

Original Research Article

STRUCTURAL MODIFICATON OF CELLULOSIC FABRIC VIA ESTERIFICATION USING *BALANITES AEGYPTIACA* SEED OIL.

Abstract

Cellulose fabrics were esterified by using varying volume of *Balanites aegyptiaca* seed oil. X-ray diffraction analysis was carried on the esterified fabrics and unesterified fabric. The crystallographs of all esterified fabrics gave almost the same profile different from that of control fabric. The control fabric gave a sharp single peak at 24.033° diffractometer angle. Esterified fabrics gave a slightly broad splitted peaks at lower diffractometer angles which ranged from $20.080 - 22.690^\circ$, suggesting that there was structural modification of cellulose. The inter-atomic distance (d-spacing) for control fabric was $3.7027 \text{ \AA}$. There was increase in d-spacing which ranged from $3.9192 - 4.4216 \text{ \AA}$ for esterified fabric. The peak width increased from 1.5° (control) to range of $1.6 - 2.8^\circ$ (esterified) fabrics. The peaks intensity increased from 5489 (control) to highest value (7798) for 30 cm^3 of oil esterified fabric. The crystallite size reduced from 9.9 nm (control) to a maximum value (9.2 nm) for 40 cm^3 and to minimum value (5.3 nm) for 10 cm^3 oil esterified fabrics. The percentage crystallinity reduced from 65% (control) to a range of $62 - 63\%$ for esterified fabrics. From the results obtained, it can be concluded that reduction in crystallite size, increase in d-spacing, intensity and peak width were due to the presence of a bulky ester group in the cellulose chain; this may also have led to the observed decrease in percentage crystallinity of the esterified fabrics. This structural modification is expected to have direct consequences on the physical and mechanical properties as well as the dyeing properties of the esterified fabrics.

Keywords: Modification, Cellulosic fabric, esterification, *Balanites aegyptiaca*, x-ray diffraction.

Introduction

In the past, Urea and melamine formaldehyde resins have been applied to improve physical mechanical and dye fastness properties of cellulosic fabric [1, 2, 3, 4].

However, these resins are not entirely satisfactory for easy-care finishes because aside from the very high cost of melamine and urea; formaldehyde is very toxic to man and the environment. The resins are not sufficiently resistant to washing and contain secondary amino groups which react with hypochlorite to form chloramines [5]. The chloramines decompose on storage with the accompanying appearance of a yellow discolouration and under the influence of ironing they give rise to hydrochloric acid which causes loss of strength to the fabric [5, 6].

Globally, increasing attention is being paid to green chemistry due to environmental degradation and economic challenges. Therefore, it has become imperative to source locally

40 available materials that are biodegradable and cheaper that could be used for easy-care finish
41 in the textile industry.

42 *Balanites aegyptiaca* is an oil seed yielding plant belonging to the family
43 zygophyllaceae. It is called desert date in English and is one of the most common, but
44 neglected wild plant species of dry land areas of Africa and South Asia [7]. It is mainly
45 cultivated for fibre and oil although many parts of the plant are used as famine foods in
46 Africa and some developing countries. It is also used for herbal medicine [8]. The oil is
47 known for its good physical and chemical properties [9].

48 This paper presents the results of powder x-ray diffraction obtained from reaction between
49 OH of cellulose and the –COO- of triglyceride in the oil via esterification. A cellulose
50 monoester was obtained with modified structural properties.

51 **Materials and Methods**

52 *Balanites aegyptiaca* fruits were obtained in Bauchi metropolis. Its identification was
53 established by Alexander Sindama of biological Sciences department, Federal University,
54 Wukari, Taraba State. A plain woven loom state 100% cotton fabric of commercial quality.
55 Chemicals of commercial grade, oven, soxhlet apparatus, weighing balance, beakers, reflux
56 condenser, Bruker D8 Advance x-ray Machine and accessories.

57 **Fabric Identification and Purification**

58 Standard methods according to ASTM [10] were employed for fabric analysis.
59 Threads were subjected to solubility and flame test to ascertain its origin. The fabric was
60 scoured, bleached and mercerized using 2% sodium hydroxide, 5% hydrogen peroxide and
61 20% sodium hydroxide solutions respectively.

62 **Extraction of Oil**

63 Extraction and characterization of the oil was based on the standard method by
64 Pearson [11]. The fruits were decoated, soaked in water for about 6 hours to dissolve the
65 sticky pulp then sun dried. The seeds were removed from the hard shells through cracking,
66 and kernels obtained were air dried then ground to fine powder.

67 The powder (50.0 g) was placed in a pre-weighed thimble and then placed in the barrel of the
68 soxhlet apparatus. 200 ml of n-hexane was poured into the flask and the apparatus set for
69 extraction and allowed to run for 6 hours. Percentage yield was calculated using equation 1;

$$70 \text{ Yield \%} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad \dots\dots\dots (1)$$

71 Esterification of fabric using 100 ml of methanol mixed with 10, 20, 30, 40, 50 and 60 ml of
72 the oil respectively. 0.5 ml of concentrated H₂SO₄ was added as catalyst and refluxed for 1

hour at 60°C. The mercerized samples were weighed and then immersed into each flask and refluxed for 3 hours at 60°C with flask and refluxed for 3 hours at 60°C with occasional shaking. The fabrics were removed and neutralized in 2% solution of Na₂CO₃ in order to destroy any acid residue that remained in the samples, while the residual oil was removed by immersing the fabrics in a very dilute detergent solution. The samples were rinsed in distilled water and dried in the oven at 60°C for 20 minutes then weighed again.

X-ray Diffraction Analysis

The control fabric measuring 1 cm x 0.5 cm was ground into fine powder. The ground sample was placed in a glass tube and this was mounted on the Bruker D8 Advance x-ray machine at the University of Kwazulu Natal, West Ville Campus 4000, Durban South Africa. The sample was positioned in the centre of the copper source monochromatic radiation ($\lambda = 1.5418 \text{ \AA}$). The diffraction pattern was generated by a radiation counter and was plotted automatically. The procedure was repeated for other fabrics esterified under varying volume of the oil. The inter-atomic distance (d-spacing) was calculated according to Bragg's law in equation 2

$$n\lambda = 2d \sin \theta \quad \dots\dots\dots (2)$$

The crystallite size was obtained from the scherrer equation with the method based on the width of the diffraction pattern.

$$D = \frac{k\lambda}{B \cos \theta} \quad \dots\dots\dots (3)$$

Where D is the size of crystallite (nm), k is the scherrer constant (0.94), λ is the x-ray wavelength, B is the full-width at half-maximum of the peaks measured in 2 θ angle [12].

The percentage crystallinity was calculated according to equation 4.

$$\text{Crystallinity (\%)} = \frac{I_c}{\sum I_a + I_c} \times 100 \quad \dots\dots\dots (4)$$

Where I_c is intensity of crystalline peak, I_a is intensity of amorphous peak.

Results and Discussion

Table 1: Effect of esterification and volumes of oils on weight of fabrics

Volume of oil (cm ³)	Weight of fabric before esterification (g)	Weight of fabric after esterification (g)	% increase in weight of fabric
10	1.0375	1.0661	2.76
20	0.9907	1.0230	3.26
30	0.9768	1.0197	4.39
40	1.0432	1.0833	3.84
50	0.9861	1.0072	2.14

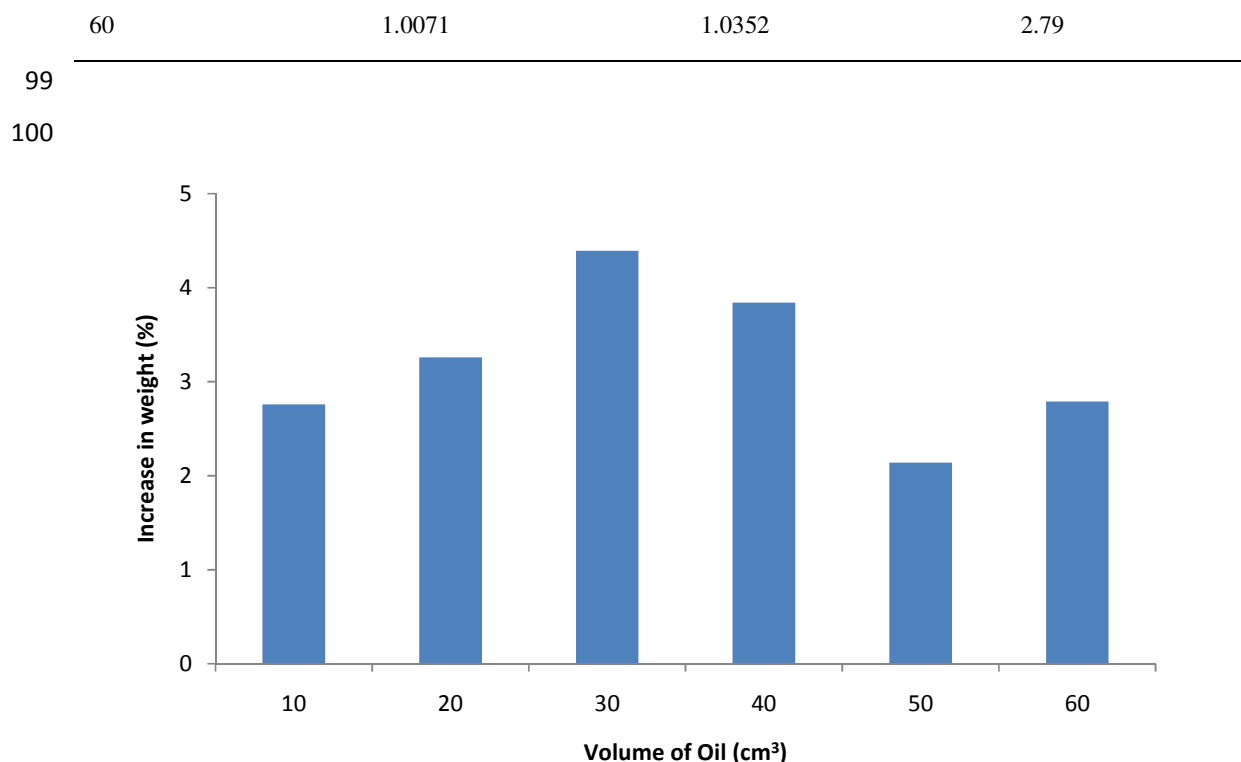


Figure 1: Effect of Esterification with varying Volume of Oil on Fabric Weight.

The result of esterification and varying volume of oil on fabrics' weight and percentage increase in weight are outlined in Table 1 and Figure 1 respectively.

The increase in weight after esterification is indication that a chemical bonding was formed between the oil and cellulose. The highest weight (4.39%) was obtained with 30 cm³ of Oil indicating that this fabric was densest.

Percentage Yield

The seeds of *Balanites aegyptiaca* contain a high amount of oil (40%) which could be highly economical in chemical industries. The oil is light yellow in colour, odourless, tasteless and liquid at room temperature. Therefore, this plant could be fully harnessed for oil production.

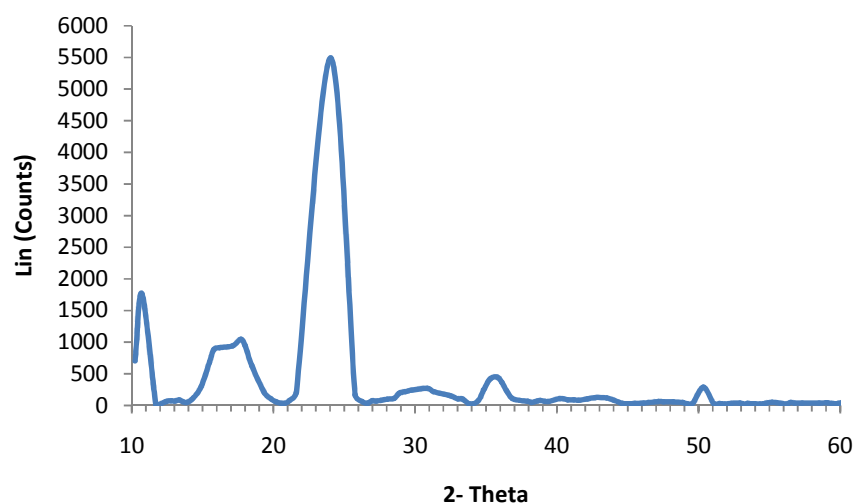


Figure 2: X-ray Crystallograph of Unesterified Fabric (Control)

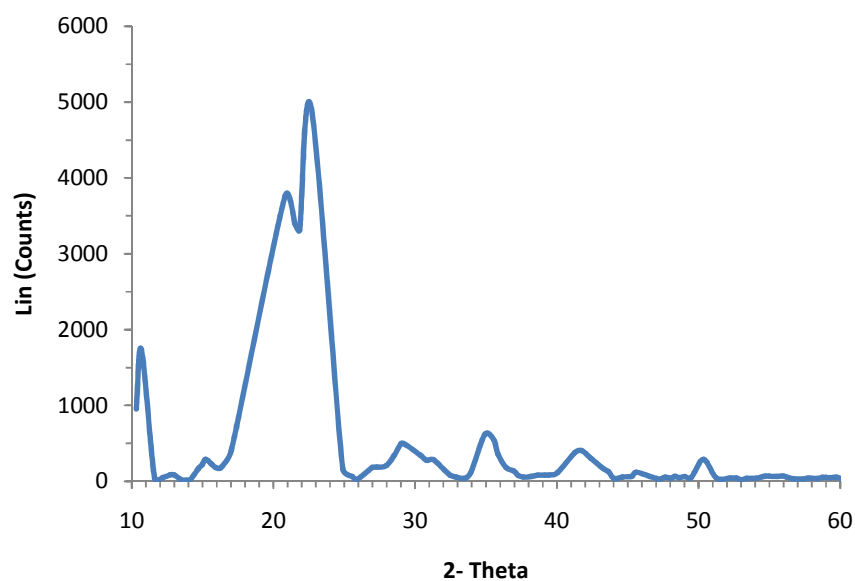


Figure 3: X-ray Crystallograph of Fabric Esterified with 10ml *Balanites aegyptiaca* oil

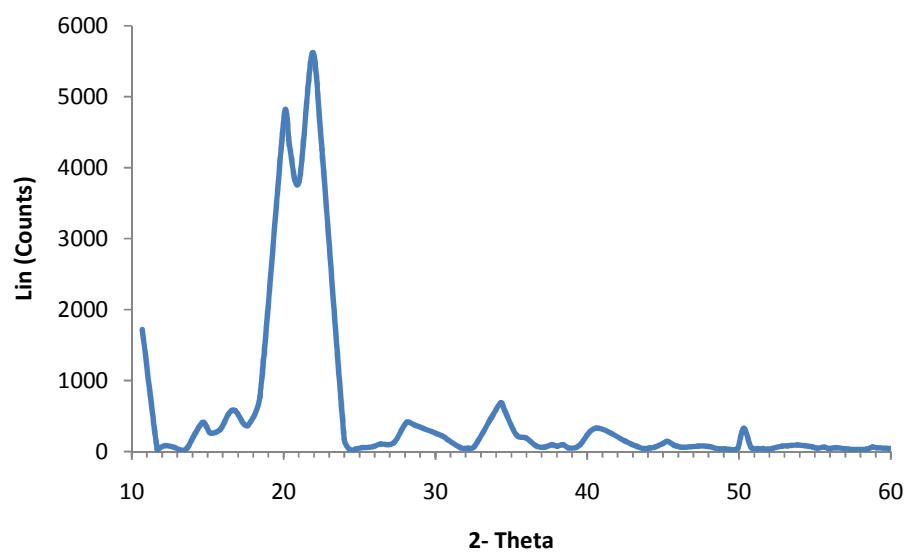


Figure 4: X-ray Crystallograph of Fabric Esterified with 20ml *Balanites aegyptiaca* oil

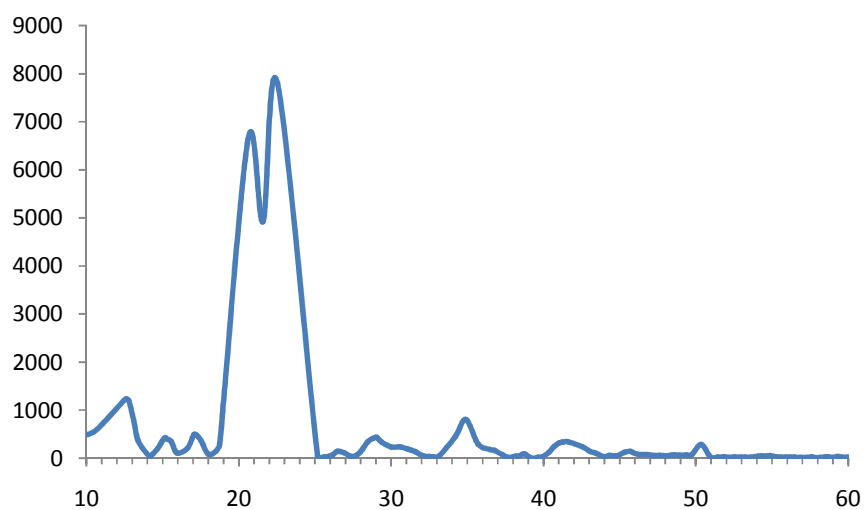


Figure 5: X-ray Crystallograph of Fabric esterified with 30ml *Balanites aegyptiaca* oil

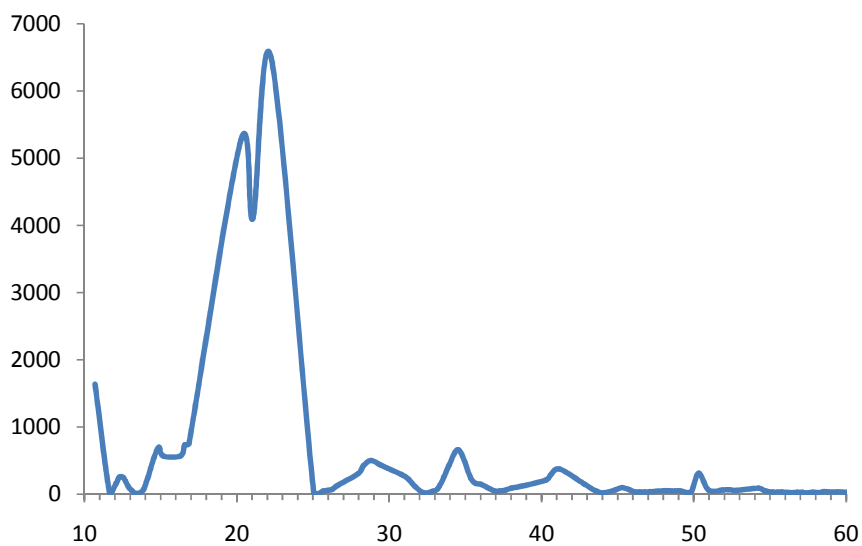


Figure 6: X-ray Crystallograph of Fabric Esterified with 40ml *Balanites aegyptiaca* oil

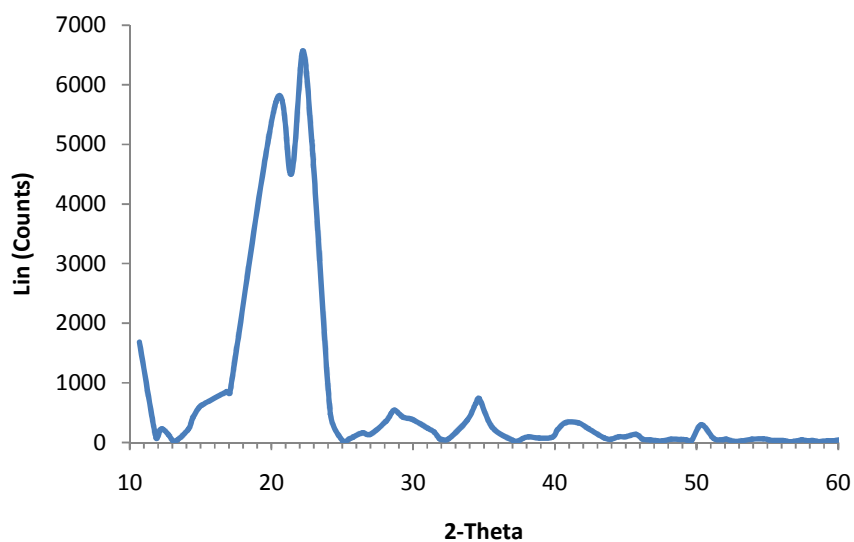


Figure 7: X-ray Crystallograph of Fabric Esterified with 50ml *Balanites aegyptiaca* oil

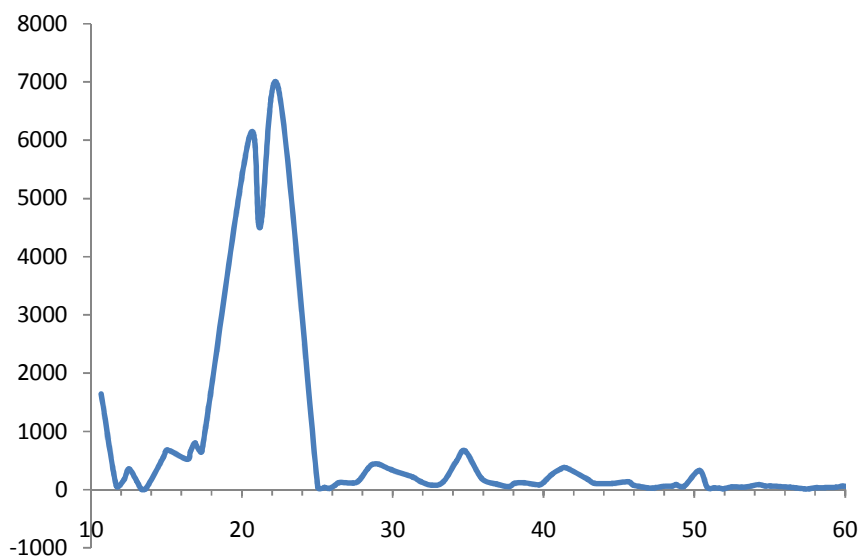


Figure 8: X-ray Crystallograph of Fabric Esterified with 60ml *Balanites aegyptiaca* oil

Table 2: X-ray Diffraction Analysis of Fabric Esterified with Varying Volume of *Balanites aegyptiaca* oil

Properties	10cm ³		20cm ³		30cm ³		40cm ³		50cm ³		60cm ³		Control
Functional groups	- O -	C = O	- O -	C = O	- O -	C = O	- O -	C = O	- O -	C = O	- O -	C = O	O - H
2-theta Angle (°)	20.827	22.690	20.080	21.912	20.642	22.537	20.261	22.272	20.326	22.215	20.471	22.423	24.033
d-spacing (Å)	4.2650	3.9192	4.4216	4.0563	4.3031	3.9452	4.3826	3.9912	4.3689	4.0016	4.3382	3.9645	3.7027
Intensity	3761	4913	4773	5617	6651	7798	5265	6485	5703	6563	6038	6886	5489
Count (%)	76.5	100.00	85.0	100.0	85.3	100.0	81.2	100.0	86.9	100.0	87.7	100.0	100.0
Peak Width (°)	2.0	2.8	1.9	2.6	2.1	2.4	1.6	2.1	2.1	2.2	2.0	2.2	1.5
Crystallite Size (nm)	7.4	5.3	7.8	5.7	7.0	6.2	9.2	7.0	7.0	6.7	7.4	6.7	9.9

With respect to Table 2 and figures 2 – 8, x-ray diffraction analysis of control and fabrics esterified with varying volume of *Balanites aegyptiaca* oil is presented.

Effect of esterification on the diffractometer angle (2-theta angle)

There was a shift of diffractometer angle from 24.033° (control fabric) at 100% count to the lowest (20.080°) at 85% count for –O- atom after esterification with 20 cm³ of oil. The highest values of diffractometer angle (20.827°) at 76.5% count and (22.690°) at 100% count were obtained at 10 cm³ optimum volume of oil for –O- and C=O respectively. These shifts in diffractometer angles may be attributed to the broadening of the diffraction peaks [13] and it is indication that certainly modification has taken place in the structure of the cellulose as a result of chemical reaction with the oil.

Effect of esterification on inter-atomic distance (d-spacing)

The result showed that d-spacing for the control fabric was 3.7027 Å. However, the effect of esterification led to an increase in values of d-spacing as the volume of oil increased. The values ranged from 4.2650 – 4.4216 Å at 76.5% and 85.0% counts respectively for –O– and 3.9192 – 4.0563 Å at 100% count for C=O. the maximum values (4.4216 and 4.0563 Å) for –O– and C=O respectively were obtained at 20 cm³ optimum volume of oil. Increase in d-spacing for esterified samples suggests that there was modification in the structure of cellulose which may consequently lead to a decrease in crystallinity of the esterified fabrics [14].

Effect of Esterification on Peaks Intensity

The control fabric recorded intensity of 5489 at 100% count. After esterification there was increase in intensity as the volume of oil increased except for fabric treated with 10 cm³ of oil. The increased values ranged from 5617 – 7798 for C=O. This may be attributed to the ester linkage in the cellulose chain which has given rise to higher molecular mass [13]. The maximum values (6651 and 7798) for –O– and C=O at 85.3% and 100% count respectively were obtained with 30 cm³ optimum volume of oil.

Effects of Esterification on Peaks Width

The peak widths were obtained from the crystallographs shown in figures 2-8 by measuring the full-width at half maximum in 2-theta angle for each peak. The smallest value (1.5°) was obtained for control fabric. This is indication that this fabric might be more crystalline than the esterified fabrics. This is because there was increase in peak widths due to esterification which ranged from 1.6 to 2.8° as the volume of oil increased. The widest peak (2.8°) and narrowest peak (1.6°) for esterified fabrics were observed for C=O and –O– from using 10 cm³ and 40 cm³ of oil respectively with 10 cm³ being the optimum volume of oil. The observed increase in peak width may be due to the presence of ester bond, it may also be as a result of increase in d-spacing and diffractometer angle [15]. This may consequently lead to decrease in crystallinity of the esterified fabrics.

Effect of Esterification on Crystallite Size

The crystallite size of unesterified fabric (9.9 nm) was obtained in this research. Clearly, there was a decrease in crystallite size after esterification which ranged from 9.2 nm for –O– at 40 cm³ is the optimum volume of oil. The observed decrease in crystallite size may be attribute to the presence of short chain ester group that may result to loss in alignment of the polymer chains. This molecular irregularity therefore, is an indication that crystallinity was reduced. (Billmeyer, 1984).

Effect of Esterification on Percentage Crystallinity

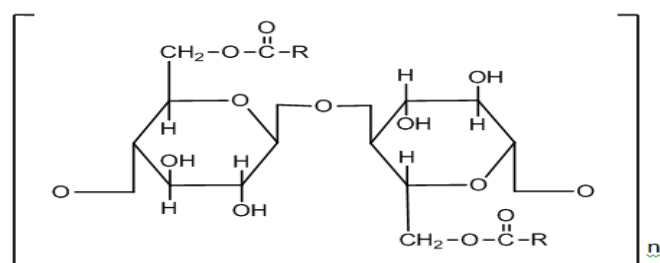
Crystallinity determines the strength [3] and other very important mechanical properties such as the ability to recover from deformation [16], it also determines the end use of any product.

Table 3: Percentage Crystallinity

Volume of Oil (cm ³)	Balanites oil esterified fabric crystallinity %
0	65
10	62
20	63
30	63
40	63
50	62
60	62

0 cm³ is for unesterified sample

With respect to Table 3, the percentage crystallinity of the control cellulose was 65%. However, after esterification there was decrease in percentage crystallinity which ranged from 62 - 63% with 20 cm³ optimum volume of oil. This decrease may be attributed to factors like increase in d-spacing, decrease in crystallite size, broadening of peak width [13, 15, 17]. The presence of bulky ester side groups and loss of alignment [18] may also be responsible for the decrease in crystallinity. The extent of esterification according to the x-ray crystallographs in Figures 2 – 8 showed that a cellulose mono-ester was produced and the bulky ester groups is attached to the primary carbon (sixth position) atom on the cellulose chain as shown in scheme below. The reduction in crystallinity also means that the fabric has become more porous which could be an advantage for easy and good dye absorption.



Where R is alkyl group in the oil.

Scheme 1: Cellulose Mono-ester

Conclusion

In this research, cellulose fabric was esterified by varying the volume of *Balanites aegyptiaca* seed oil. X-ray diffraction of the samples proved that there was structural modification leading to the formation of cellulose monoester. However, there was a slight decrease in percentage crystallinity, increase in d-spacing, peak width, fabric weight and reduction in crystallite size. Based on these findings it is recommended that oils from *Balanites aegyptiaca* which is cheap, non-toxic, biodegradable and environmentally friendly be used to replace amino resins for improvement of easy-care finish in the textile industry. The cellulose ester produced will be suitable for shirt making and drape.

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