

References

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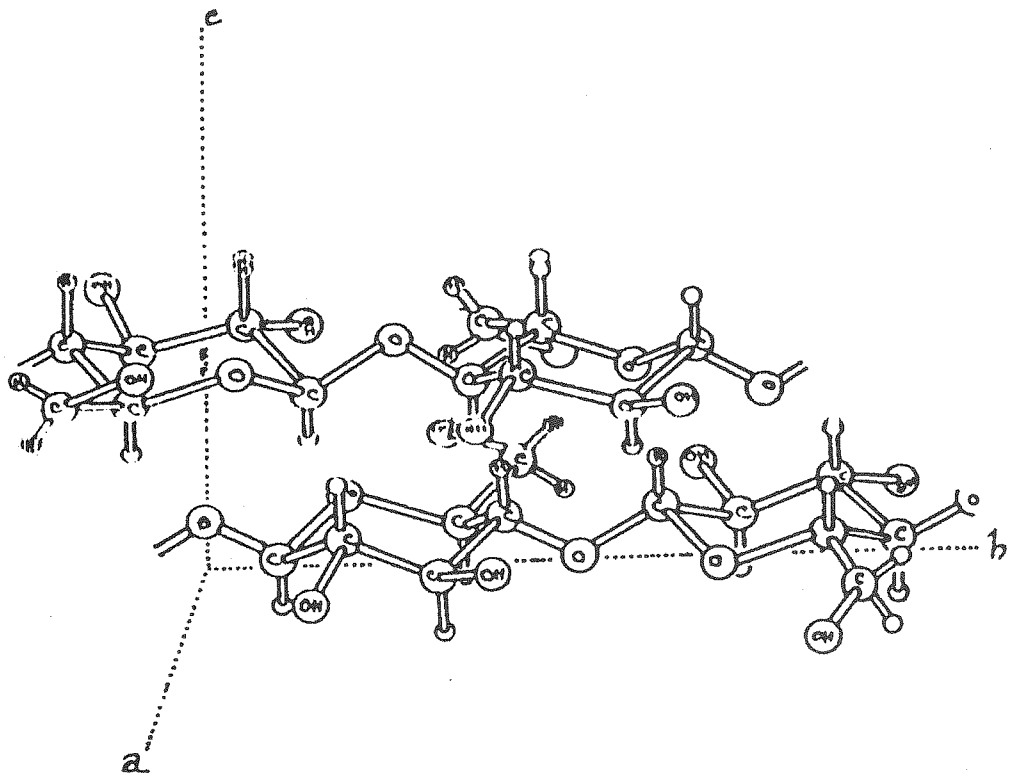


Figure (5) Crystal Structure of Cellulose as Proposed by Meyer and Mish [1]

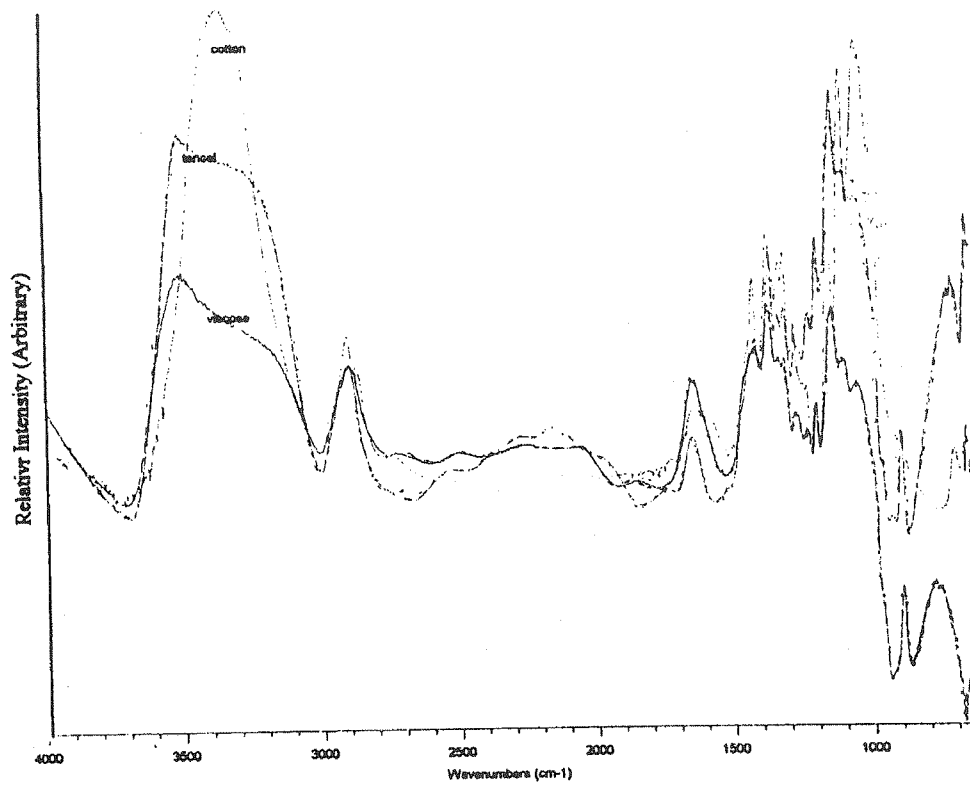


Figure (6) A Comparison of FTIR Spectra of Cotton, Viscose and Tencel Fibres in the Region 650-4000 cm^{-1}

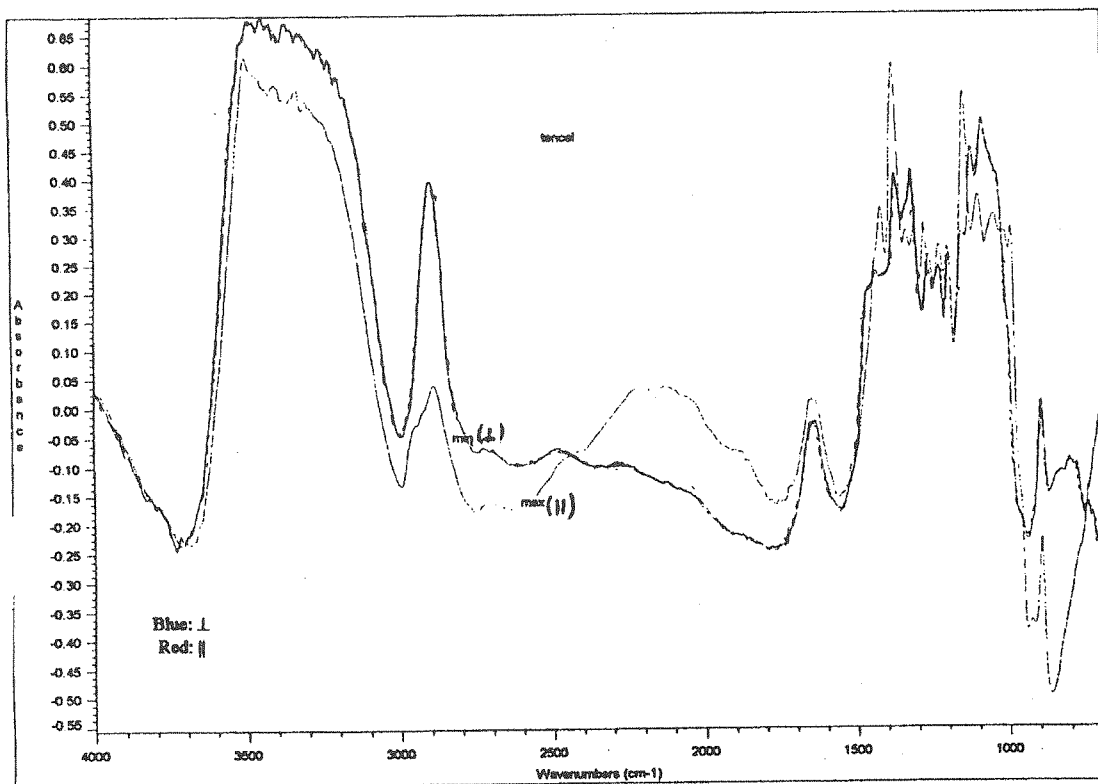
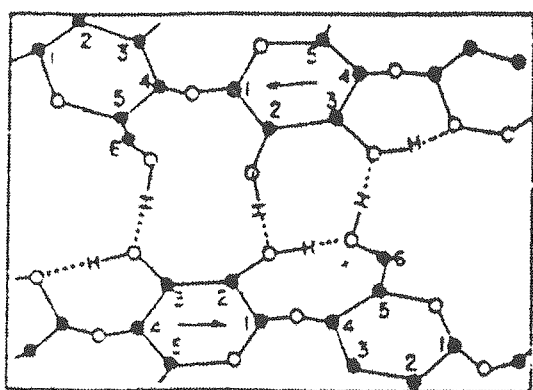


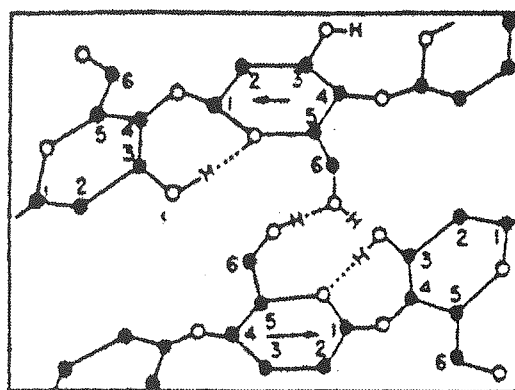
Figure (3) Polarized FTIR Spectra of Tencel Fibre

CELLULOSE II (101̄ PLANE)



INTRAMOLECULAR $O_3H \rightarrow O'_5$
 $O_2H \rightarrow O'_6$

Mann and Morrison.



INTRAMOLECULAR $O_3H \rightarrow O'_5$ (2 KINDS)

Marchessault and Liang

Figure (4) Inter and Intramolecular Hydrogen Bonds in Cellulose [8]

while those bands are weaker and less resolved for the viscose. This shows that the crystallinity of cotton and tencel is higher than that of viscose. The crystallinity index of cotton measured by Nelson and O'Connor's proposed method is higher than that

of tencel.

Based on a comparison of the appearance of the band at 1111 cm^{-1} among cotton, viscose, and tencel, it may be concluded that tencel has a crystalline structure of cellulose II similar to that of viscose.

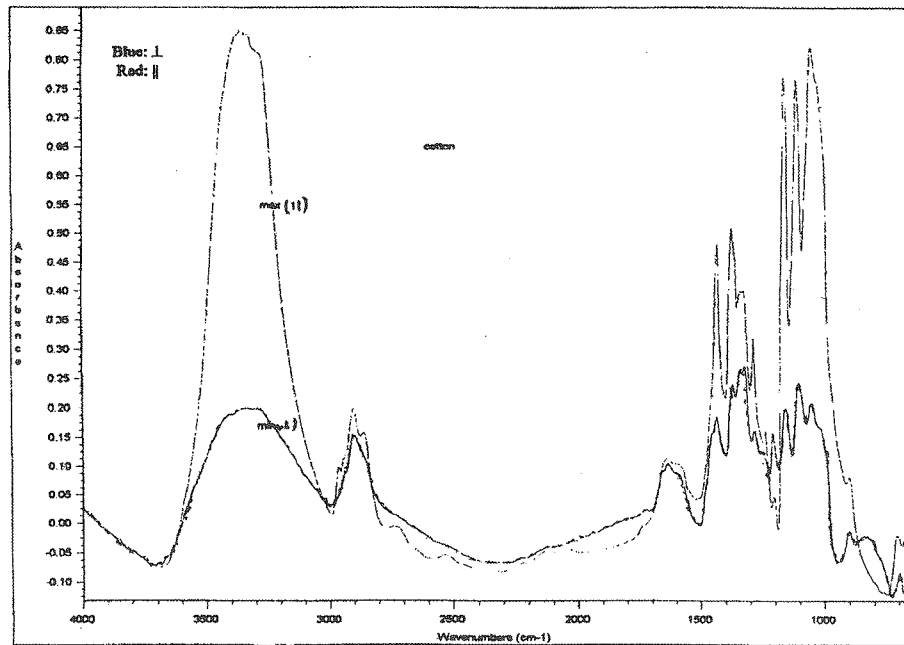


Figure (1) Polarized FTIR Spectra of Cotton Fibre

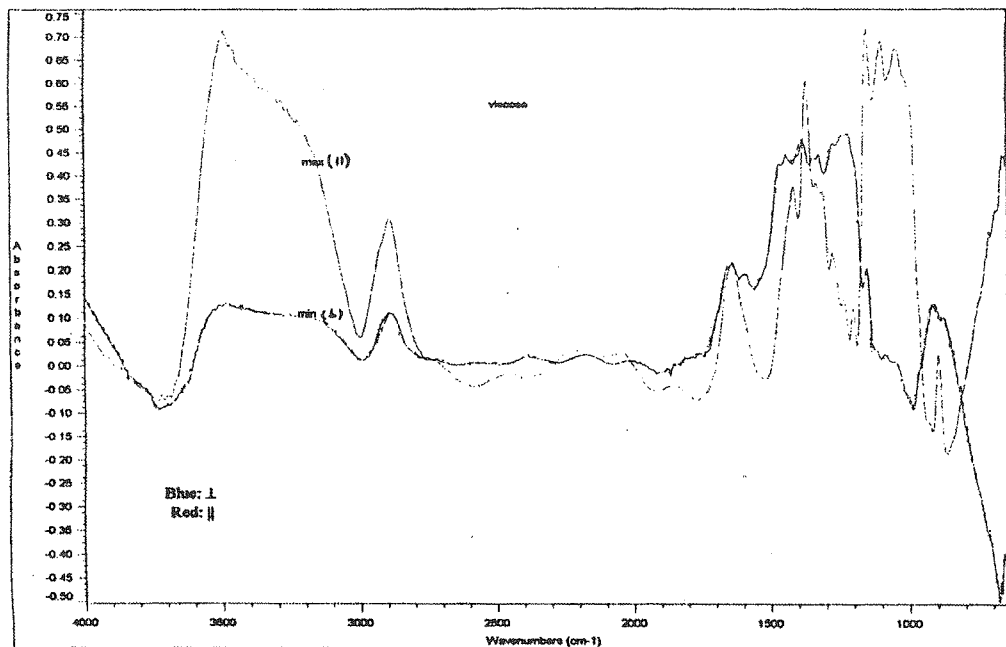


Figure (2) Polarized FTIR Spectra of Viscose Fibre

Therefore, based on a comparison of the absorptions at 1111 cm^{-1} band among cotton, viscose, and tencel, it may be concluded that tencel has a crystalline structure of cellulose II similar to that of viscose.

The intensity of the band at 1640 cm^{-1} , which has been attributed to absorbed water [1] is higher in viscose than cotton and tencel. It is higher in cotton than tencel. As expected, viscose absorbs, more water than cotton and tencel.

Evaluation of Orientation in Tencel Fibre by Polarized Spectra

The Herman orientation function of tencel fibre, obtained by birefringence and refractive index measurements, coupled with IR dichroic measurements of absorption were used to calculate quantitative values for the transition-moment angles. The results are shown in Table III.

Table (3) The results of transition-moment angles measurements

ν (cm^{-1}) 	\perp	$R=A_{ }/A_{\perp}$	R_0	ψ (degree)
897	899	0.58	0.53	62.72
1095		0.66	0.62	60.90
1085				
1154		1.56	1.62	47.70
1158				
1372		1.34	1.39	50.15
1377				
1421		1.14	1.16	52.71
1421				
2900		0.62	0.58	61.79
2895				
3354		0.75	0.72	59.05
3352				
3401		0.80	0.77	58.10
3403				

Conclusion

In the polarized spectra of cotton and viscose, the O-H stretching regions show strong parallel dichroism, but in that of tencel perpendicular dichroism is seen. It shows that the intramolecular hydrogen bonds exist between the C3 hydroxyl group of one glucose residue and the ring oxygen of the next residue (O'5) and between the C6 hydroxyl group and the bridge oxygen in cotton and viscose fibres and in tencel fibre, respectively. The perpendicular dichroism of CH₂ symmetrical stretching and bending bands indicates that the O6- O'2 intramolecular hydrogen bond are formed in tencel structure. The bands indicates that the O6-O'2 intramolecular hydrogen bond are formed in tencel structure. The bands in the region 900-1200 cm^{-1} which are attributed to vibrations including C-O and C-C stretching modes show parallel dichroism in cotton and viscose, but perpendicular dichroism in tencel expect at 992 and 1154 cm^{-1} . This means that it is possible that the C-O bond in tencel makes a larger angle with the chain axis than that of cotton and viscose.

In comparison of Cotton, Viscose, and Tencel FTIR Spectra:

The absorption bands in the O-H stretching region appear, sharper and centred to lower frequency in the cotton spectra than that of viscose and tencel. Presumably, cotton has a higher degree of order than that of viscose and tencel. The broader band in this region indicates existence of the less hydrogen bond, in the case of the tencel spectrum this suggests that tencel has more hydrogen bonds than viscose. Highly intense and well resolved bands appear at 1372, 1315, 1270, and 1225 cm^{-1} in cotton and tencel spectra,

plane. This means that the band associated with the C-H stretching vibration should be polarized perpendicular to the fibre axis.

The perpendicular band near 2903 cm^{-1} in the tencel spectra and the parallel bands at 2901 cm^{-1} in the spectra of cotton and viscose are related to CH stretching. In the cotton spectra the parallel bands at 2853 cm^{-1} and 1427 cm^{-1} have been assigned to CH₂ symmetric stretching and bending, respectively. The CH₂ antisymmetric stretching modes at 2942 and 2969 cm^{-1} show parallel dichroism. The perpendicular band at 2877 cm^{-1} and the parallel band at 1421 cm^{-1} are related to CH₂ symmetric stretching and bending modes, respectively, in the tencel spectra. In the spectra of tencel the bands at 2932 and 2954 cm^{-1} show perpendicular dichroism. This suggests that the C6 hydroxyl in the tencel may be engaged in an intermolecular hydrogen bond, contrary to that of cotton where it is assumed that the C6 hydroxyl is engaged in an intermolecular hydrogen bond and is not intramolecularly bonded to the C2 hydroxyl of the next residue.

Comparison of Cotton, Viscose, and Tencel FTIR Spectra.

Figure 6 shows the spectra of cotton, viscose, and tencel fibres in $4000\text{-}650\text{ cm}^{-1}$ region. A broad absorption peak near 3350 cm^{-1} was found for all cellulose materials. This has been assigned to the vibrations due to stretching of the O-H groups [10]. The intensity and frequency of this band are closely related to the hydrogen-bonding system [2]. As shown in Figure 6, the absorption band appears, sharper and centred more to the right in the cotton than it does in the viscose and tencel fibres. Presumably, cotton has a higher degree of order

than that of viscose and tencel. In the case of the viscose spectrum, the O-H stretching region appears broader than that of tencel. This suggests that tencel has more hydrogen bonds than viscose. Figure 7 shows the spectra of these samples in $1900\text{-}650\text{ cm}^{-1}$ region. As shown there, the spectra of all the samples are rather similar. However, on careful examination certain differences in the sharpness or intensity of several absorption bands are appeared. Highly intense and well resolved bands appear at 1372 , 1315 , 1270 , and 1225 cm^{-1} for the cotton and tencel, while those bands are weaker and less resolved for the viscose. It is believed that the intensity and resolution of these bands related to the crystallinity of cellulose materials [10]. The crystallinity index values, measured by Nelson and O' Connor's proposed method, are listed in Table II. As expected, cotton shows the highest value among these samples.

Table (II) Crystallinity index measurements of the samples

Sample	Crystallinity Index
Cotton	0.66
Viscose	0.41
Tencel	0.57

The band at 1111 cm^{-1} is seen to be strong in the spectra of cotton, but appears only as a shoulder in the spectra of viscose and tencel due to the development of a strong, broad band near 1090 cm^{-1} . Nelson and O'Conner [8] reported that the 1111 cm^{-1} band was relatively strong in the spectrum of cellulose I and appeared as a shoulder in cellulose II and amorphous cellulose.

key: ν , frequency; I, intensity; D, dichroism; vs, very strong; s, strong; m medium; w, weak; sh, shoulder; str., stretching; def., deformation.

As may be seen in the Figures 1, 2, and 3 strong dichroism are observed almost in the whole range of the spectra of the samples. In the spectra of cotton and viscose, the O-H stretching regions show strong parallel dichroism, but in that of tencel perpendicular dichroism is seen. Marchessault and Li-gang [2] reported that cellulose I and II differ considerably as regards intensity and shape of the O-H absorption bands, suggesting that a rearrangement of the hydrogen bonds has occurred as a result of going from cellulose I to cellulose II. They suggested that inter-and intramolecular hydrogen bonds in the O-H stretching region could give rise to strong parallel dichroism. There are two types of intramolecular hydrogen bonds [6, 7]: the first type is the hydrogen bond between the C3 hydroxyl group of one glucose residue and the ring oxygen of the next residue (O'5), and the second type is the hydrogen bond between the C6 hydroxyl group to the bridge oxygen. Alternative proposal was made by Man and Marrinan [8] for the second type of hydrogen bond, namely that the C6 hydroxyl group may be bonded to the C2 oxygen of the next glucose residue. Liang and Marchessault [2] and Liang [9] presented considerable evidence against the existence of the $O_6-O'_2$ hydrogen bond in either cellulose I or II. For cellulose I, Liang stated that the IR CH_2 symmetrical stretching and bending bands would not show parallel polarization, if the $O_6-O'_2$ hydrogen bond were formed. Figure 4 shows models of the

possible inter and intramolecular hydrogen bond according to Marchessault and Liang and Man and Marrinan observed band polarization [8, 9]. It seems highly probable that the first type of intramolecular hydrogen bond is presented in cotton and viscose but in tencel, the second type of intramolecular hydrogen bond may be formed because the CH_2 symmetric stretching bonds show perpendicular dichroism.

There are many strong bands in the region $900-1200\text{ cm}^{-1}$. These bands are attributed to complicated vibrations including C-O and C-C stretching modes. Tsuboi [1] reported that all the bands in the polarized spectra of flax and ramie in this region show parallel dichroism. He proposed that since every C-O bond makes a smaller angle with the chain axis than with either of the other two axes, parallel rather than perpendicular dichroism might be expected in this region. In the spectra of cotton and viscose all the bands in this region show parallel dichroism but in that of tencel all the bands show perpendicular dichroism except the bands at 992 and 1154 cm^{-1} . This means that it is possible that the C-O bond in tencel makes a larger angle with the chain axis than that of ramie, flax, cotton, and viscose, in the crystal structure proposed by Meyer and Misch [1]. Figure 5 shows the configuration and orientation of cellulose unit cell with respect to the crystallographic axes. In the fibres the crystals are considered to be arranged with their b axes in the fibre axis and with a and c axes oriented at random in the plane perpendicular to the fibre axis. Tsuboi [1] reported that there are twenty C-H bonds (i.e. five in each glucose residue) in the $C\rightarrow C-H$ and $O\rightarrow C-H$ structures which are directed perpendicularly to the ab

1145	vs	II							Antisymmetric Bridge
1158	sh	II	1154	s	1160	s	II		oxygen str. [2, 3]
1200	w	II	1202	w	1207	w	⊥		OH in-plane-bending
1232	m	II	⊥		1234	w	II		[2]
			1231	m	1247	m	II		
			⊥						
			1261	m					
1261	m	II	1278	m	1280	m	II		CH bending [2]
			⊥						
1311	m	⊥	1312	m	1317	m	II		CH ₂ wagging [2]
			⊥						
1334	m	⊥	1336	m	1337	m	II		OH in-plane- bending
			⊥						[2]
1375	s	II	1372	s	1368	m	II		CH bending [2]
			II						
1420	m	II	1420	m	1428	m	II		CH ₂ bending [2]
1443	sh	II	⊥		1453	m	II		
			1445	sh					
			⊥						
1469	sh		1469	sh					OH in-plane-bending
⊥			⊥						[2]
1637			1639		1635				Absorbed H ₂ O [1, 2]
1650					1658				
2853	w	⊥			2858	m	II		CH ₂ Symmetric str. [3]
2877		sh	2875	sh					
⊥			II						
2891		s	2891	sh					
⊥			II						
2904		s	2899	m	2901	m	II		CH str. [2, 3]
⊥									
2932		sh	2933	sh	2942	sh	II		CH ₂ Antisymmetric str.
⊥			II						[3]
2954		sh	2958	sh	2966	w	II		
⊥			II						
3304		s	3176	s	3304	vs	II		OH str. (Intermolecular
⊥			II		3333	s	II		hydrogen bonding) [2,
			3307	s					3]
			II						
3354		s	3354	s	3355	s	II		
⊥			II						
3375		s							
⊥			II						
3401		vs			3401	vs	II		
⊥									
3437		s	3436	s					
⊥			II						
3459		s	3458	s	3447	s	II		OHstr. (Intramolecular
⊥			II		3488	s	II		hydrogen bonding) [2,
3480	vs		3475	vs	II				3]

to calculate quantitative values for the transition moment angle (θ).

Experimental

The Tencel fibres used in this study were manufactured in 1993 and supplied by Courtaulds Plc. They were in the form of bright, continuous tow of 1.7 dtex per filament. In this study FTIR spectra were obtained using a Nicolet Magna IR spectrophotometer equipped with a microscope and "Omnic" control and data-manipulation software.

The polarized FTIR spectra of cotton, viscose, and tencel samples were obtained from single fibre in the standard atmospheric condition ($20 \pm 3^\circ\text{C}$ and 65% rh). The IR beam passed first through a wire-grid polarizer and then through the sample before reaching the detector. The spectra were obtained either by rotating the fibre, or by rotating the polarizer, which yielded the same results. In order to avoid errors associated with rotating the sample or polarizer, the sample must be accurately positioned with

respect to the polarizer.

In FTIR micro-spectroscopy the optics are designed to give coincident light beams and IR beams, so that IR spectra may be recorded for the exact region that is viewed optically. In this technique sample preparation is easy and specific regions of the sample can be viewed routinely. It is an effective technique for obtaining the polarized IR spectra of fibres.

Results and Discussion Comparison of Cotton, Viscose, and Tencel Polarized Spectra

The polarized spectra of cotton, viscose, and tencel fibres are shown in Figures 1, 2, and 3, respectively. The blue curves represent absorption with the electric vector perpendicular to the fibre axis, and the red curves absorption with the electric vector parallel to this direction. The frequency, assignment, and polarization (dichroism) of all the bands in the deconvoluted spectra of these fibres are collected in Table 1.

Table (1) The result of polarized FTIR spectroscopy of tencel, viscose, and cotton

Tence $\nu(\text{cm}^{-1})$	Viscose		Cotton		Band Assignment	
	I	D	I	D		
740	m	II	760	m	II	OH out - of-plane def. [1, 2]
897	m	\perp	897	m	\perp	CH ₂ rocking; Ring breathing(C ₁ group frequency) [2]
965	s	II	966	m	II	C-O str. [1, 2]
992	s	II	994	s	II	C-C str. [1]
1004	s	\perp	1002	s	II	
1015	s	\perp	1013	s	II	
1030	s	\perp	1038	s	II	
1059	s	\perp	1053	s	II	
1075	vs	\perp	1073	s	II	
1117	vs	\perp	1112	s	II	Ring str. [2]

For each vibrational mode of a molecule, there is a transition moment vector. The intensity of the IR absorption band depends on the angle that the electric vector of the incident radiation makes with the transition moment. For liquids and gases, the movement of the molecules is sufficient to yield a random orientation of transition moment vectors and for solids there is often a preferred orientation of the molecules. When the electric vector of polarized IR radiation is parallel to the transition moment vector, strong absorption occurs and when the electric vector is perpendicular to the transition moment, no absorption occurs. The dichroic ratio may be considered to be characteristic of the directional orientation of the segments of the molecule. For fibres, the dichroic ratio, R , is defined as $R = A_{\parallel} / A_{\perp}$, where A_{\parallel} is the absorbance parallel to the fibre axis, and A_{\perp} is absorbance perpendicular to the fibre axis. For highly oriented fibres the dichroic ratio may approach either infinity or zero, depending on the alignment of the transition moment vector with respect to the molecular chain axis. The alignment of the chain segments can be determined from dichroic ratio measurement if the inherent polarization are known. For fibres that have a low level of orientation the magnitude of the dichroic ratio is close to 1. For uniaxially drawn fibres these dichroic parameters can be related to the Herman orientation function, F ; $F = 3 \langle \cos^2 \theta \rangle - 1/2$.

The orientation angle θ is the angle between the draw direction and the local molecular chain axis. The Herman function is equal to 1 when the chain axis is parallel to the fibre orientation 0 when the system is randomly oriented, and 0.5 when the chain

axis is perpendicular to the fibre orientation direction. This function can be calculated from measurements of the dichroic ratio by using $F = (R-1)(R_0+2)/(R+2)(R_0-1)$ [5] where R_0 is the dichroic ratio for perfect uniaxial order. The value of the constant R_0 is unknown and can be different for every IR band studied. For perfect uniaxial order it is assumed that the polymer chains are all oriented parallel to the draw direction, and the transition moments associated with the vibrations lie on a cone with a semiangle ψ to the chain axis direction. The dichroic ratio is then expressed by $R_0 = 2 \cot^2 \psi$.

As ψ varies from 0 to $\pi/2$, R_0 varies from ∞ to 0. For $\psi = 54^\circ 44'$, no dichroism will be observed. In practice, the orientation of the polymer chains is imperfect and is often described in terms of f_p , the fraction of fibre that is perfectly oriented, while the remaining fraction $(1-f_p)$ is randomly distributed. The dichroic ratio is

$$R = f_p \cos^2 \psi + (1/3)(1-f_p) / \{ [(1/2)f_p] \sin^2 \psi + (1/3)(1-f_p) \}$$

A method of defining the imperfect orientation is to suppose all the molecular chains are displaced from parallelism with the draw direction by the same angle θ . The expression for R then becomes:

$$R = [2 \cot^2 \psi \cos^2 \theta + \sin^2 \theta] / [\cot^2 \psi \sin^2 \theta + (1 + \cos^2 \theta)/2]$$

If the direction of the transition moment with respect to the chain axis is known, the average orientation of the chain segments can be determined from the measured dichroic ratio. The Herman orientation function, F , can be determined by a number of independent techniques, including X-ray diffraction, birefringence, and refractive index measurements. These methods, coupled with IR dichroic measurements can be used

Polarized IR Spectra of Tencel Fibre

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Abstract

This study describes a comparison of polarized FTIR spectra of cotton, viscose and tencel fibres. Polarized FTIR micro-spectroscopy has been applied to improve resolution of overlapping bands to help in band assignment and crystallinity measurements of these fibres. It is also useful to determine chain conformational and micro-structural differences of these fibres. An evaluation of orientation has been done by dichroism and transition-moment angles measurements.

Keywords

polarized spectra, FTIR micro-spectroscopy, Tencel fibres

Introduction

For oriented polymers much useful structural information can be obtained by study of the spectra obtained with polarized infra-red radiation. Tsuboi [1] studied IR absorption spectra of flax and ramie fibres using polarized radiation. Marchesault and Liang [2] determined the polarization properties of doubly oriented mercerized ramie and fortisan crystallites. Liang and Marchesault [3] also studied the IR spectra of oriented films of valonia cellulose and of ramie and bacterial cellulose crystallites. They found that the polarization properties differences between bacterial and ramie crystallites are attributed to percent crystallinity and orientation effects. Marchesault

et al. [4] showed the oriented outer portion of the secondary walls a separate phase, with the direction of orientation parallel to that of the cellulose microfibrils in hardwood fibre.

FTIR micro-pectroscopy is an effective technique for obtaining the polarized IR spectra of fibre. An IR spectrometer can be equipped with a wire-grid polarizer. The beam passed first through the polarizer and then through the sample before reaching the detector. Polarized transmission measurements can be used to:

- I) assist in the determination of chain conformation and structure;
- II) help in band assignment;
- III) improve resolution of overlapping bands in oriented polymers;
- IV) estimate overall orientation and orientation of crystalline and amorphous zones.