

The Chain Orientation of Cellulose Flat and Tubular Films Prepared from *N*-Methylmorpholine *N*-Oxide Solutions

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ABSTRACT: Cellulose flat and tubular films were made from cellulose-aqueous *N*-methylmorpholine *N*-oxide solution system by casting method on nonwovens and blow-extrusion technique, respectively. An attempt was made to disclose the chain orientation of the new cellulose films. It was found that the (1 $\bar{1}$ 0) lattice planes of the flat and tubular films have an uniplanar orientation mode with respect to the film surface. For flat films, the (110) lattice planes are almost unoriented with respect to the machine direction. However, the (110) planes of tubular films have axial orientation with respect to the machine direction. With increasing blow up ratio, both the axial orientation and the crystallinity of tubular films increase. With increasing draw down ratio, only the axial orientation increases while the crystallinity does not change significantly. The three dimensional orientation parameters from polarized Fourier transform infrared spectrometry (FT-IR) spectra by sample tilting indicate that the uniplanar orientation of cellulose chain with respect to the surface of flat film increases when the casting speed increases. Moreover, no axial orientation was found within the plane parallel to the flat film surface. For tubular films, the uniplanar orientation with respect to the film surface increases with the blow up or draw down ratio.

KEY WORDS Cellulose Film / Orientation / *N*-Methylmorpholine *N*-Oxide / Pole Figure / Fourier Transform Infrared Spectrometry (FT-IR) /

Recently, *N*-methylmorpholine *N*-oxide (NMMO) as a new organic solvent has been used to dissolve cellulose to prepare novel cellulosic products with improved mechanical properties when compared to materials prepared by the conventional viscose process.^{1–3} Disadvantages of the more than one century old viscose technology are its complicated multi-step processing line and the serious environmental problems arising from the use of CS₂. However, the new NMMO process has no chemical reaction and byproducts. It is possible to prepare the cellulose films from NMMO solution using casting method as well as blow-extrusion process in our laboratory. The super-molecular structures of the two types of films must be different due to the different fabricate method. Especially for the blown films, the process of film formation includes two processes simultaneously, that are drawing-down and blowing-up processes. Furthermore, the blowing-up process is a two-dimensional elongation process. Therefore, the combination of drawing-down ratio and blow-up ratio may affect the orientation or crystallization of cellulose film.

It is known that X-Ray diffraction is a powerful characterization tool for the elucidation of crystalline microstructure. Nevertheless, it is inaccessible to estimate the degree of orientation in the amorphous phase, which is a very important parameter influencing material properties of polymers. Infrared spectroscopy is a complementary method since vibrational absorptions

can arise from chain segments in both amorphous and crystalline phases. In the present paper, X-Ray diffraction techniques are used to reveal and characterize orientation modes in the crystalline regions of the two types of films. In addition, polarized FT-IR spectra for them are also obtained to confirm the changes of orientation for the molecular chains of cellulose.

EXPERIMENTAL

Film Preparation

Cellulose sample was purchased from Shanghai Fengxian Pulp Co., China. Fifty percent *N*-methylmorpholine-*N*-oxide (NMMO) water solution obtained from BASF was used as the solvent after concentrating it to 87 wt% (NMMO/H₂O = 87/13, expressed as NMMO monohydrate). Moreover, 0.5 wt% *n*-propylgallate (supplied by Shanghai Reagents Co., China) was added as an antioxidant to avoid oxidation and degradation during the cellulose dissolving process.

The mixing and dissolving of dried cellulose pulp in NMMO monohydrate were carried out at 85°C in a container equipped with stirring rake and heating jacket. The cellulose concentration were 9 wt% and the dope was degassed at 90°C for 4 h before use.⁴

The flat films were obtained by traditional casting method as shown in Figure 1 using the casting ma-

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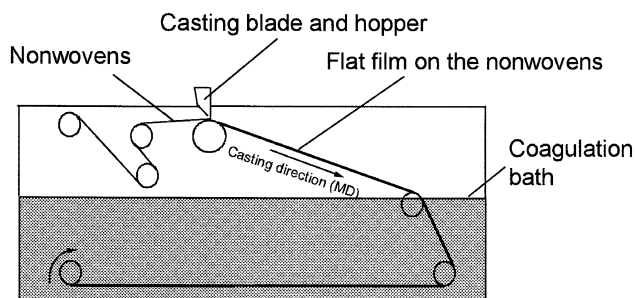


Figure 1. Scheme of the casting process for the preparation of cellulose flat film.

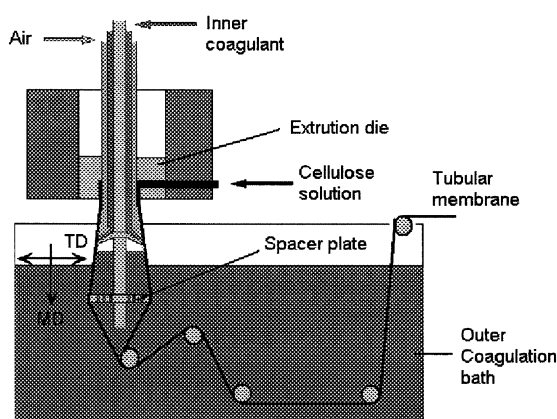


Figure 2. Scheme of the blow extrusion process for the preparation of cellulose tubular film.

chine made by our group. Firstly, the cellulose solution was cast into flat film form on nonwovens fabricated by polyethylene terephthalate (PET) at room temperature. Then the solution with the nonwovens was immersed into pure water bath with the temperature of 25°C and wound on a roller.

The tubular films were prepared by the blow-extrusion process. The principle of the new route is illustrated in Figure 2. A dope of cellulose with concentration of 9 wt% in the solvent of NMMO monohydrate was extruded out through a circular blow nozzle with a diameter of up to 30 mm and temperature of about 90°C, which shapes the dope in a tube-like fashion. Before coagulated in the coagulation bath, the tube of the highly viscous and elastic dope passed an air-gap about 150 mm. In the air gap, the tube-like shaped dope can be drawn down in machine direction (MD) by adjusting the winding speed and blown up in transverse direction (TD) by controlling the air pressure inside the tube. Both the inner and outer coagulants are pure water with the temperature of 25°C.

All the films were washed with running water for 24 h to remove the excess solvent completely before being air-dried with a given dimension for at least 24 h at ambient temperature.

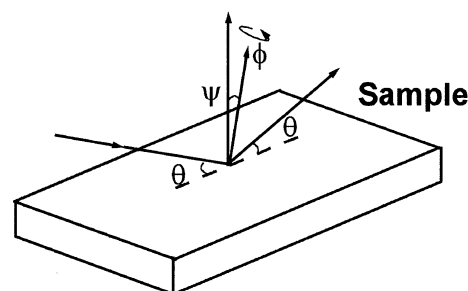


Figure 3. Pole figure measurement.

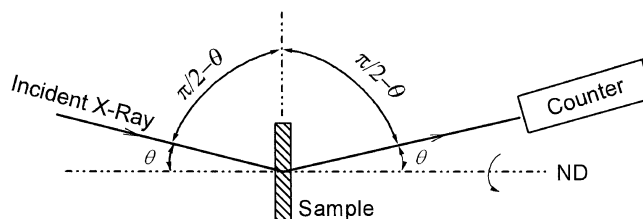


Figure 4. Geometrical arrangement of specimen with respect to X-Ray source and counter for diffractometry in symmetrical transmission method.

X-Ray Diffraction Analysis

X-Ray diffraction patterns of cellulose films were measured by reflection and transmission methods on an X-Ray diffraction apparatus with scintillation counter (Rigaku D/Max-III A).⁵ All experiments were carried out using Nickel filtered Cu- $K\alpha$ radiation under moderate resolution conditions for 2θ from 6 to 35°. The crystallinity index was calculated according to the Segal's method.^{6,7}

Texture measurements (pole figure) were used to determine the orientation distribution of crystalline grains in polycrystalline cellulose samples. A pole figure is often plotted in polar coordinates consisting of the tilt and rotation angles with respect to a given crystallographic orientation. It is measured at a fixed scattering angle and consists of a series of ϕ -scans (in-plane rotation around the center of the sample) at different tilt or Ψ (azimuth) angles, as illustrated in Figure 3. The pole figure data are displayed as contour plots or elevation graphs with zero angle in the center. Details of X-Ray texture investigations are given in ref 8.

A crystalline orientation parameter, π , of films was estimated from diffraction strength for azimuthal directions by fixing scintillation counter at $2\theta = 20.0^\circ$ (corresponding to (110) plane) and by rotating a sample around the normal direction (ND) of film in symmetrical transmission method. The geometrical arrangement of specimen was shown in Figure 4. The π was calculated from the following equation:⁹

$$\pi = (180 - \Psi_{1/2})/180 \quad (1)$$

where $\Psi_{1/2}$ means the half-height width (degree) of

diffraction intensity. In this paper, cellulose lattice parameter notations were made according to the general crystallographic rule. According to this rule, the c -axis coincides with the molecular chain axis and the b -axis is larger than the a -axis for a monoclinic unit cell.¹⁰

FT-IR Analysis

Infrared (IR) spectroscopy is particularly useful for measuring molecular orientation in semicrystalline polymers since IR absorptions frequently exist which are characteristic of amorphous phase material. The degree of chain orientation in the amorphous phase is a very important parameter influencing material properties and is inaccessible to many other characterization techniques such as wide-angle X-Ray scattering. In many polymers, infrared spectra exhibit absorption bands assignable to vibrations of specific chain segments, chemical groups or localized conformations. Each vibrational mode of a molecule has a transition moment vector M associated with it. When infrared radiation is plane-polarized such that the electric vector E is parallel to the transition moment vector, strong absorption occurs; when it is perpendicular, no absorption occurs.

The dichroic ratio, which is used in many references, is a two-dimensional measurement. To completely characterize the orientation of films, three-dimensional measurements are required.

If a highly oriented film sample is sufficiently thin to allow transmission infrared measurements, it has been shown that precise three dimensional orientation information may be obtained by tilting the sample films with respect to the incident infrared beam.¹¹ The three principal axes of the film may be defined with y being the machine direction (MD), x the transverse direction (TD), and z the direction perpendicular to the film surface (ND). The axes of the fixed space coordinate are defined with Y being the vertical direction, X the horizontal direction, and Z the direction perpendicular to the XY plane. An angle α is defined to be the angle of rotation around the x -axis. The experimental geometry is shown in Figure 5. The absorbance of bands in three directions (A_x , A_y , A_z) can be determined by measuring the following four spectral quantities: (a) A_x , y -axis vertical and incident polarization parallel to the X -axis; (b) A_y , y -axis vertical and incident polarization parallel to the Y -axis; (c) A_t^0 , y -axis tilted at α from the vertical axis Y and incident polarization parallel to the X -axis, (d) A_t^0 , y -axis tilted α from the vertical axis Y and incident polarization parallel to the Y -axis. A_z then can be calculated from the following equation^{11, 12}

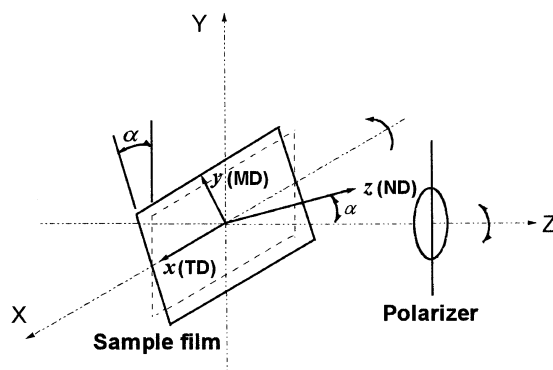


Figure 5. The sample geometry used in the three dimensional orientation measurement.

$$A_z = \frac{A_t^0(1 - \sin^2 \alpha/n_z^2)^{1/2} - A_y(1 - \sin^2 \alpha/n_z^2)}{\sin^2 \alpha/n_z^2} \quad (2)$$

where n_z is the index of refraction of the film in the yz plane. Its value may be measured from the following expression^{11, 12}

$$n_z = \left(\frac{\sin^2 \alpha}{1 - (A_x/A_t^{90})^2} \right)^{1/2} \quad (3)$$

for these cellulose films, a value of 1.4 for n_z was determined and a value of 45° for α was chosen in our experiments.

The classical dichroic ratio in this reference system is $R_{yx} = A_y/A_x$. Another important factor

$$A_0 = (A_x + A_y + A_z)/3 \quad (4)$$

represents the absorbance of the band exclusive of contributions due to orientation of the polymer.¹³ This factor is proportional to the amount of chemical structure giving rise to the infrared absorption. The three dimensional orientation parameters: A_y/A_0 , A_x/A_0 , and A_z/A_0 can be constructed to determine molecular orientation. For these parameters to have any physical meaning, the direction of the transition moment vector of vibration mode must be known.

The peak band at 1159 cm^{-1} of the cellulose FT-IR spectra was used to estimate the orientation since it is attributed to anti-symmetrical bridge $C_1\text{--O--}C_4$ stretching band. In particular, the band can be interpreted as representing molecules aligned parallel to the molecular axis and exhibits parallel dichroism.^{14, 15}

RESULTS AND DISCUSSION

The Crystalline Orientation of Cellulose Films Obtained from X-Ray Diffraction

It is well known that c -axes of cellulose II crystals tend to orient parallel to a drawing direction in y -axis

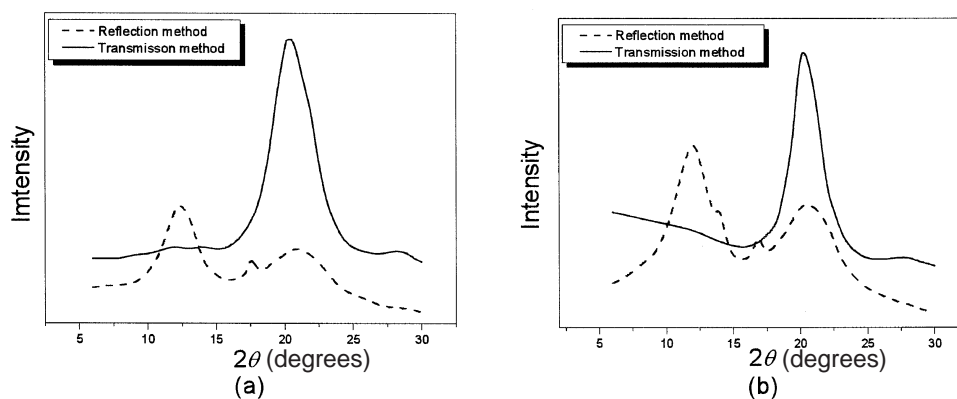


Figure 6. X-Ray diffraction patterns of cellulose films measured by reflection method and transmission method, (a) flat film, (b) tubular film.

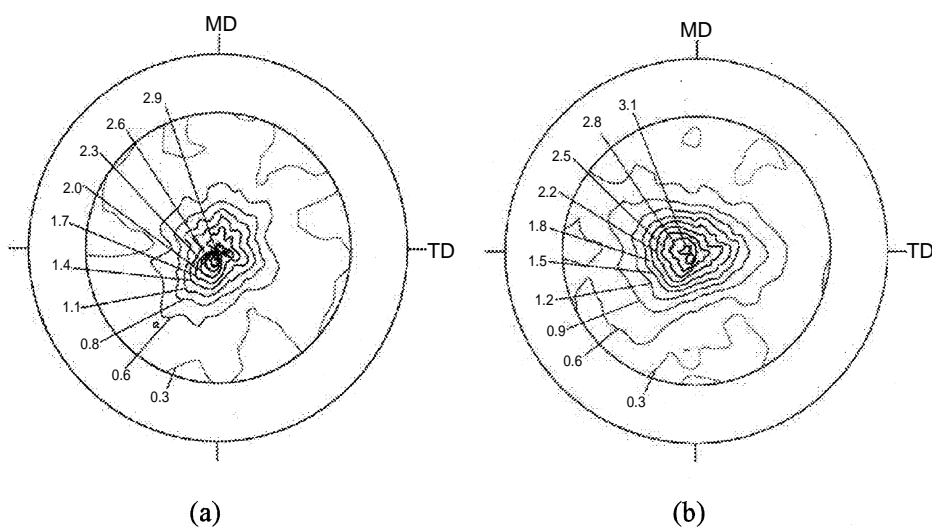


Figure 7. WAXD pole figures of the $(1\bar{1}0)$ lattice planes of cellulose films corresponding to Figure 6. (a) flat film, (b) tubular film, draw down ratio in machine direction larger than transversely.

and $(1\bar{1}0)$ planes prefer to orient parallel to the film surface (reference plane). However, in many references¹⁶ the former orientation (classified as uniaxial orientation) has only been concerned in relation to mechanical properties and processing conditions of regenerated cellulose fibers and films, though the latter orientation (classified as selective uniplanar orientation) could also have important influence on the mechanical properties of cellulose products.

Figure 6 shows the difference of X-Ray diffraction patterns of cellulose films measured using reflection and transmission methods. For the flat and tubular films, the peak intensity corresponding to the $(1\bar{1}0)$ plane at $2\theta = 12^\circ$ obtained by reflection method is higher than that obtained by transmission method. However, the peak intensity corresponding to the (110) plane at $2\theta = 20^\circ$ obtained by reflection method is less than that obtained by transmission method. Normally, the normal of (110) plane encloses an angle of about 85° to the normal of the planar-oriented $(1\bar{1}0)$ lattice-plane.^{17,18} It is also well known that the diffraction

peak corresponding to the $(1\bar{1}0)$ crystal plane of cellulose exhibits chain orientation parallel to the top surface of the films.¹⁹ Consequently, the orientation of the $(1\bar{1}0)$ plane contributes to the high diffraction peak at $2\theta = 12^\circ$ of the intensity curve by reflection method; the orientation of the (110) plane contributes to the high diffraction peak at $2\theta = 20^\circ$ of the intensity curve by transmission method.

Mode of orientation of the cellulose films was estimated from X-Ray pole figures of the $(1\bar{1}0)$ lattice planes obtained with the texture goniometer in reflection method (Rigaku-Dmax-IIIC). It is recorded with the texture goniometer by moving the sample stepwise around the three axes at a fixed Bragg angle ($2\theta = 12^\circ$). The sample is characterized by the fixed coordinate system with MD, TD, and ND. The $(1\bar{1}0)$ pole figures for selected flat and tubular films are shown in Figure 7. It can be seen from Figure 7 that a very high concentration of poles exists in the immediate neighborhood of the normal to the polymer film. This means that the great majority of the polymer crystallites are oriented with

their $(1\bar{1}0)$ planes nearly parallel to the surface plane of the polymer film. From the sharp peak in the center of the $(1\bar{1}0)$ pole figures, it is concluded that there is an uniplanar orientation mode in both the flat and tubular films, which can generally be found in cellulose films. This means that the $(1\bar{1}0)$ lattice planes preferably orient towards the macroscopic film surface. For the flat film, a near-circular distribution of the various intensity-levels was achieved (Figure 7a). One of the possible reasons is that the cellulose solution was adhered on the nonwovens and there is no strong stretching in both MD and TD. Therefore, a balanced uniplanar orientation was obtained. However, the pole figure of the blown film has an elliptical intensity distribution which indicating a higher degree of uniplanar orientation in MD than TD (Figure 7b).

In order to investigate whether there is an axial orientation of cellulose chains in the films, the intensity distributions in azimuthal scan of (110) planes were measured in transmission method. The results were shown in Figures 8 and 9.

It is interesting that the intensity of the (110) reflection of the flat films (Figure 8) were very constant as

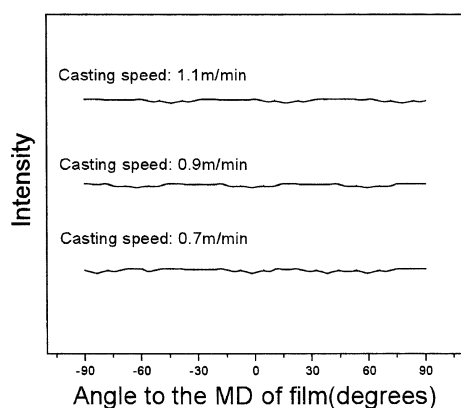


Figure 8. Azimuthal intensity tracings of the (110) arc of the flat films prepared with different casting speed.

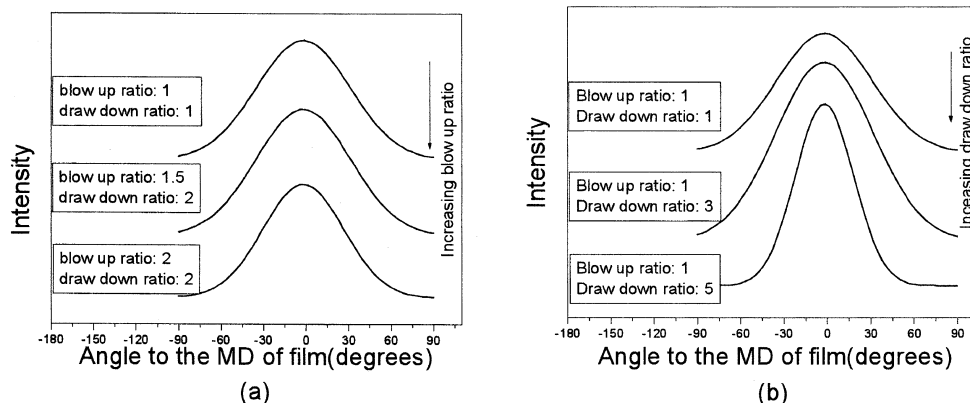


Figure 9. Azimuthal intensity tracings of the (110) arc of the tubular films prepared with different blow up ratio (a) and draw down ratio (b).

a function of the angle to the MD of film. The casting speed has also no influences on the intensity distributions. That means the (110) plane is almost unoriented to the casting direction (MD). A possible explanation is that the polymer chain was stretched nearly equally in both MD and TD, since cellulose solution is adhered on the nonwovens all through the casting, coagulation and drying procedures. It also should be noticed that the moving speed of the nonwovens is very low in our experiments.

Figure 9 shows the resolution of the (110) azimuthal profiles, which have typical Gaussian distributions, of the tubular films. That means that the (110) planes of the tubular films have preferred axial orientation to MD, which is not observed in the flat films. The orientation parameter, π , analyzed from WAXD patterns (Figure 9) at (110) planes, and the crystallinity index are shown in Figure 10. The data of Figure 10a show that both the axial orientation and the crystallinity of tubular films increase when the blow up ratio increases. However, the effect of the draw down ratio to the super-molecular structure is somewhat different from that of the blow up ratio. As shown in Figure 10b, the axial orientation increases while the crystallinity does not change significantly even while the draw down ratio increases. That is reasonable because the blowing-up process is a two dimensional elongation process, higher blow up ratio results in greater stretching effect in both MD and TD. Consequently, the normal strain on the cellulose chain within the film surface also increases. Therefore, both higher degrees of axial orientation with respect to MD and uniplanar orientation with respect to the film surface were obtained. The higher degree of the three dimensional order of cellulose chain may contribute to higher crystallinity of the tubular film. However, larger draw down ratio results in greater stretching effect on cellulose chain in MD, which only leads to the predominant increase of the axial orientation with respect to

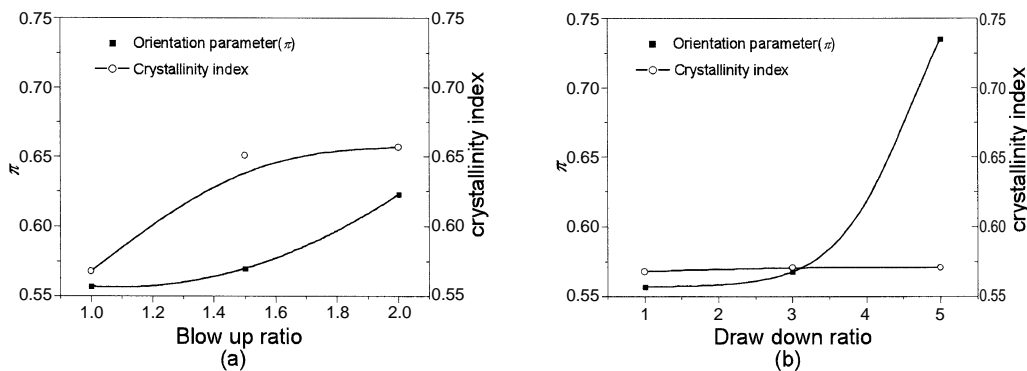


Figure 10. The effects of blow up ratio (a) and draw down ratio (b) to the orientation parameter and the crystallinity index of the tubular films.

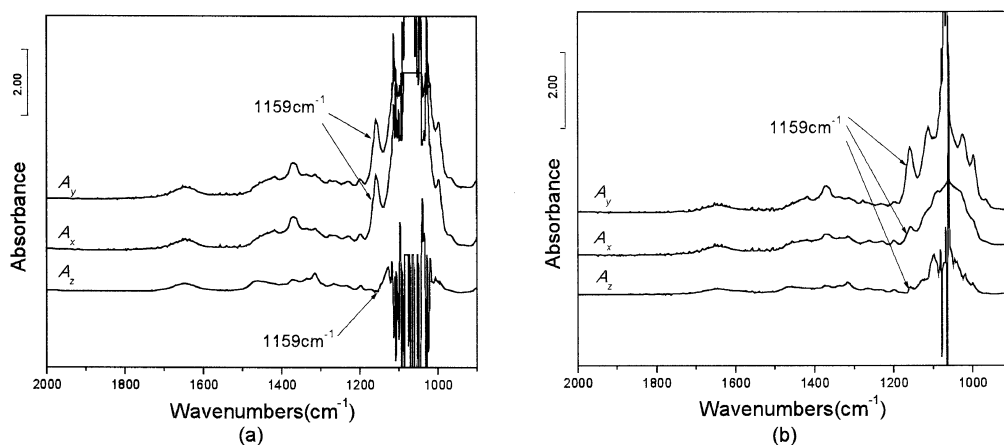


Figure 11. Determination of A_x , A_y , and A_z via sample tilting and spectral subtraction for the cellulose films. (a) flat film, (b) tubular film.

MD. The increase of the two dimensional order of cellulose chain has little contribution to the crystallization.

The Molecular Orientation of Cellulose Films Obtained from FT-IR

In order to confirm the changes of orientation for the molecular chains of cellulose films, polarized FT-IR spectra were obtained using a Nicolet Nexus-670 Fourier transform infrared spectrometer equipped with a polarizer. Operating parameters were chosen such that the wave number accuracy was $\pm 0.02\text{ cm}^{-1}$ and the spectral resolution was 2 cm^{-1} . The thickness of the films is about $15\text{ }\mu\text{m}$. Complete A_x , A_y , and A_z can be calculated using the software available on the computer associated with the FT-IR.

The polarized spectra obtained for the two types of cellulose films are shown in Figure 11. For well-assigned parallel vibrations (1159 cm^{-1}) the absorbance measured in MD (A_y) almost equals to the transverse component (A_x) for flat film (Figure 11a). This suggests that there is no axial orientation in the xy plane of the flat film. However, as shown in Figure 11b, A_y value of 1159 cm^{-1} is much higher than that of A_x . This implies the molecular chains of tubular film have

axial orientation to MD. In addition, the small A_z values found in both figures indicate that the molecular chains are perpendicular to the normal of the film plane for both flat and tubular films. In other words, the cellulose chains of these two types of films have uniplanar orientation to the film surface, which coincides with the results from X-Ray diffraction as described before.

From the basic principles of polarized FT-IR analysis focused on 1159 cm^{-1} , it is known that larger value of A_y/A_x means preferentially orientation to the y -axis and lower value of A_z/A_0 means preferentially uniplanar orientation to the xy plane. Figure 12 illustrates the effect of the casting speed on the three dimensional orientation of flat films. That the dichroic ratio of the sample plane (A_y/A_x) equals 1 in despite of the increasing casting speed definitely suggests the higher casting speed has no effect on the random orientation within the xy plane. It can also be found that the value of A_z/A_0 decreases while the values of A_y/A_0 and A_x/A_0 increase when the casting speed increases. This means that the degree of uniplanar orientation increases in the case of higher casting speed. This is reasonable because the higher casting speed, the thinner of the film and the larger strain within the film surface plane dur-

ing the coagulation and drying procedure with a given dimension.

For tubular films, the three dimensional orientation parameters A_y/A_0 , A_x/A_0 , A_z/A_0 , and A_y/A_x are listed in Table I.

By comparing the film of C50 M and C40 M, it can be seen that larger blow up ratio results in less A_z/A_0 value and little increase of A_y/A_x value under the same draw down ratio condition. Consequently, the larger uniplanar orientation of cellulose chain to the xy plane and larger axial orientation to the y -axis were obtained when the blow up ratio increases. After the cellulose dope is extruded out from circular nozzle, the polymer chains were stretched in both MD and TD. When the blow up ratio increases, greater stretching effect of the two directions may result in preferential uniplanar orientation of cellulose chains to the film surface. The little increase of A_y/A_x from 1.54952 to 1.57932 and ob-

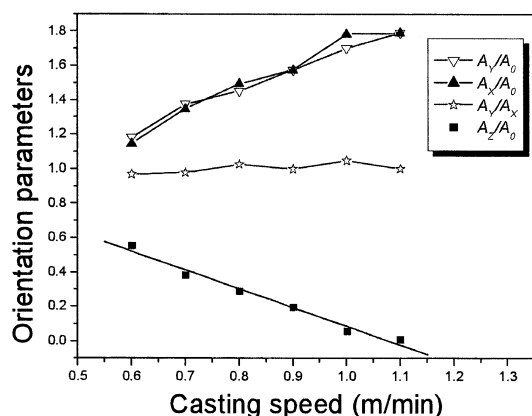


Figure 12. The effect of casting speed on the three dimensional orientation parameters of flat films.

Table I. The three dimensional orientation parameters of tubular films

Film	Blow up ratio	Draw down ratio	A_0	A_x/A_0	A_y/A_0	A_z/A_0	A_y/A_x
C50M	2	2	0.91471	1.24739	1.97002	0.23492	1.57932
C40M	1.5	2	0.86708	1.08295	1.67805	0.42438	1.54952
C40F	1.5	3	0.66018	1.10424	1.83282	0.35878	1.65981
C25M	1	5	0.46413	0.52786	2.33122	0.48853	4.41633

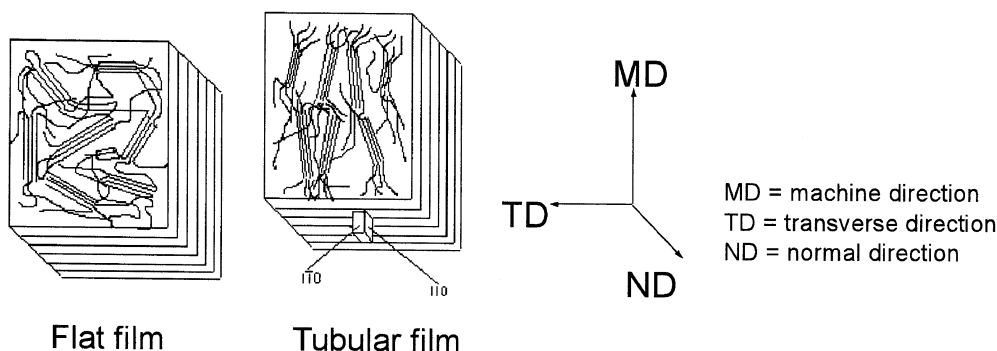


Figure 13. Schematic representation for the two modes of orientation for flat and tubular films.

vious decrease of A_z/A_0 from 0.42438 to 0.23492 suggest that the contribution of blow up ratio to the uniplanar orientation is larger than the contribution of blow up ratio to the axial orientation. In addition, it can be found that both A_x/A_0 and A_y/A_0 increase while A_z/A_0 decreases from the comparison of C40 M and C50 M. This is because less polymer chains parallel to the ND must result in more polymer chains parallel to the xy plane. Moreover, there are more polymer chains parallel to the y -axis than the x -axis within this plane.

By comparing the film of C40 M and C40F, it can be found that larger draw down ratio also results in larger A_y/A_x value and somewhat less A_z/A_0 value under the same blow up ratio condition. The data indicate that predominant axial and a little higher degree of uniplanar orientation can be obtained in the case of higher draw down ratio. For the film of C25 M that has high value of draw down ratio, the very large A_y/A_x value suggests that draw down ratio is a dominant factor to influence the axial orientation to the y -axis.

From the comparison between the entire column of blow up ratio and A_x/A_0 , it can be seen that A_x/A_0 becomes larger with increasing of blow up ratio. Similar result can also be found by comparing the entire column of draw down ratio with A_y/A_0 . These two relationships suggest that blowing up contributes to the chain orientation in TD and drawing down contributes to the chain orientation in MD.

CONCLUSION

The schematic representation for the two modes of orientation for flat and tubular films is shown in Figure 13. There is an uniplanar orientation mode in both

the flat and tubular films and the $(1\bar{1}0)$ lattice planes preferentially orientate towards the macroscopic film surface.

For flat films, the (110) plane is almost unoriented with respect to the casting direction (MD). Polymer chain orientation is predominantly in the xy plane. Within this plane very little preferential x or y orientation exists. The uniplanar orientation of cellulose chain to the film surface increases when the casting speed increases.

For tubular films, the (110) planes have preferential axial orientation with respect to the machine direction. With increasing blow up ratio, both the axial orientation and the crystallinity of tubular films increase. With increasing draw down ratio, the axial orientation increases while the crystallinity has no obvious change. The uniplanar orientation of cellulose chain with respect to the surface increases with the blow up or draw down ratio. Blowing up contributes to the molecular orientation in the transverse direction and drawing down contributes to the molecular orientation in the machine direction.

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