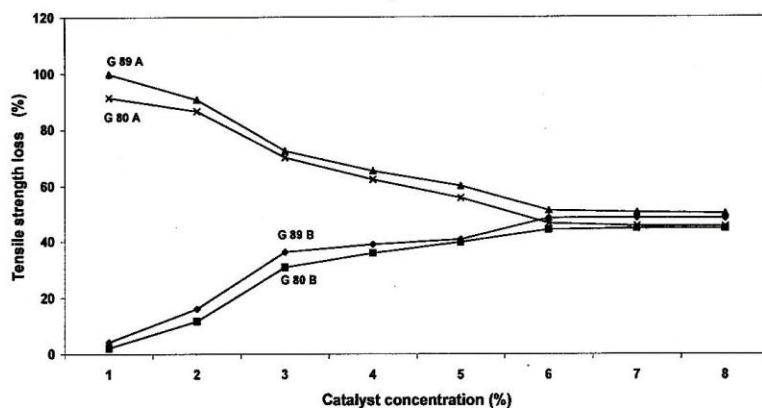


Figure 2. The percentage tensile strength loss due to (A) crosslinking and (B) degradation for Giza89, and 80 fabric treatment using buffered commercial catalyst

The plots of the percentage of total tensile strength loss due to the cellulose degradation and crosslinking for cotton fabrics treated with DMDHEU and cured using the activated catalyst system for Giza 89 and Giza 80 are shown in Figure 3. The percentage of total tensile strength loss due to the cellulose degradation increases whereas that due to crosslinking decreases continuously over the entire range of catalyst concentrations used. The percent contribution to the tensile strength due to the crosslinking were lower and those due to the cellulose degradation which were higher for cotton fabrics treated with DMDHEU, and the activated catalyst system than that for the buffered catalyst system discussed above. The overall percentage of tensile strength loss due to cellulose degradation does not level off as was observed above but increase continuously over the concentration range. The organic acid present in the activated catalyst systems promotes and increased cellulose degradation with increased catalyst concentration. In order to further understand the effect of the catalyst on the tensile strength loss, fabric samples were treated separately with both commercial catalysts, activated and buffered in the absence of the DMDHEU crosslinking agent.

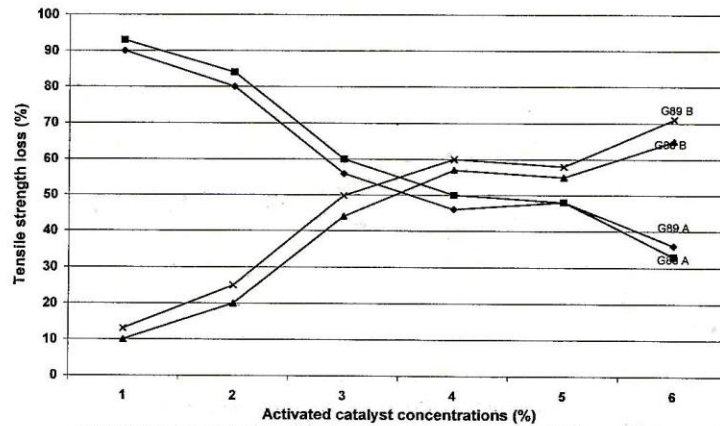


Figure 3. The percentage tensile strength loss due to (A) crosslinking and (B) degradation for Giza89, and 80 fabric treatment using activated catalyst

Effect of the catalysts

The percent tensile strength loss for cotton fabrics treated with the commercial buffered catalyst and with the activated catalyst system, both at a 3% concentration, as a function of curing temperature is presented in Figure 4 for Giza 89 and Giza 80 respectively. The loss of the tensile strength increases with increasing the curing temperature, similar to that observed with the crosslinking of cellulose with DMDHEU. Whereas there is a very little tensile strength loss when the fabric treated with the buffered catalyst cured at 130°C, over 70% of the fabric tensile strength is lost when the fabric is cured at 180°C. Evidently, the MgCl₂ catalyst alone causes significant reduction in the fabric strength. When the cotton fabric was treated with just the activated catalyst system the tensile strength loss was found to be much more severe, even at a relatively moderate cure temperature (130°C), the fabric loss over 65% of its original tensile strength. The tensile strength loss becomes greater than 90% when the fabric is cured at 180°C. This

activated catalyst system obviously induces more damage to cellulose than does the buffered catalyst. The pH of the activated catalyst bath was 2.85.

The increased degradation due to citric acid contained in the catalyst system is due to the exposure of cotton fabric treated with polycarboxylic acids at elevated temperatures reducing the fabric tensile strength due to acid-catalyzed depolymerization. It has also been reported that HCl can be released when cotton is treated with a system consisting of ethyleneurea and a mixture of metal chloride and an acid. A second possible explanation is that $MgCl_2$ is more effective in catalyzing cellulose degradation at lower pH, since this chloride hydrolysis in aqueous solution releasing HCl thus increasing H^+ ion concentrations.

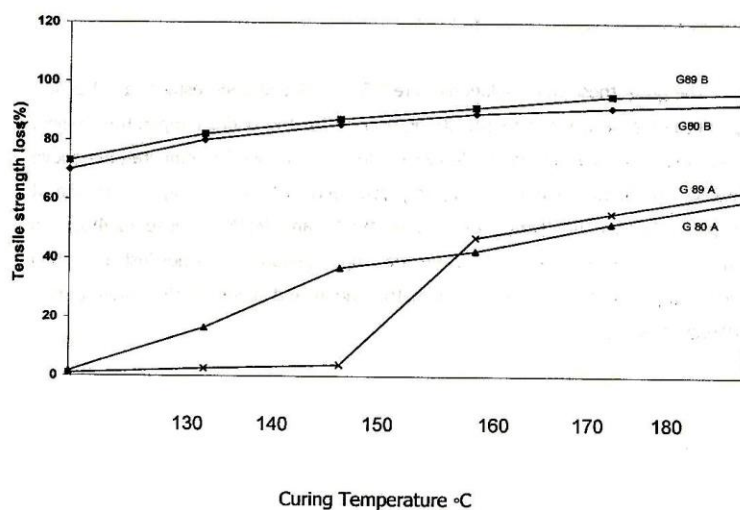


Figure 4. The tensile strength loss for cotton fabric treated with the buffered catalyst (A) and with the activated catalyst (B) at different cure temperatures

The effect of changing the catalyst metal ion on the percent of tensile strength loss is presented in Figure 5 for Giza 89 and Giza 80 respectively treated with 0.5% MgCl_2 , and with 0.5% ZnCl_2 , and then cured at different temperatures for 3 minutes. Interestingly, the fabric strength loss was greater when ZnCl_2 was used as compared to MgCl_2 over the entire temperature range. The 0.5% ZnCl_2 solution was found to have a slightly higher pH than the 0.5% MgCl_2 solution, 6.2 versus 5.99. Thus, the difference in strength loss between the two metal ions cannot be just explained based on the catalyst bath pH.

The catalyst anions also were found to influence the degree of fabric strength loss. The percent tensile strength loss for fabrics treated with three different magnesium salts, 0.5% MgCl_2 , 0.78% $\text{Mg}(\text{NO}_3)_2$, and 0.75% $\text{Mg}(\text{Ac})_2$, (all are 0.053M), and cured at various temperatures for 3 minutes is presented in Figure 6 for Giza 89 and Giza 80 respectively.

The pH of these three solutions were 5.51, 5.59, and 6.95 respectively. $\text{Mg}(\text{Ac})_2$ produces the least fabric tensile strength loss over the entire temperature region, and MgCl_2 produce the highest fabric tensile strength loss for temperatures above 170°C. The fabric treated with $\text{Mg}(\text{Ac})_2$ loses only 4.7% of its original strength at 180°C, whereas the fabric treated with MgCl_2 , and $\text{Mg}(\text{NO}_3)_2$ lose 62.4%, and 57.2% respectively. It is obvious that the fabric strength loss is not just a function of solution pH, but depends on both the cation and anion of the catalyst used (Pierce *et al.* 1970).

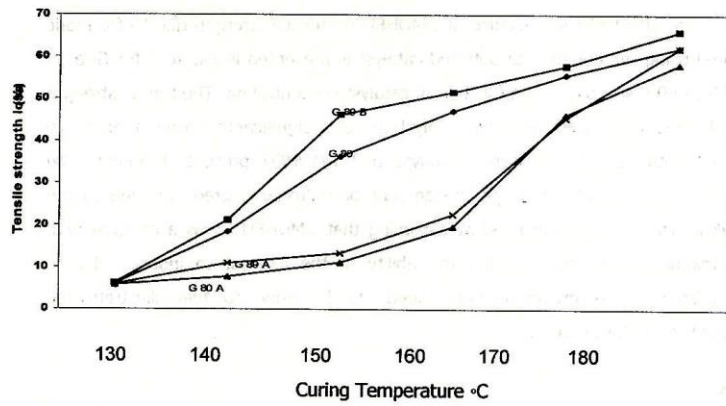


Figure 5. The tensile strength loss for the cotton fabrics treated with $MgCl_2$ (A), and $ZnCl_2$ (B) and heated at different temperature

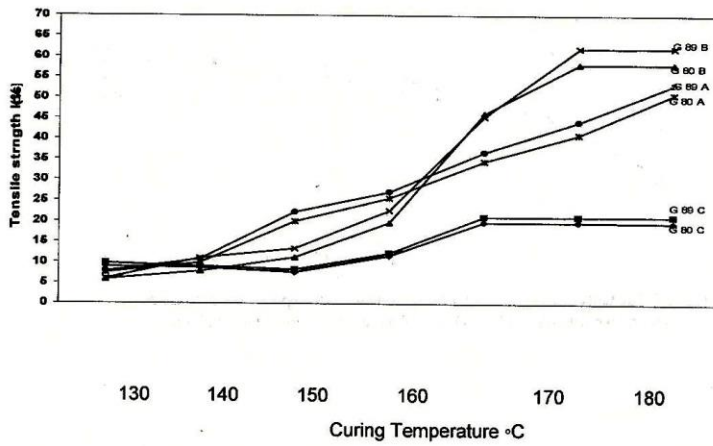


Figure 6. The tensile strength loss for the cotton fabric treated $MgCl_2$ A, $Mg(NO_3)_2$ B, and $Mg(Ac)_2$ C of equal mole concentration 0.005M and cured at different Temperatures

The effect of the presence of DMDHEU on tensile strength due to for fabric treated using the commercial buffered catalyst is presented in Figure 7 for Giza 89 and Giza 80 respectively as a function of catalyst concentration. The tensile strength loss for fabrics treated with the catalyst alone is significantly higher than those treated with both the buffered catalyst and DMDHEU present. Evidently, the presence of DMDHEU reduces the amount of cellulose degradation due to the catalyst. This may be explained by assuming that DMDHEU forms a complex with the magnesium cation, reducing the ability of the catalyst to induce cellulose degradation. However, more work needs to be done to fully illustrate the mechanism of this process.

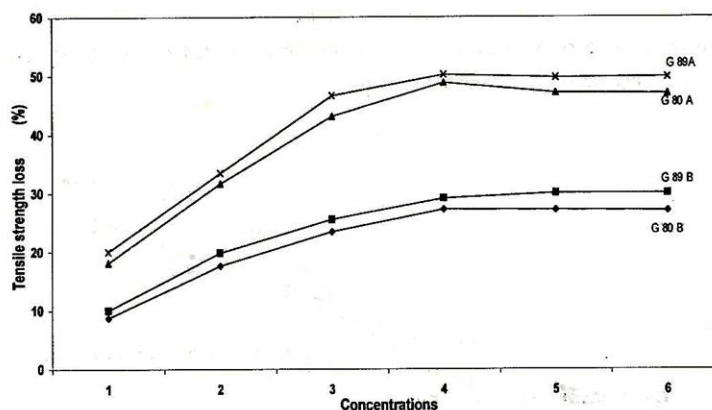


Figure 7. The tensile strength loss for the cotton fabric treated with the catalyst (A) and treated with DMDHEU and the catalyst (B) at different concentrations

CONCLUSION

The results obtained during this study reveal the following:

- 1- The WRA and DP of Egyptian cotton Giza 89 fabric treated with DMDHEU increased more than Giza 80 fabric with increasing the concentration of the catalytic system till 2% at 160°C in 3 minutes.
- 2- The strength loss of the cotton fabrics used increased in the presence of the catalytic system (activated or buffered) to reach the maximum loss 80% with the activated catalyst.
- 3- DMDHEU concentration is critical for optimizing the tensile strength retention of finished fabrics.
- 4- The magnitude of fabric strength loss is affected by the temperature, time, concentration of the catalyst, and on both of cation and anion used as the catalyst.
- 5- Activated catalyst, which includes an organic acid caused more severe fabric strength loss due to additional cellulose degradation induced by the organic acid in the catalyst system.

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تأثير عوامل الحفز علي فقد المتانة لبعض أصناف القطن المصري

صلاح منصور صالح

مركز البحوث الزراعية- معهد بحوث القطن- الجيزة- ج.م.ع

الملخص

يعتبر تناقص متانة الخيوط القطنية أثناء معاملات التجهيز النهائي (المقاومة للإجهاد - Durable press) باستخدام مادة ثنائي ميثيل ثنائي هيدروكسي إيثيلين يوريا من المشاكل التي تواجه الصناعة المصرية. يهدف البحث الي دراسة إضافة العامل الحفاز (النشط أو المتعادل) أثناء معاملات المقاومة للإجهاد و تأثيرها علي المتانة.

أستخدم في هذه الدراسة أقمشة مصنوعة من صنفين من الأقطان المصرية (جيزة ٨٩ و جيزة ٨٠) والتي تم الحصول عليها من شركة مصر للغزل و النسيج - المحلة الكبرى لموسم ٢٠٠٠-٢٠٠١ و بحيث تتراوح عدد الخيوط القطنية بين ٧٤ و ٩٣ (العدد القياسي للخيوط في ٢,٥ سم عرض من القماش لقياسات المقاومة للإجهاد و المتانة) و ذلك بعد إجراء معاملات إزالة البوش و الغلي في القلوي ثم التبييض و قد أوضحت الدراسة الآتي:-

- ١- تزداد قيم زاوية التجعد و كذلك نسبة المقاومة للإجهاد لصنف جيزة ٨٩ عن صنف جيزة ٨٠ بزيادة تركيز العامل الحفاز المتعادل عن العامل الحفاز النشط حتي ٢% و ذلك باستخدام مادة ثنائي ميثيل ثنائي هيدروكسي إيثيلين يوريا لمدة ثلاث دقائق في درجة حرارة ١٦٠ مئوية.
- ٢- وجد أن المتانة تتناقص بوجود كل من العامل الحفاز النشط أو المتعادل و وجد أن أعلي نسبة تناقص بوجود العامل الحفاز النشط تصل الي (٨٠%) لكل الأصناف المستخدمة.
- ٣- زيادة تركيز مادة ثنائي ميثيل ثنائي هيدروكسي إيثيلين يوريا في وجود العامل الحفاز (النشط و المتعادل) يؤدي الي ثبات المتانة و ذلك بتفاعل هذه المادة مع الأيون الموجب للعامل الحفاز مما يؤدي الي أقل نسبة فقد في المتانة عند تركيز (٨%) من هذه المادة.
- ٤- بدراسة تأثير درجات الحرارة المختلفة علي المتانة لكلا الصنفين (باستخدام مادة ثنائي ميثيل ثنائي هيدروكسي إيثيلين يوريا بتركيز (٨%) لمدة ثلاث دقائق) بوجود العامل الحفاز المتعادل فأن المتانة لا تتأثر حتي درجة ١٣٠ مئوية و يزداد التناقص في المتانة حتي يصل الي ٧٠% عند درجة حرارة ١٨٠ مئوية بينما وجد إن المتانة تتناقص لتصل الي ٩٠% في درجة حرارة ١٨٠ مئوية في وجود العامل الحفاز النشط
- ٥- بدراسة تأثير الأيون الموجب المكون للعامل الحفاز (الماغنسيوم أو الزنك) في درجات الحرارة المختلفة فأن المتانة لكل الأصناف المستخدمة تتناقص نتيجة تغيير الأس الهيدروجيني (pH) لحوض التفاعل.
- ٦- بدراسة تأثير الأيون السالب المكون للعامل الحفاز (الكلوريد- النترات- الأسيتات فأن أقل مقدار للفق في المتانة يصل الي ٤,٧% باستخدام أسيتات الماغنسيوم كعامل حفاز نشط. وكنيجة نهائية لهذا البحث فقد وجد أن أفضل الطرق لمعاملات التجهيز النهائي (المقاومة للإجهاد) لكل من الأصناف المستخدمة نون للتأثير الشديد علي متانة الخيوط الا في حدود ٤,٧% هو استخدام تركيز ٨% من مادة ثنائي ميثيل ثنائي هيدروكسي إيثيلين يوريا في درجة حرارة حوض المعاملات ١٣٠ مئوية و درجة الأس الهيدروجيني ٥,٩١ لمدة ثلاث دقائق و باستخدام تركيز ٠,٥٣ مول من أسيتات الماغنسيوم كعامل حفاز نشط.