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Dynamic elastic modulus of modified cotton fibres

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The dynamic elastic modulus of three cultivated varieties of *G. hirsutum* Linn, namely Samaru 26J Nigeria, Samaru 26J Glasgow and an unspecified American upland has been studied at different stages of fibre maturity using visco-elastomer. The dynamic modulus is found to be strongly dependent on both the maturity and the optical orientation angle. To eliminate the effect of convolutions on both the dynamic modulus and the helix angle, fibres are treated in liquid ammonia to get Cellulose III lattice structure and revert back to Cellulose I lattice structure using distilled water. Both the X- ray diffractograms and the scanning electron micrographs also confirm this finding. Maturity ratio is shown to have a very strong effect on the dynamic elastic modulus and not the age of the fibre. Fibres of similar maturity ratio show similar dynamic modulus, irrespective of the environmental conditions. Cellulose III and Cellulose I regenerated fibres have about the same dynamic modulus values. This shows that treatment does produce profound changes in the gross structure and calls for a fresh look at the swelling mechanism in both structures, a possible disruption of the H- bonding systems of cellulose by both treatments.

Keywords: Birefringence, Cellulose III, Dynamic elastic modulus, *G. hirsutum* Linn, Helical angle, Lattice structures, Regenerated cellulose I

Dynamic elastic modulus is a useful measure of resistance to small deformations and orientation of the molecular chains in polymeric materials. Unlike static modulus, dynamic elastic modulus is measured with stress and strain varying sinusoidally with time. Importantly, it characterizes two features in polymeric materials, namely elastic response and internal friction (dissipation factor or loss tangent), both of which are important properties in determining the performance of fibres[1].

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Study on the dynamic elastic modulus of cotton has received little attention over the years despite its versatility in the field of fibre blends and composites. This may be due to the presence of convolutions and helical arrangement of the fibrils. If these convolutions can be safely removed by liquid ammonia treatment, the true mechanical properties of these fibres can be elucidated.

In cellulosic fibres, the organization of plant cell wall determines the mechanical properties of the cell[2-4]. The fibrils form a helical arrangement in these fibres which persists even when the fibres are mercerized or treated in liquid ammonia, both of which are important technological processes [5,6]. The effect of liquid ammonia on the mechanical properties has received very little attention over the years as compared to caustic soda or ethylamine treatments [7-11] The helical orientation of these fibres without convolutions can be measured by optical means, which measures the overall orientation of the crystalline and non-crystalline regions[2]. The values obtained can be compared with the tensional modulus at different stages of cell wall development.

Treatment of cotton fibres with liquid ammonia under controlled condition ensures complete conversion from cellulose I(native) to cellulose III conformation. This treatment is known to reduce sample variations between variety and within variety [7-9]. This process is also known to be less drastic than treatment with caustic soda [10,11]. Cellulose I can be regenerated in distilled water under certain conditions without any recrystallization occurring and free of convolutions [10-14]. Cellulose III and cellulose I regenerated fibres would then be compared with the theoretical model that regards fibre as a solid, cylindrical body [15,16]. The aim of this work is to determine the dynamic elastic modulus of these fibres free of convolutions and to ascertain the effects of both maturity and orientation on the elastic modulus. These are useful properties to know, especially now, that the cotton fibres are used excessively in fibre blends[3] and in composites.

Experimental

Three cultivated varieties of *G. hirsutum* Linn cotton plant, viz Samaru 26J Nigeria, & Samaru 26J

Glasgow, and an American upland were grown in Glasgow in a greenhouse. Nigerian samara 26J was also field grown in Nigeria. Cotton bolls were harvested at different stages of maturity. That is, a ten days interval from 20 days after flowering until ball opening. An open ball of *G. barbadense* Linn variety (Ashmouni) was also used in this investigation for comparison. Ramie fibres were also investigated being the most oriented cellulosic fibres[2-4]. Detail description of the set up and the procedure of liquid ammonia treatment of fibres are reported elsewhere [17].

Measurement of Refractive Indices and Helix Angle Calculation

To determine the refractive indices of fibres by the 'Becke-line' technique, series of colorless immersion liquids were prepared. The refractive indices increase steadily in steps of 0.005, as calculated by using the following formula:

$$n = \frac{n1V1+n2V2}{V1+V2}$$

where n_1 and n_2 are the refractive indices; and V_1 and V_2, the volume of liquids 1 and 2 respectively. The liquids used in this investigation are paraffin (refractive index 1.481 at 20°C) and α-monobromonaphalene (refractive index 1.658 at 20°C). The mixture has high temperature coefficient of about 0.0004 per °C (refs 2-4). The experiments were performed in a conditioned environment. The refractive indices of series of liquid mixture were measured using a calibrated Abbe refractometer and carefully labelled.

Two liquids from the series, whose refractive indices were roughly those of the fibre parallel (n_{11}) and perpendicular ($n_\perp$) to the fibre axis respectively, were determined by immersing single fibres in a liquid of known refractive index and observed in a plane polarized light. If the refractive index of the immersion liquid equals to that of the fibre, the edges of the fibre will disappear. If the refractive index of the immersion liquid differs from that being measured, a bright line, called 'Becke line' appears at the two edges of the fibre. Defocusing the fibre image by raising the microscope objective lens slightly will cause the 'Becke line' to move into the medium of higher refractive index. Defocusing by lowering the object slightly will produce the opposite result. Liquids of different refractive indices are tried, in turn, on fresh fibres until we get a liquid that matches the refractive index of the fibre that is being determined.

The mean refractive indices from the group of 20 fibres each of n_{11} and $n_\perp$ per sample was used to calculate the helix angle θ, using the following relationship:[2]

$$cos^2\theta = \frac{(n_\parallel - n_\perp)_{65}}{(n_1 - n_2)_{65}} \times \frac{(n_1)^2}{(n_\parallel)^2} \times \frac{(n_\parallel + n_\perp)_{65}}{(n_1 + n_2)_{65}}$$

where ($n_1 - n_2$) is the birefringence of an ideally oriented fibre. Ramie fibres were used (its orientation is almost ideal and crystallinity is almost 100% as indicated by x-ray diffraction) [2]

Cellulose Chain Transformations

Using Scanning Electron Microscope (SEM)

SEM was used to visualize the penetration and diffusion of the swelling agent and to see whether the micrographs will reveal the absence of convolutions at least in the matured fibres. This was done by observing fibres both longitudinally and when sectioned transversely.

Using X-ray Diffraction Technique

X-ray diffraction was used to ascertain the extent of conversion to cellulose III during the liquid ammonia treatment and in the restoration of cellulose I lattice on treatment with distilled water. Sample exposure time varied from 2h to 4h. Immature or less well oriented fibres took longer time to produce diffraction spots of measurable density. The peaks from the three principal equatorial reflections (101, 10$\bar{1}$ and 002) were obtained.

Measurement of Dynamic Elastic Modulus

A direct reading dynamic visco-elastometer called "Rheovibron DDV II C (Toyo measuring Instrument, Tokyo, Japan) was used. This versatile instrument is not suitable for fibres with irregular cross-section like cotton fibres. For this reason, only fibres that were free of convolutions after the liquid ammonia treatment, were used. The minimum requirement of specimen cross- sectional area from the vibron instrument is 10^{-5} cm^2. The average cross-section for a fibre is 1.85×10^{-6} cm^2. To achieve this requirement, 10 specimens per sample, each containing 10 examined fibres, were prepared.

All the specimen were normally conditioned and investigated on the instrument in a conditioned environment. The instrument setting of tan δ range/amplitude factor of 50/10 and a frequency of vibration of 110Hz was used. The static strain just sufficient to obtain consistent reading on the instrument was used. The instrument gave a direct

reading of tan δ and dynamic force (D). These were used along with the known cross-sectional area (S, cm^2) and length (L, cm) of the fibre specimen to calculate the dynamic elastic modulus (Y), using the following equations:

$$|E| = \frac{2}{ADK} \cdot \frac{L}{S} \times 10^8 \text{ Pa}$$

where

$|E|$ = Complex dynamic modulus
A = Amplitude factor = 10
K = Instrument constant = 16.0×10^5 (cm/N)
Y = $|E| \tan \delta$

Results and Discussion

The scanning electron micrographs reveal the absence of convolutions in mature fibres after the liquid ammonia treatment to cellulose III lattice structure and subsequent regeneration to cellulose I lattice structure [Figs 1(a)-(c)]. Figures 1(d)-(f) show the micrographs of the cross-section of native cotton, cellulose III and regenerated cellulose I respectively. A magnification of ×640 was used to observe clearly the level of deconvolution. Figure 2(a) shows the x-ray diffractograms of native cotton cellulose (A), after 2 h of treatment (B) and after 4 h of treatment (C). Figure 2(b) shows the diffractograms of cellulose III cotton (A), after 15 h in boiling water (B) and after 24 h in boiling water(C). Only partial reversion (about 40%) was observed after 15 h. Both cotton and Ramie are found to behave similarly in boiling water (C). Mittal *et al.*[12] observed similar peaks for cellulose III and cellulose I lattice structures.

Birefringence and Helical Angles of Cotton Fibres

Cellulose I (Untreated Fibres)

Table 1 shows the mean values of n_{11}, $n_{\perp}$, birefringence (n_{11} - $n_{\perp}$), and helical angles of three different cottons harvested at various stages of maturity. It is evident from the graph (Fig. 3) that the birefringence values of the fibres show a gradual increase with maturity ratio. Between the maturity ratios 0.2 and 0.4, the birefringence increase is found to be fairly rapid; this corresponds with the period of elongation of fibres. Between 0.4 and 0.7 maturity ratio, the increase is found to be gradual. And from 0.7 onwards, the birefringence went up again. This probably means that cellulose deposition and chain alignment do not take place simultaneously. Fibres as early as 20 days after flowering are found to be birefringent. The helical angles show a corresponding decrease from 63° for 20 days old cotton to 35° for open Samaru 26J cotton grown in Nigeria. The Samaru

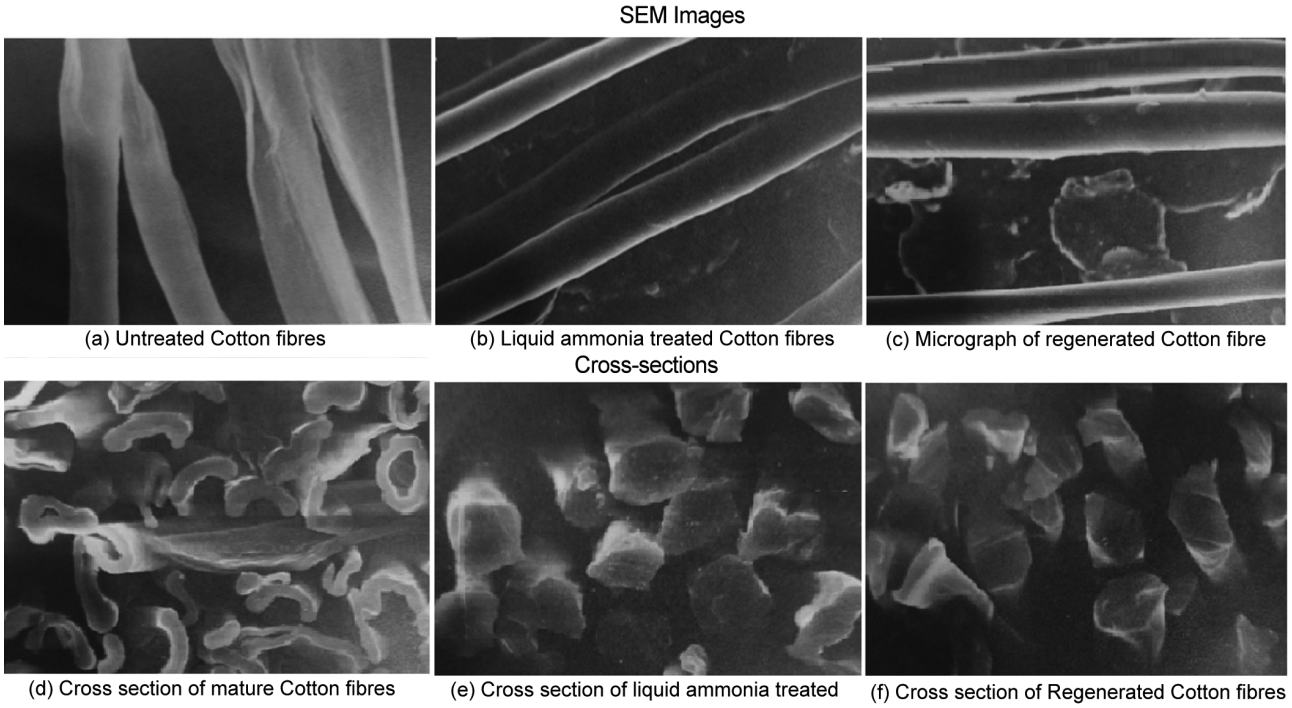

Fig. 1 — Scanning electron micrographs (×640) of (a) untreated, (b) liquid ammonia treated and (c) regenerated; and cross-sections of the (d) untreated mature, (e) liquid ammonia treated and (f) regenerated cellulose 1 fibres respectively.

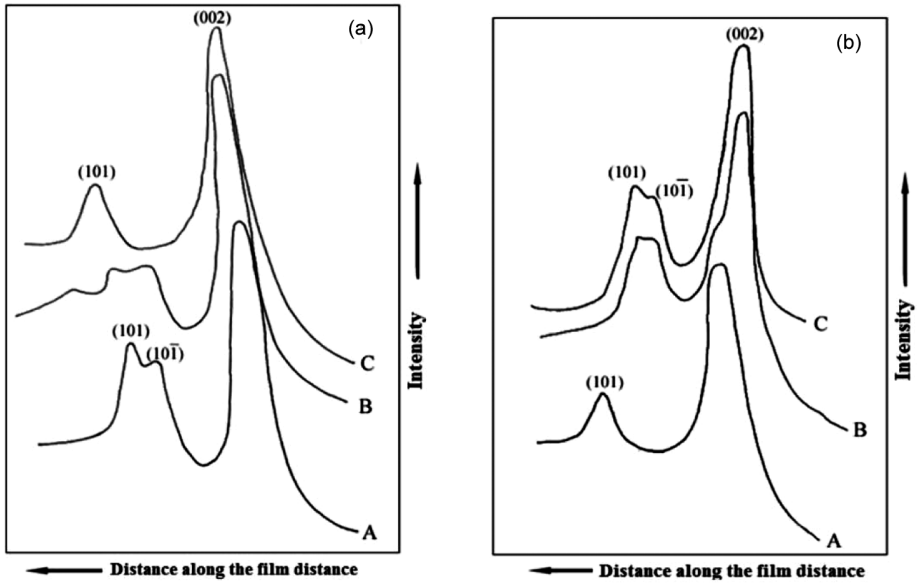

Fig. 2 — X-ray diffractograms of (a) cellulose I [(A) untreated, (B) after 2h of treatment, and (C) after 4h of treatment; and (b) cellulose III [(A) untreated, (B) after 15 h of treatment and (C) after 24 h of treatment

Table 1 — Refractive indices, birefringence and helix angles of fibres at different stages of maturity (untreated fibres)

Fibre age, days	Maturity ratio	n_{11}	$n_{\perp}$	Birefringence	Helix angle (α^o), deg
		Samaru 26J, Nigeria			
20	0.32	1.5520	1.5395	0.0125	63
30	0.60	1.5540	1.5340	0.0200	49
45	0.76	1.5700	1.5340	0.0350	42
60 (open)	0.80	1.5740	1.5320	0.0420	35
Ashmouni	0.93	1.5760	1.5300	0.0460	32
		Samaru 26J, Glasgow			
30	0.35	1.5540	1.5283	0.0260	50
40	0.53	1.5608	1.5330	0.0278	49
50	0.76	1.5650	1.5330	0.0320	45
60	0.79	1.5640	1.5310	0.0330	43
70	0.83	1.5660	1.5310	0.0350	42
Open	0.88	1.5690	1.5300	0.0390	38
		American Upland, Botanic Garden			
30	0.30	1.5507	1.5270	0.0237	52
40	0.55	1.5530	1.5285	0.0245	51
50	0.71	1.5640	1.5305	0.0335	44
78	0.79	1.5640	1.5300	0.0340	42
Open	0.83	1.5690	1.5310	0.0380	39

26J grown in Glasgow, on the other hand, shows a decrease from 50° for 30 days cotton to 38° for an open ball. This difference of about 20% is attributed to the effect of environment; it does modify orientation [4,5].

The decrease in the measured helical angle with increase in maturity shows that the Becke-line (immersion) method may not be limited to measurement of the fibre surface as previously suggested[5]. The helix angle of 63°, recorded for the 20 days old fibre suggests that they are mainly made up of primary wall.

Cellulose III Fibres (Liquid Ammonia Treated)

Table 2 shows the mean values of the fibre length (cm), cross-sectional area ($\times 10^{-5}$ cm^2), dynamic elastic modulus (Y), helix angle (θ^o) and the respective fibre age in days. The values of the cross-sectional area is calculated using the mean width (d) of each specimen from the formula ($\frac{\pi d^2}{4}$). The values of the dynamic modulus are found to increase with increase in maturity. This seems to agree quite well with the helix angle values, a measure of the general arrangement of

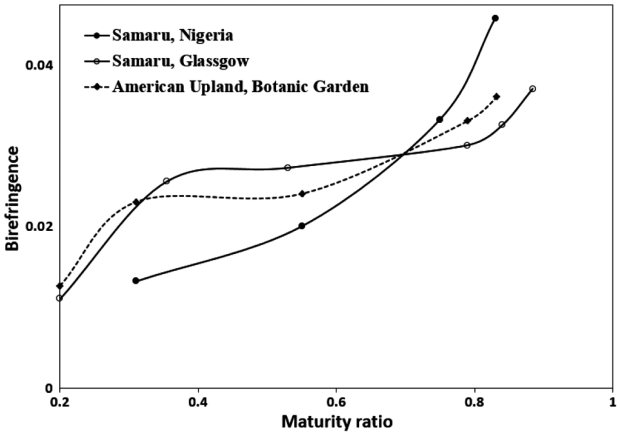

Fig. 3 — Relation between birefringence and maturity ratio

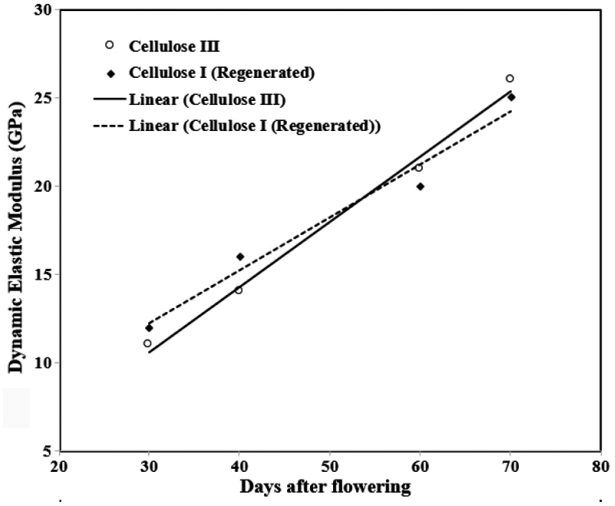

Fig. 4 — Relationship between dynamic elastic modulus and maturity of cellulose III and cellulose I(regenerated)

Table 2 —Cellulose III fibres at different stages of maturity

Fibre age days	Specimen length cm	Cross-sectional area ($\times 10^{-5}$) cm^2	Dynamic modulus calculated (Y) GPA	Helix angle (α^o) deg
Samaru 26J, Nigeria				
30	1.064	2.23	19 ± 1.05	40
45	1.103	2.21	21 ± 1.09	37
Open	1.172	2.14	31 ± 0.95	32
Ashmouni	1.201	2.14	32 ± 0.85	28
Cellulose III stretched	1.102	1.94	36 ± 0.92	16
Ramie III	1.102	4.50	56 ± 0.08	7
Samaru 26J, Glasgow				
30	1.035	2.00	11 ± 1.13	55
40	1.203	1.98	14 ± 1.15	49
60	1.200	2.03	21 ± 0.97	42
Open	1.206	1.96	26 ± 0.70	38

Table 3 — Regenerated Cellulose I at different stages of maturity

Fibre age days	Specimen length cm	Cross-sectional area ($\times 10^{-5}$) cm^2	Dynamic modulus calculated (Y) GPA	Helix angle (α^o) deg
Samaru 26J, Nigeria				
30	1.108	2.18	15 ± 1.05	51
45	1.093	2.10	17 ± 1.08	40
0pen	1.107	2.02	26 ± 0.96	36
Ashmouni	1.171	2.06	28 ± 0.98	33
Ramie	1.146	4.09	46 ± 0.86	7
Samaru 26J, Glasgow				
30	1.042	2.00	12 ± 1.06	49
40	1.261	1. 97	16 ± 1.03	44
60	1.271	2.01	20 ± 0.95	41
0pen	1.208	1.98	25 ± 0.93	38

chains in the fibre. The helix angles are found to decrease with maturity. It is interesting to note that the helix angle of cellulose III (Ashmouni) decreases from 27.7° for unstretched fibres to 15.7° when stretched 8% during treatment. Similar observations have also been reported [8&9].

Woo and Postle[1] also found a profound increase in dynamic modulus with maturity using pulse propagation method. It may be observed that the values obtained for Nigerian Samaru fibres are generally higher than those obtained for Samaru Glasgow of similar age. However, fibres of similar maturity ratio show similar dynamic modulus. Therefore, differences in the environmental conditions show differences in growth rates but maturity ratio shows strong effect on the dynamic elastic modulus (Fig. 4). Expectedly, mature fibres generally show higher modulus values than the immature fibres for the same reason. It is interesting, however, to note that immature fibres show reasonably high modulus values. It is well known that fibres build up stress on drying and the stress relaxes on treatment. Immature fibres show greater response to swelling due to their having a smaller amount of material in the cell wall and a large lumen. For this reason, the fibrils have more space to move to relieve these stresses and, therefore, more organization of cellulose chains may be expected with a general reduction in the major and minor weak areas. This may be responsible for the general high level of the modulus of these fibres. It may also be recalled that high birefringence values are recorded for these young fibres.

Regenerated Cellulose I Fibres (Boiled in Water for 24 h)

Table 3 shows the mean values of the fibre length (cm), cross-sectional area ($\times 10^{-5}$ cm^2),

dynamic elastic modulus (Y), helix angle (θ^{o}) and the respective fibre age in days. The dynamic modulus values obtained for cellulose III fibres are slightly higher than those obtained for cellulose I(regenerated) fibres (Fig. 4). But the general evidence is inconclusive and we take it that Cellulose III fibres and the regenerated fibres have about the same dynamic modulus values. Similar observation has been made earlier on the rigidity modulus[18]. This shows that the treatment does produce profound changes in the gross structure, and since wall layers differ in optical properties they could also differ in the swelling behavior. This finding calls for a fresh look at the swelling mechanism in both structures, the possible disruption of the H- bonding systems of Cellulose by both treatments.

It is inferred that the cotton fibre maturity depends on the environmental conditions. But it is the maturity ratio and not the fibre age that controls the mechanical properties. The scanning electron micrographs reveal the absence of convolutions and the central lumen in mature fibres. X-ray diffractograms confirm Cellulose III conversion and the reversion to Cellulose I lattices. Dynamic elastic modulus is dependent on both the fibre maturity and the orientation angle. It increases with decrease in the helix angle and increase in maturity. Cellulose III and Cellulose I regenerated from it show the same dynamic modulus values. This calls for a fresh look at the swelling mechanisms in both structures and the H-bonding linkages.

References

1 Woo J L & Postle R, *Text Res J*, 48(2) (1978)68.

2 Meredith R, *J Text Inst Trans*, 37(9) (1946)T205.

3 Hearle J W S, *Physical Structure and Properties of Cotton Fibres* (Cambridge Woodhead Publishing Ltd), 2007, 35.

4 Preston R D, *Physical Biology of Plant Cell Wall* (Chapman and Hall), 1974.

5 Kljun A, El-Dessouky H M, Benians, T A S, Goubet F, Meulewaeter F, Knox J P & Blackburn R S, *Eur Polym J*, 51(2014)57.

6 Betrabet S M, Pillay K P R & Iyengar R L N, *Text Res J*, 33(9) (1963)720.

7 Lewin M & Roldan L, *J Polym Sci*, 36(1) (1971)213.

8 Rousselle MA, Nelson ML, Hassenboehler CB & Legendre DC, *Text Res J*, 46(4) (1976)304.

9 Hebert J J & Boylston E K, *Text Res J*, 54(1) (1984)23.

10 Sarko A, Southwick J & Hayashi J, *Macromolecules*, 9(5) (1976)857.

11 Hebert J J, Muller L L, Schmidt R J & Rollins M L, *J Appl Polym Sci*, 17(2) (1973)585.

12 Mittal A, Katahira R, Himmel M E & Johson D K, *Biotechnol Biofuels* , 4 (2011) 41.

13 Dornyi B, Csiszar E, Somiai C & Sajo I, *Text Res J*, 76(8) (2006)629.

14 Haga T & Tagagishi T, *J Appl Polym Sci*, 80 (2001) 1675

15 Koyuncu M, Karahan M, Karahan M & Nawab Y, *Fibers Text East Eur*, 24(4) (2016)105.

16 Wada M, Chanzy H, Nishiyama Y & Langan P, *Macromolecules*, 37 (2004)8548.

17 Ishaq A, *Structural and Mechanical Properties of some Native and Modified Cotton Fibres,* PhD Thesis, University of Strathclyde, Glasgow, 1984.

18 Ishaq A & Peacock N, *J Appl Polym Sci*, 51 (1994) 967.