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Graft Copolymerization of Methylmethacrylate Onto Cellulosic Cotton Fabric: Effects of Pretreatments and Monomer Concentration

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ABSTRACT

Graft polymerization of methylmethacrylate (MMA) on to enzyme desized, scoured, bleached, and mercerized cellulosic cotton fabric was studied in 0.1M nitric acid using ceric ammonium nitrate (CAN) as an initiator. The investigation was carried out to study the possibility of grafting methylmethacrylate on to cellulosic cotton fabric at various stages of processing. Two sets of five different samples were used, four of them passed through the pretreatment stages of desizing (D), desizing and scouring (DS), desizing, scouring and bleaching (DSB), desizing, scouring, bleaching and mercerizing (DSBM) and one was kept as grey (G). The first set of the samples including the grey were grafted with 3.5 ml of MMA and 0.05 M of CAN at 50 °C for 3 hrs. In the second set of samples the graft polymerization was carried out under varying concentrations of monomer, while keeping all other factors constant. The second set has all passed through the final stages of pretreatment (DSBM). The results of FTIR (Infrared spectroscopy), water absorption, dimensional stability, crease recovery properties, tearing strength indicated that there was improvement in the physical and chemical properties of the cellulosic cotton fabric as a result of the graft polymerization. Tearing strength and water absorption of the grafted sample showed considerable decrease. The dimensional stability and crease recovery characteristics of the cotton fabric were generally improved.

Key words: cellulose, graft copolymerization, methylmethacrylate, pretreatments.

1. INTRODUCTION

Modification of polymers has received much attention recently. Graft co-polymerization is an attractive method through which a

variety of functional groups can be introduced into the cellulosic polymer. This results in the modification of its physical and chemical properties (Haruna, 1998). Grafting allows the introduction of vinyl

monomers on to the cellulose backbone thus incorporating the properties of the added polymers while retaining the basic traits of the cellulosic material. It also allows the development of a material with a tailor made properties for a variety of applications (Amar *et al.*, 2012). Cellulose is a renewable biodegradable product which can be modified through chemical reactions in a variety of ways to obtain novel characteristics (Kulicke *et al.*, 1996). This is made possible through the creation of grafts (branches) of polymers on the cellulose backbone that imparts the desired properties without destroying its basic characteristics (Hebeish, 1981).

Modification of cellulose through graft co-polymerization has been conducted over the years using different methods. Typical of these methods include ionic and ring opening polymerizations, living radical and free radical polymerizations (Habibu, Sarih, & Mainal, 2018). Among these methods free radical polymerization received the greatest attention (Sebenik, 1998). In this technique free radicals are created through reaction with initiator on the cellulose backbone. The free radical thus formed can add to the monomer to create a covalent bond between the monomer and the cellulose. This reaction is then followed by propagation leading to the formation of macromolecules and subsequently termination. The process is usually carried out by a combination of two growing radical chains (Athawale, 1999; Berlin, 1992). Graft polymerization of cellulose using vinyl monomers is one of the most extensively studied using a wide range of initiators such as $\text{KMnO}_4\text{-HNO}_3$ redox system, KMnO_4 /Citric acid redox system, and CAN initiation (Deo, 1999; Vijay, 2009; Khullar et al., 2008). Ceric ammonium nitrate (CAN) initiation technique was favored because of its simplicity, availability, and better yield. Modification of cellulose through graft co-polymerization has a bright future and their development is practically boundless. The use of ceric ammonium nitrate to initiate graft

copolymerization of vinyl monomers on to various cellulosic materials such as cotton, jute, flax, rayon, wood pulp and paper has gained considerable attention. Ceric ion is a powerful oxidizing agent and possess high efficiency on both grafting and oxidation of cellulose (Neetu *et al.*, 2011). In the presence of nitric acid, ceric ammonium nitrate (CAN) is an efficient initiator for graft polymerization of vinyl monomers on to cellulose. A number of scholars have worked on the prospects of graft copolymerization on natural cellulosic fibers applying advance techniques of characterization to evaluate their properties, (Kumar *et al.*, 2005). A wide variety of monomers either hydrophobic or hydrophilic has been grafted on to cellulose (Zahran *et al.*, 2003), but generally acrylic monomers are the most widely used. Few of the recent areas of applications of cellulose graft copolymers are wood plastic composites, dispersion stabilizers, and film development etc. (Gürdağ & Sarmad, 2013; Jiang, Pan, Zhang, & Fang, 2019; Kumar, Sharma, & Singh, 2018). At this point, you need to state briefly, what the paper is reporting.

2. EXPERIMENTAL

All the chemicals used in this investigation were of laboratory grade. The cellulosic cotton fabric was procured from Kwari market in Kano Nigeria and was analyzed at the African Textile Manufacturers Limited; Challawa Industrial Estate, Kano, to have the following specifications: Fabric width 51.1inches; picks/inch 68 and ends/inch 72; warp count 24.6 and weft count 28.1; weight/meter 168.79 g.

2.1 Pretreatment of the cotton fabric

The cotton fabric was thoroughly treated prior to the graft polymerization reaction.

2.1.1 Desizing

A 10gm of the sample was treated at 45 °C with 5 g/l of enzyme, 3 g/l common salt, and 2 g/l wetting agent. The process involved soaking the fabric in the prepared solution for 3 mins. It was then removed folded and

wrapped in a polythene bag for 24 hrs. The fabric was removed, washed thoroughly with hot, warm, then cold water respectively and finally dried.

2.1.2 Scouring

The scouring was carried out on a 10 g sample of fabric using a programmable electrical thermostatic water bath with NaOH 4 g/l, Na₂CO₃ 2 g/l and liquor to material ratio of 1:30. The temperature was raised to 90 °C and kept for 2hrs. The fabric was removed, washed thoroughly with hot, warm, then cold water respectively and finally dried (Kathirvelan *et al.*, 2000).

2.1.3 Bleaching

The scoured fabric was treated for 60 minutes in a solution containing 5g/l hydrogen peroxide, caustic soda 1g/l, sodium silicate 3g/l, and wetting agent 2g/l at 90 °C using a liquor ratio of 1:30 (Nkeonye, 2009). The fabric was properly washed with hot, warm, then cold water respectively and finally dried.

2.1.4 Mercerization

In this process 10g sample was passed through a 27 % solution of caustic soda at room temperature for a period of 60 seconds. The fabric was washed thoroughly with hot, warm, then cold water respectively and finally dried after neutralization with acetic acid (Remzi, 2010).

2.2 Graft copolymerization

The graft co-polymerization was conducted using the procedure adopted by Kazaure M.A., (1996) and Danbatta M.H. (1998). The ceric ammonium nitrate (CAN) solution was prepared by dissolving the required amount in 0.1 M nitric acid. The material was introduced into the 250 ml conical flask and kept in a thermostat water bath at a temperature of 50 °C for 15mins; the material to ceric solution ratio was 1:50. Samples of both grey and treated samples were placed inside the solution and after a period of 15mins the required amount of the

monomer was added. The flask was covered with a stopper and the contents stirred at intervals during the polymerization period of 3hrs. The samples were then removed, washed thoroughly in acetone, and the occluded homopolymer was removed using Soxhlet extraction in methanol for 24hrs. The co-polymer was then dried at 40 °C under vacuum to constant weight. This procedure was repeated on the mercerized cotton fabric with varying concentrations of monomer.

2.3 Analyses of the grafted cotton fabric

2.3.1 Fourier Transform Infra-Red Spectroscopy (FTIR)

The FTIR spectra of the grafted and ungrafted cellulose cotton fabrics were recorded on 8400-S Fourier Transform Infrared Spectrophotometer using KBr pellet technique in the range 4500 – 400 cm⁻¹ with a resolution of 2 cm⁻¹.

2.3.2 Determination of dimensional stability

The length of the samples was taken in both warp and weft direction before the test. The samples one after the other was immersed in boiling water each for 3 mins, they were then removed without squeezing and dried. The measurement was again taken in both warp and weft direction.

2.3.3 Determination of crease recovery angle

The test samples of 40 mm x 15 mm dimensions with ten samples cut in warp direction and ten in weft were conditioned for 24 hrs at 20 °C ± 2 °C and RH (Relative Humidity) of 65 % ± 2 %. Half the number of the test specimens in the warp direction were folded face to face and the other half back to back, same applied for those in the weft direction. The crease recovery angle was measured across the length (warp direction) face to face and back to back and the angle was also measured along the width

(weft) of the fabric face to face and back to back according to (ISO/R 2313) standard.

2.3.4 Determination of tear strength

Five samples of 10.5 cm x 7.5 cm in both warp and weft directions were prepared. The machine has upper and lower jaws. A cut was made in the sample to form two tongues and lines were marked indicating the point where the tear should reach, one tongue was fixed to the upper jaw and the other to the lower. The machine was then put on to tear the fabric up to the reference point. The reading was taken for each of the five samples in both warp and weft directions. The average tearing strength was then recorded.

3. RESULTS AND DISCUSSION

3.1 Analyses of the pre-treated cotton fabric

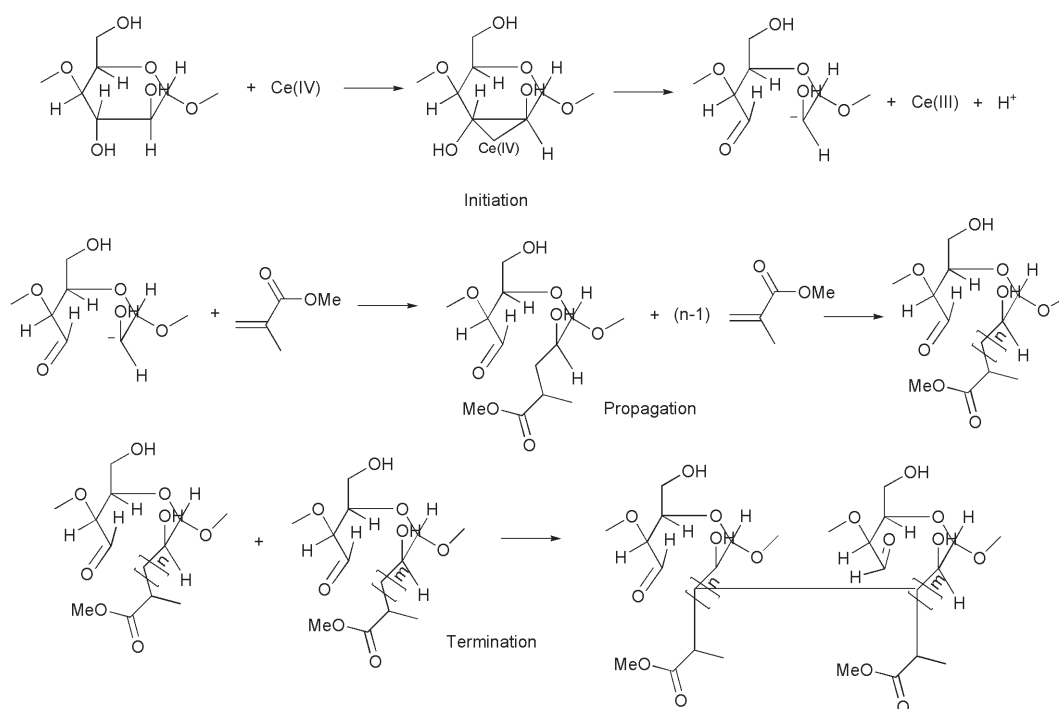
The size mixtures present on the cellulosic cotton fabric has been removed as a result of the desizing process carried out. This was further confirmed through testing with

iodine solution. When a drop of iodine solution was placed on the desized cotton fabric a yellow color was observed indicating that the size had been degraded and removed. The impurities both natural and added present on cotton fabric prior to scouring had been removed. This is evident from the increased absorbency observed on the fabric. The natural coloring matter had been degraded and decolorized during the bleaching operation and removed in the subsequent washing treatment. Increased water absorbency, strength, and luster has been observed indicating proof of mercerization.

After the copolymerization reaction (Scheme 1), the graft percent yield was calculated using the relationship:

$$\% \text{GY} = \frac{\text{final cellulose wt.} - \text{initial cellulose wt.}}{\text{initial cellulose wt.}} \times 100$$

And the result is presented in Table 1 and 2 below:



Scheme 1: Mechanism of graft copolymerization of MMA onto cellulose

Table 1: effect of pretreatments on the percentage yield of cotton cellulose grafted-co-MMA.

Sample	MMA(ml)	Graft % Yield
G	„	8.26
D	„	9.46
DS	„	11.17
DSB	„	13.33
DSBM	„	14.34

Table 2: Effect of Monomer Concentration on the yield cotton cellulose grafted-co-MMA.

Sample	MMA(ml)	Graft % Yield
DSBM	0.0	0.00
DSBM	1.0	9.06
DSBM	2.5	12.11
DSBM	3.5	14.34
DSBM	4.0	15.52
DSBM	5.0	13.93

From Table 2, the grafting reaction was studied under varying concentrations of monomer keeping all other factors constant. The mercerized (DSBM) sample was used as such the natural and added impurities which might affect the grafting process have been removed. The graft percent yield increased up to a monomer concentration of 4.0 ml. In addition to the pretreatment this may be attributed to the generation of more monomer radicals to react on to the reactive sites on the cellulose backbone. After reaching the optimum value, the percent graft yields decreased and this may not be unconnected with the predominance of homopolymer over graft polymerization, (Kumar *et al.*, 2005). The highest graft percent yield was obtained on the DSBM samples. This happened as a result of the mercerization and removal of all the impurities present on the cotton fabric prior to the grafting reaction. The graft percent yield increased with increasing accessibility due to greater availability of physically

absorbed monomer on the more accessible sites on the substrate, (Hebeish, 1981). It is therefore evident that the graft percent yield obtained on grafting (MMA) on to mercerized cotton fabric is higher.

3.2 Water absorbency

The water absorbency test result is presented in Table 3 below. It was observed that there is a considerable decrease in water absorption of the methyl methacrylate grafted cotton fabric.

Table 3: Effect of Pretreatments on Water Absorbency of Cotton cellulose grafted-co-MMA.

Sample		Water Absorbency (s)
Control		3.5 ml MMA
G	20 x 60	22.11 x 60
D	10 x 60	23.09 x 60
DS	5 x 60	22.67 x 60
DSB	12	24.31 x 60
DSB M	06	29.81 x 60

It can be observed from the above table that the more the number of pretreatments on the fabric, the higher the water absorption; The best result of 6 seconds; was obtained with the DSBM samples, which is attributed to the mercerization and efficient removal of impurities present on the fabric prior to grafting. Before grafting, a wetting time of 6 seconds was recorded, but after grafting with methylmethacrylate, a wetting time of 29.81 minutes was observed with the mercerized (DSBM) sample. This clearly indicates that the absorption of water by methylmethacrylate grafted samples had greatly decreased.

Table 4: Effect of Monomer concentration on Water Absorbency of Mercerized Cotton cellulose grafted-co- MMA.

Monomer Concentration	n	Water Absorbency (secs)
DSBM	1.0	22.60 x 60
DSBM	2.5	22.60 x 60
DSBM	3.5	29.81 x 60
DSBM	4.0	32.07 x 60
DSBM	5.0	26.60 x 60

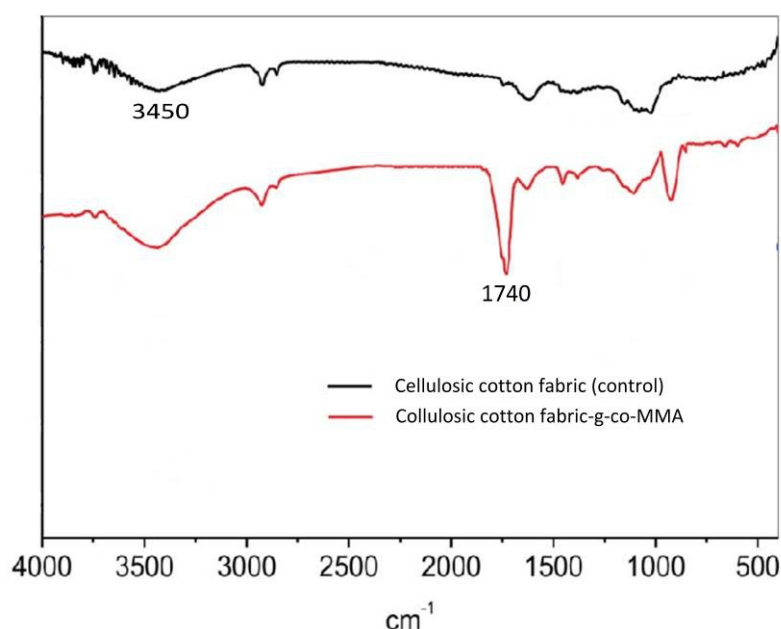
Further decrease of water absorption was also recorded with DSBM of the varying concentrations of monomer grafted samples

as can be seen from Table 4, above. The graft copolymerization carried out on the fabric has made it more hydrophobic resulting in decrease water absorption (Negishi *et al.*, 1965).

3.3 Results of the analyses carried out on the Unmodified and grafted cotton fabrics

3.3.1 FTIR Spectroscopy

The result for the FTIR spectra of the raw cellulose as well as the grafted cellulose is presented in Figure 1 and Table 6.

**Figure 1:** FTIR spectrum of cellulosic cotton fabric and cellulosic cotton fabric**Table 65:** FTIR Absorption Frequencies (cm^{-1}) of Cellulosic Cotton Fabric (Control) and Cellulosic Cotton Fabric – g-co-MMA

Control Sample		Grafted Sample	
Assignment	Functional Group	Assignment	Functional Group
3500-3200	O-H (H-bonded)	3500-3200	OH(H-bonded)
-	C-H(Stretch)	2899	CH(Stretch)
-		1703	C=O(Esther)
-		1709	C=O(Esther)
-		1708	C=O(Esther)
-		1708	C=O(Esther)

Control Sample		Grafted Sample	
Assignment	Functional Group	Assignment	Functional Group
-		1430	C-CH ₃ (Bending)
1315	CH ₂ (rocking)	1130	CH ₂ (Bending)

From the results it can be seen that both control and grafted cellulosic cotton fabrics have a common –OH stretching vibration in the region 3500-3200 cm⁻¹ corresponding to hydrogen bonded substances and 2890-2899 cm⁻¹ of C-H stretch. This is regardless of the stage of pretreatment at which the cotton fabric was grafted. This clearly suggests that not all the OH groups of the cellulosic cotton fabric have been replaced by methylmethacrylate groups. However, in the case of methylmethacrylate grafted cotton fabric an additional peak appears at 1703.2, 1709.95 cm⁻¹, 1708.02 and 1708.99 cm⁻¹ which is peculiar to the Carbonyl group (>C=O) of ester stretching. This suggests

that MMA has been grafted on to the cellulosic cotton fabric through covalent linkages. Other peaks at 1430.26 (O-CH₃ bending of MMA), 1329.96 (C-CH₃) and 1132.25 - (CH₂) bending of MMA support this assumption (Kazaure et al., 1999).

3.3.2 Dimensional Stability

After drying, the samples were measured again and the length in both warp and weft directions remained unchanged. The test was conducted for both the control and the grafted samples and the results are presented in the Table 7 below:

Table 7: Effect of pretreatment on the dimensional stability of Cotton cellulose grafted-co-MMA.

Sample	Dimensional Stability			
	Control		3.5 ml MMA	
	Warp	Weft	Warp	Weft
G	4.30	9.80	0.00	0.00
D	6.10	11.40	0.00	0.00
DS	7.20	17.80	0.00	0.00
DSB	10.00	21.60	0.00	0.00
DSB	11.80	27.10	0.00	0.00
M				

Table 8: Effect of Monomer concentration on Dimensional Stability of Mercerized Cotton cellulose grafted-co-MMA.

Concentration	Shrinkage (%)	
	Warp	Weft
1.00	0.92	1.76
1.00	0.16	1.02
1.00	0.00	0.00
1.00	0.00	0.00
1.00	0.00	0.00

It can be observed from tables 7 and 8 that the methyl methacrylate-grafted cotton fabric has a satisfactory dimensional stability.

3.3.3 Tearing Strength

This is the force required to tear the fabric. It is the average force required to continue a tear previously initiated in a fabric by twice the length of tear. Graft copolymerization of methyl methacrylate produced a marked increase in some desirable properties such as dimensional stability, crease recovery, and thermal stability of the grafted cellulosic cotton fabric, (Hebeish and Guthrie, 1981). However certain undesirable effects such as reduction in tearing strength are also observed. The grafted fabric samples were arranged according to the sequence of processing; desized (D), desized and scoured (DS), desized, scoured and bleached (DSB), desized, scoured, bleached and mercerized (DSBM), the result is presented in the Table 9.

Table 9: Effect of pretreatment on the Tear Strength of Cotton cellulose grafted-co-MMA.

Sample	Tear Strength (kg)			
	Control		3.5 ml MMA	
	Warp	Weft	Warp	Weft
G	16.21	134.4	111.8	87.2
D	154.2	126.1	125.2	80.8
DS	155.9	125.7	97.6	71.2
DSB	149.2	125.7	97.6	71.2
DSB	157.7	125.7	118.7	93.6
M				

It could be observed from Table 9 that the tearing strength remained fairly stable prior to grafting, but after grafting a considerable reduction in the tearing strength was recorded. The tearing strength of the control samples seemed to be good and this might be connected with the mercerizing and efficient removal of size mixtures from the fabric following enzyme desizing. It can also be observed that the grafted samples show a considerable reduction in tearing strength when compared to control samples. This was due to the increase in stiffness of the fabric as a result of grafting with MMA (Masazo, 1964).

Table 10: Effect of Monomer concentration on the Tear Strength of Mercerized Cotton cellulose grafted-co-MMA.

Concentration (ml)	Tear Strength (kg)	
	Warp	Weft
0.00	157.7	125.8
1.50	118.7	93.6
2.50	126.4	74.4
3.50	116.4	87.6
4.00	101.2	64.6
5.00	91.2	57.6

From Table 10, it could be observed that the tearing strength of the grafted samples continued to decrease progressively reaching its lowest level. The tearing strength of the grafted samples decreased progressively as the monomer concentration was increased. The overall reduction in the strength of all the treated samples was believed to be as a result of the stiffening of the cloth following methylmethacrylate grafting. A similar decrease of the tearing strength of the grafted cellulosic fabric was reported by Hebeish and Guthrie, (1981).

3.3.4 Crease recovery angle

Crease recovery denotes that property of fabric to go back to its original shape or position after creasing. It is a measure of crease resistance specified in quantitative terms of crease recovery angle. If the angle is 0° then recovery is zero and if the angle is 180° recovery is full. The results are given in the following tables:

Table 11: Wrinkle Recovery Angle (WRA), deg. of the Control Samples

Sample	Warp			Weft			Total WRA	
	Face Face	to	Back to Back	Face Face	to	Back to Back	Warp	Weft
G	6.40		5.20	7.20		6.80	11.6	14.0
D	19.0		17.6	17.6		18.0	36.4	35.6
DS	18.7		21.1	20.3		19.6	39.8	39.9
DSB	19.4		19.0	19.8		19.2	38.4	38.6
DSBM	19.1		20.0	22.4		21.5	39.1	42.4

Table 6: *Wrinkle Recovery Angle (WRA), deg. of the Constant Concentration of Monomer Grafted Samples (3.5ml)*

Sample	Warp		Weft		Total	
	Face to Face	Back to Back	Face to Face	Back to Back	Warp Weft	
G	22.8	22.6	23.2	22.6	45.4	45.8
D	24.2	22.2	22.4	24.2	46.4	46.6
DS	24.6	23.2	23.0	23.0	47.8	46.0
DSB	24.1	24.0	23.8	23.3	41.1	47.1
DSBM	26.0	25.6	23.8	23.8	51.6	47.6

Table 13: *Wrinkle Recovery Angle (WRA), deg. of the Varying Concentrations of Monomer Grafted samples*

Monomer Concentration	Warp		Weft		Total	
	Face to Face	Back to Back	Face to Face	Back to Back	Warp Weft	
1.0	21.2	19.0	21.6	17.4	43.8	39.0
2.5	25.0	24.8	24.9	19.8	49.8	44.7
3.5	20.8	28.8	23.2	20.6	49.6	43.8
4.0	25.0	25.6	26.2	23.8	50.6	50.0
5.0	20.8	19.0	23.2	17.4	43.8	39.0

It can be seen from the control (Table 11) that the crease recovery angle was low compared to that of the grafted samples. It was observed that the crease recovery angles increased with the increase in the number of pretreatments reaching its optimum value on the mercerized (DSBM) cotton fabric as can be seen on Table 12. The second set of samples in their final stages of pretreatment were grafted using varying concentrations of monomer (1 ml, 2.5 ml, 3.5 ml, 4.0mls and 5.0 ml) keeping all other factors constant (Table 13). The crease recovery angle (WRA) was fairly good for all the samples reaching maximum at monomer concentration of 4.0 ml. The pretreatments given to the fabric have effectively removed all the natural and added impurities from the fabric which might otherwise interfere with the grafting process.

4. CONCLUSIONS

Modification of the cellulosic cotton fabric through graft copolymerization allows the elimination of several drawbacks associated

with cotton fabrics, and brings about improvement in comfort, ease of maintenance, dimensional stability, crease recovery, and water repellency. The present study was carried out with these aims in mind and the results of experimental analyses proved that the objectives had been achieved. In addition, we were able to prove that graft co-polymerization of methylmethacrylate using ceric ammonium nitrate as initiator can be conducted on cellulosic cotton fabric at various stages of pretreatments. At one stage varying amount of concentrations of the methylmethacrylate was grafted on to the fabric. Infrared spectroscopy (FTIR) was conducted to further establish the proof of grafting. Methylmethacrylate (MMA) was grafted on to cellulosic cotton fabric at various stages of pretreatments. The optimum grafting conditions were obtained by studying the effect of pretreatments and varying concentrations of MMA. The effect of these factors was investigated by calculating the graft percent yield. The highest percent yield

of 14.34% was achieved at MMA concentration of 4.0mls on the fabric at its final stage of pretreatment. The result of the study of wrinkle recovery properties, water absorption, dimensional stability, and tearing strength of the grafted samples confirms the grafting of MMA on to the cellulosic cotton fabric. The characterization of the grafted cotton fabric was also confirmed using FTIR Spectroscopy.

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