

Crystallization, Orientation Morphology, and Mechanical Properties of Biaxially Oriented Starch/Polyvinyl Alcohol Films

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ABSTRACT: Biaxially oriented starch/polyvinyl alcohol (PVA) films were prepared by stretching starch/PVA blend precursor films that were fabricated by extrusion casting via a twin-screw extruder. Investigations on crystallization, orientation morphology, and mechanical properties of extrusion cast and stretched starch/PVA films were carried out by using differential scanning calorimetry, scanning electron microscope, wide angle X-ray diffraction (WAXD), and tensile testing. The fresh extrusion-cast starch/PVA films, which were almost amorphous, can crystallize spontaneously when aged at room condition. A good compatibility between starch and PVA was obtained by extrusion-casting technology. The well-developed mo-

lecular orientation, which did not occur along the machine direction during the extruding process, was observed in stretched film samples. Stretching unaged films can induce crystallization and the orientation of crystalline structures during stretching, resulting in the changes in diffraction peaks of WAXD patterns. The effect of stretch ratio and the orientation distribution in the plane of the film on mechanical properties of stretched films was studied, and the equal biaxially oriented films were found to exhibit in-plane isotropy. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 523–530, 2008

Key words: PVA; starch; crystallization; orientation

INTRODUCTION

Over the last few years, there has been a renewed interest in biodegradable plastics and plastics made from annually renewable natural polymers.¹ Of these materials, starch is the most attractive candidate because of its low cost, easy availability, and high production from annually renewable resources.² However, packaging films composed entirely of starch lack the strength and rigidity to withstand the stresses to which many packaging materials are subjected, and so the extensive application is limited.^{3–5} Therefore, many attempts^{6–10} have been made to overcome these problems by blending starch with synthetic polymers. Much interest lies in blending starch with polyvinyl alcohol (PVA) as a hydrophilic, biodegradable, and crystalline polymer.

Some researches^{10–14} have been done on the properties of starch/PVA films fabricated by solution casting, spray coating, or blow extrusion. A ubiquitous problem is that the properties of the blend films deteriorate as starch proportion in the film formulation increase, particularly in mechanical and optical

properties. This might result from a poor compatibility between starch and PVA¹ and phase separation during film preparation.⁸ Therefore, the ways for increasing the compatibility between starch and PVA have been paid widely attention, including adding plasticizers to the blends,^{15,16} crosslinking by UV radiation or crosslinking agents,^{17,18} chemical grafting,¹⁹ and physical blending²⁰ modifications. They have been proved as effective measures to improve the properties of starch/PVA films.

In this study, instead of the conventional solution casting, spray coating or blow extrusion, starch/PVA mixture was melt blended through a twin-screw extruder to prepare extrusion-cast starch/PVA films (precursor films) and then the precursor films were biaxially stretched at a certain temperature to obtain the final film products for packaging applications. The crystallization, orientation morphology, and mechanical properties of either the unstretched or the stretched extrusion-cast starch/PVA films were investigated.

EXPERIMENTAL

Materials

The raw materials used in our experiments are available as commercial products. The potato starch, a

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white fine powder with an amylose content of 25%, was purchased from Qingdao Zhengtian Food Co., Ltd., China. PVA-1788 was supplied by Beijing Organic Chemical Factory (China) with a hydrolysis degree of 87–88% and the polymerization degree of 1700. The glycerol (purity = 99%) was used as a plasticizer and supplied by Shanghai Jieren Chemical Co., Ltd., China.

Films preparation

The blend containing 35% potato starch, 15% PVA, 35% distilled water, and 15% glycerol was chosen to make films. Water and glycerol were utilized as plasticizers to improve the brittle of starch.^{21,22} The calculated amounts of distilled water and glycerol were first mixed, and the mixture was slowly added to the mixture of starch and PVA at room temperature with stirring. The blend was continuously stirred for 10 min and then immediately sealed in glass containers. Ten hours were needed to ensure that the liquid phase was completely absorbed by the solid phase. The precursor film was prepared via a twin-screw extruder ($\Phi = 20$ mm, $L/D = 29$) equipped with a 160 mm wide sheet casting T-die head. The melt temperature at the die was controlled at 90°C, and the screw speed was 100 rpm. The precursor film was rapidly quenched on a chill roll, whose temperature was maintained at 15°C with the help of a water circulating temperature control unit. To prevent orientation into the machine direction (MD), the ratio between the extrusion speed and the winding speed by a cooling roll was fixed at 1. The precursor film was cut in the size of 100 mm \times 100 mm, and oriented into MD at the speed of 1000%/min using the lab stretcher and then oriented into the transverse direction (TD) at 60°C. The stretch ratio ($\lambda_{MD} \times \lambda_{TD} = (L_{MD}/L_{MD}^0) \times (L_{TD}/L_{TD}^0)$) was associated with the changes in length (L) from the initial value (L^0) along two principal stretch directions (MD and TD). The stretched films were heat-set for 2 min under tension at the stretch temperature, cooled down below their glass transition temperature with an air blower, and then taken out from the clamps. The last step was important to maintain the dimensions of the stretched films.

Morphological analysis

To analyze the morphology of the precursor film and the stretched film, the samples were fractured in liquid nitrogen and the fracture surfaces were sputter coated with gold–palladium alloy. The morphology was observed using a scanning electron microscope (SEM, JSM-6360LV, Japan).

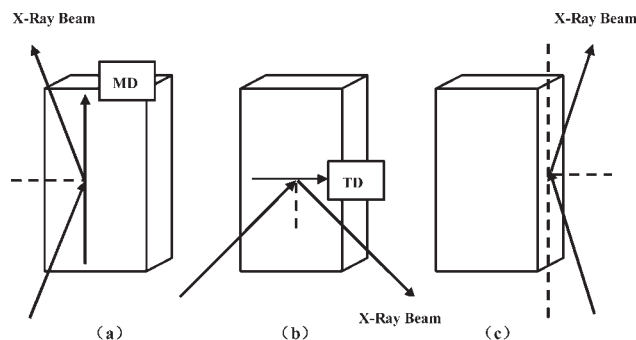


Figure 1 Scheme of three incidence directions in WAXD experiments on the oriented film samples.

Thermal measurement

Differential scanning calorimetry (DSC) was utilized for determining various thermal properties of extrusion-cast starch/PVA films. Heating scans were made from 30 to 250°C at a rate of 20°C/min in nitrogen atmosphere by the model STA-449C DSC (NETZSCH Company, Germany).

Wide angle X-ray diffraction

The crystallization of PVA resin, starch, and starch/PVA film samples were investigated by means of wide angle X-ray diffraction (WAXD) technique at room temperature. X-ray patterns were obtained by WAXD diffractometer 2 θ scans using a Rigaku X-ray generator model. The Cu K α X-ray radiation ($\lambda = 1.5406$) was obtained at 40 kV and 200 mA and filtered by reflecting X-ray beam on the inserted crystal monochromator. Geometrical arrangement applied in our WAXD experiments was symmetrical reflection. The thin film was stacked into a suitable thickness with careful attention given to their directionality. For unoriented samples, crystallinity was determined by integration of the areas under the curve. For oriented film samples, experiments of three orthogonal incidence directions were done and the specific direction was showed in Figure 1. The preparation of the film sample tested in the (C) direction included following steps: (1) the stretched film was folded over two-hundred layers and then compacted and fixed with clamp to form a film block (about 1 cm thickness), (2) the test side of the film block was cut into a formal plane and set in the sample frame.

Water content

The weighted fresh film sample was put into an air-blast oven at 100°C until its weight did not change anymore. The percent weight loss obtained by analytical balance was the water content of the fresh precursor film. The water contents of aged films

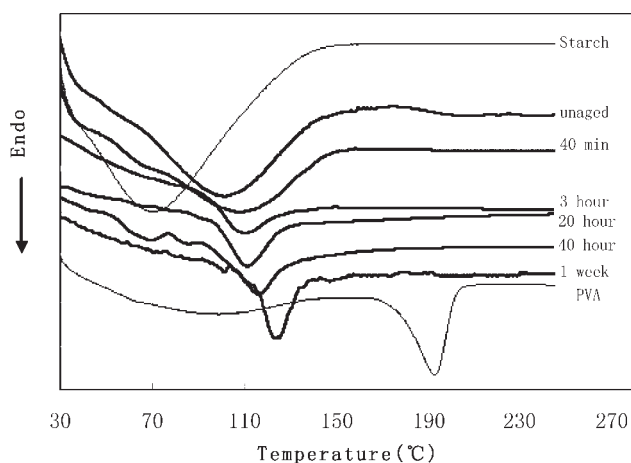


Figure 2 DSC thermograms of starch and PVA resin and unstretched extrusion-cast starch/PVA film versus aging time.

were calculated by the weight loss of film samples during the aged time.

Mechanical properties

Mechanical properties of starch/PVA film samples were measured by means of Instron 1185 tensile tester at room condition (22–23°C and 22–31% RH). The test samples were cut in the desired directions and then tested at a strain rate of 50 mm/min. At least three samples were tested for each condition and direction, and the results were averaged.

RESULTS AND DISCUSSION

Stretchability of extrusion-cast starch/PVA films

The extrusion-cast starch/PVA film which was obtained by extruding at about 90°C with a 15°C chill roll was successfully biaxially stretched into films up to a stretch ratio of $\lambda_{MD} \times \lambda_{TD} = 3.0 \times 2.0$ without showing necking propagation when they were not aged. However, films aged at room condition (22–23°C and 22–31% RH) for more than 1 day showed low elasticity and could not be stretched to high extension ratios. In general, crystallization is one of the most possible reasons to deteriorate the ductility of extrusion-cast films and make them more rigid.²³ Therefore, crystallization behaviors of the extrusion-cast starch/PVA film during aging were measured.

Aging of the extrusion-cast film

The unstretched extrusion-cast film ($\lambda_{MD} \times \lambda_{TD} = 1.0 \times 1.0$) was aged at room conditions to investigate changes in thermal properties and crystallization behaviors with respect to the aging time. Figure 2 showed the DSC thermograms of starch and PVA

resin and both the unaged and aged extrusion-cast films.

From the thermograms exhibited in Figure 2, we can see that pure PVA had a T_m of 192.1°C, but starch did not have a definite T_m and just showed a broad endothermic peak mainly assigned to the gelatinization from 30°C up to 150°C.²⁴ However, in blended starch/PVA films the characteristic peaks of starch and PVA disappeared because their original crystals or gel structure was broken because of the present of great amount of plasticizers and strong shear provided by twin-screw extruder.^{24,25} With regard to the single endothermic peak newly appeared in the curves of unaged and aged films, there was different explanation. It is considered that the rather broad endothermic peaks of the fresh extrusion-cast film and films aged for a shorter time did not belong to melting peak, and the reason was that the fresh extrusion-cast film and films aged for a shorter time were being in a highly amorphous state, which will be verified by the following WAXD analysis. Therefore, those broad peaks were basically assigned to volatilization of water, because there was still some free water in those films according to the data in Table I. When the aging time was more than 20 h, the films exhibited narrower range of endothermic peaks. From Table I we can see that water content in the film aged for more than 20 h was almost constant, which meant that the effect of volatilization of free water on the peak shape was very little; therefore, the narrower peaks should be mostly reflected to the melting of crystallites. The similar aging behavior has been observed with extrusion-cast PVA films and PVA hydrogels.^{26,27}

To research the change of microstructure of films during aging, WAXD experiments on unaged and aged films were carried out. From Figure 3, we can see that the WAXD patterns of both unaged film and the film aged for 3 h showed an obvious amorphous diffusion peak, which was consistent with the fact that the unaged precursor film and films aged for a short time did not exhibit endothermic peaks of crystallites melting in Figure 2. However, with the

TABLE I
Water Content and Melting Temperature of the Unaged and Aged Starch/PVA Extrusion-Cast Films

Samples	Water content (%)	Melting temperature (°C)
Mixed material	35.0	–
Fresh precursor film	20.7	–
Aged film		
40 min	18.2	–
3 h	16.9	–
20 h	15.4	111
40 h	15.1	116
1 week	15.0	123

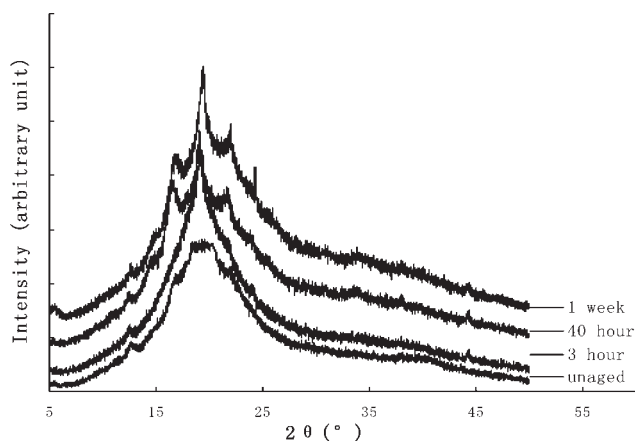


Figure 3 WAXD patterns of unaged and aged starch/PVA extrusion-cast films.

aging time, a group of sharp crystalline diffraction peaks appeared in WAXD patterns of the films aged for a long time and the peak intensity are increasing. This phenomenon approves the formation of some ordered crystalline structure in film samples during aging and also explains why the narrower peaks in DSC thermograms of the films aged for over 20 h should be assigned to the melting of crystallite.

These DSC and WAXD results indicate that the extrusion-cast starch/PVA film can gradually crystallize during storage at room condition even if it has been rapidly quenched into a highly amorphous state. Crystallization would make the chains have lower free volume and less molecular movement during stretching process,²³ and therefore, the stretchability of aged films decreased.

We can also see from Figure 2, for aged extrusion-cast starch/PVA films, the melting peak became narrower and narrower with respect to the aging time. The endothermic peak was in the range from 95 to 124°C for the film aged for 20 h and from 121 to 135°C for the film aged for 1 week. The sharpening phenomenon of the melting peak with respect to the aging time maybe result from the presence of better-defined crystals and the decrease of the distribution width of the crystallite sizes.²⁶

In addition, as shown in Figure 2 and Table I, on aging, the endothermic peaks grew and shifted toward higher temperatures from 111 to 123°C. The increase of the melting temperature of the aged film with increasing aging time can be interpreted in terms of morphological changes mainly involving a growth of the dimensions of crystallites.²⁸

Blend morphology and effect of stretch ratio

The morphology of a starch/PVA blend precursor film was shown in Figure 4. The precursor film was

not stretched and the thickness was 180–200 μm. Figure 4(a) was the cross-sectional view of the precursor film and Figure 4(b) was the perpendicular sectional view to Figure 4(a). It can be found that there was no much difference in both patterns. It means that no orientation occurred along the MD during the extruding process because the ratio between extrusion and winding speed was fixed at 1. This morphology may be advantageous to the starch/PVA precursor film for deforming into platelets when two dimensionally stretched.²⁹

In addition, we can find that, from Figure 4, unlike the reported fact that phase separation occurred during film preparation by solution casting and spray coating technology,^{1,8} There is no phase separation observed in the present study, indicating a good compatibility between starch and PVA by extrusion-casting technology. This result can be also verified by the DSC thermograms in Figure 2. As we can see, either the unaged or aged starch/PVA extrusion-cast film just exhibited a single melting temperature unlike those immiscible blends which show two distinct melting temperatures. The compatibility of starch and PVA was reported by Ke and Sun.²⁰ The

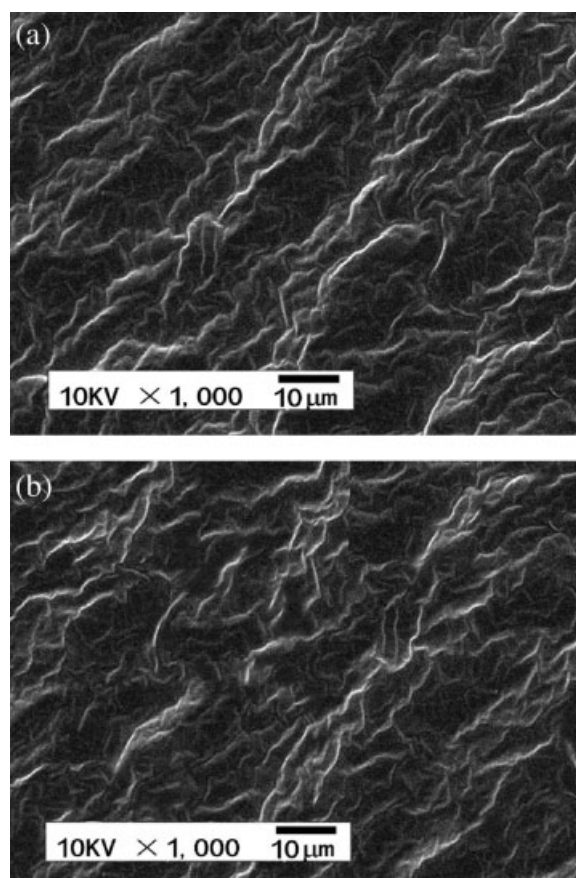


Figure 4 SEM photomicrographs of the fracture surface of the starch/PVA blend precursor film: (a) transverse sectional view of the precursor film; (b) perpendicular view to (a).

good compatibility may be attributed to the facts that the hydrogen bond interactions between starch and PVA^{30,31} and a twin-screw extruder can provide the mixture with high temperature, high pressure, and strong shear during extrusion casting,³² and make the starch and PVA blend in molecular level.

Figure 5(a,b) illustrated the morphology of the starch/PVA films stretched from a lab stretcher with the different stretch ratios. The thickness of the stretched film in Figure 5(a) was 90–100 μm with the stretch ratio of $\lambda_{\text{MD}} \times \lambda_{\text{TD}} = 2.0 \times 1.0$, and the thickness of the stretched film in Figure 5(b) was 60–65 μm with the stretch ratio of $\lambda_{\text{MD}} \times \lambda_{\text{TD}} = 3.0 \times 1.0$. Comparing Figure 4 with Figure 5, we can find that obvious orientation occurred in stretched films, particularly in Figure 5(b) which represented a well-developed fibrous morphology. This phenomenon confirms that the film is deformed from random to fibrous morphology during stretching, and the fibrous arrangement in one stretch direction is more and more ordered with the increasing stretch ratio in the same direction.

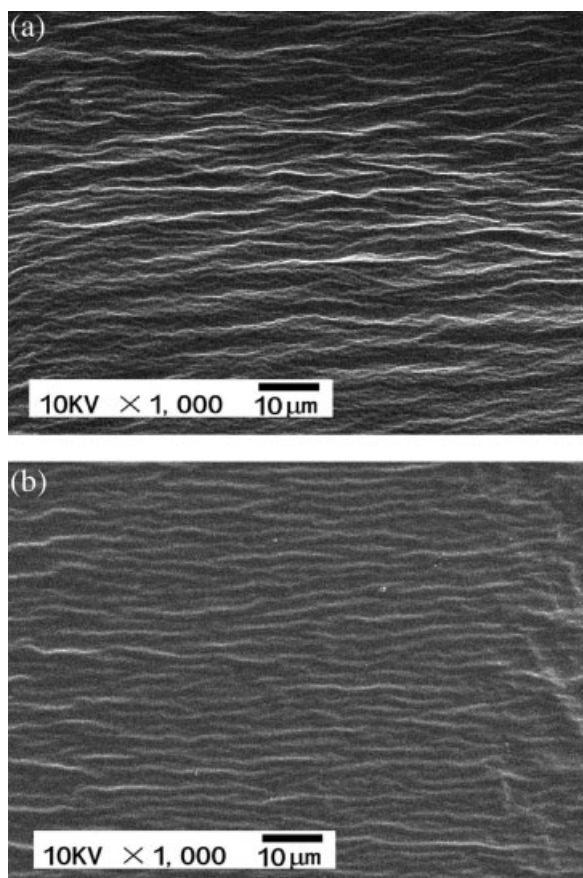


Figure 5 SEM photomicrographs of the fracture surfaces of the stretched starch/PVA films: (a) $\lambda_{\text{MD}} \times \lambda_{\text{TD}} = 2.0 \times 1.0$; (b) $\lambda_{\text{MD}} \times \lambda_{\text{TD}} = 3.0 \times 1.0$.

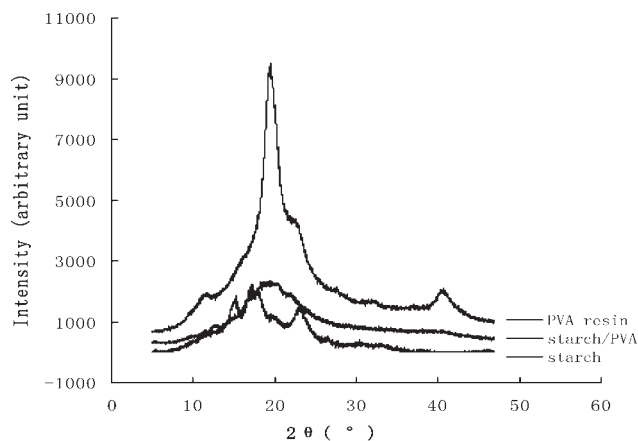


Figure 6 X-ray diffractograms of PVA resin, potato starch and the unaged starch/PVA precursor film.

WAXD characterization and effect of orientation

X-ray diffraction analysis was used to study the crystallization behavior of starch, PVA resin, and the unstretched or the stretched extrusion-cast starch/PVA films.

The X-ray diffractograms of PVA resin, potato starch, and the unaged starch/PVA precursor film were presented in Figure 6. Crystallinity and X-ray diffraction data were shown in Table II. From Figure 6, it can be known that the sharp crystalline diffraction peak of PVA appeared mainly at $2\theta = 19.74^\circ$ and those of starch appeared at $2\theta = 14.68^\circ$, 17.41° , and 23.21° , and the data of their other small diffraction peaks were listed in Table II. It is well known that both PVA and starch are the polymers containing many hydroxyl groups, so they have the higher crystallinity of 37.8 and 26.8%, respectively, which were evaluated by integration of the areas under their WAXD curve. Comparing the diffractogram of starch/PVA unaged precursor film with those of starch and PVA, we can find that those inherent diffraction peaks of PVA and starch had disappeared in WAXD of the precursor film after the processes of extrusion casting and quenching. The diffractogram of the precursor film just showed a wide amorphous diffusion peak and its estimated crystallinity value was less than 4%. The crystalline structure of PVA and starch in the precursor film was destroyed and transferred into amorphous structure, on one hand, because the hydroxyl bonds between starch and PVA were broken down during the process of plasticizing and extruding, on the other hand, the amylopectin content of the starch increased intermolecular distance and decreased the chance to form hydroxyl bonds between starch and PVA and between starch themselves.³²

Changes of 2θ in the WAXD patterns of the starch/PVA films with respect to stretch ratio were

TABLE II
WAXD Data and Crystallinity of PVA Resin, Starch, Aged Film, and the Unstretched and Stretched Starch/PVA Films

Samples	2 θ values (°)						Crystallinity X_{XRD} (%)
	11–13	14–16	17	18	19	21–23	
PVA	11.42 (7.74 Å)	–	–	–	19.74 (4.49 Å)	22.56 (3.94 Å)	37.8
Starch	–	14.68 (5.99 Å)	17.41 (5.14 Å)	18.09 (4.92 Å)	19.75 (4.46 Å)	23.21 (3.83 Å)	26.8
Fresh precursor film	12.67 (6.98 Å)	–	–	–	–	21.88 (4.06 Å)	<4.0
Films aged for 1 week	12.31 (7.06 Å)	16.45 (5.38 Å)	–	–	19.42 (4.57 Å)	22.02 (4.03 Å)	–
Starch/PVA	–	–	–	–	–	–	–
$\lambda = 1.5 \times 1.0$	11.96 (7.39 Å)	–	–	–	19.87 (4.46 Å)	23.20 (3.83 Å)	–
Stretched film	–	–	–	–	–	–	–
$\lambda = 3.0 \times 1.0$	11.20 (7.89 Å)	15.77 (5.62 Å)	–	–	19.32 (4.59 Å)	22.63 (3.93 Å)	–
$\lambda = 2.0 \times 2.0$	–	–	–	–	19.56 (4.53 Å)	–	–

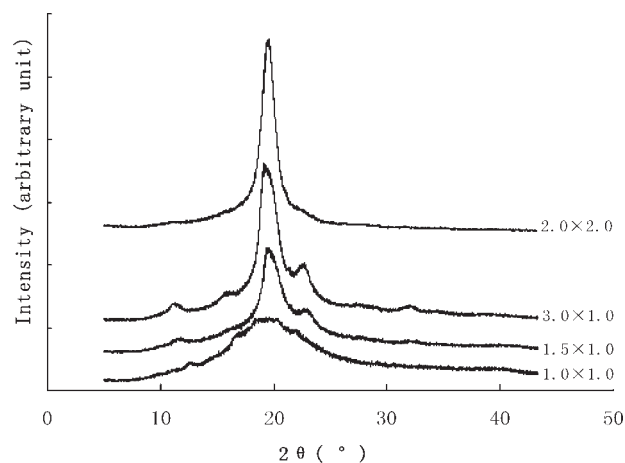


Figure 7 X-ray diffractograms of stretched starch/PVA films with different stretch ratio.

demonstrated in Figure 7. Firstly, we can see that a main crystalline diffraction peak, which disappeared in the precursor film, appeared at about $2\theta = 19^\circ$ for each stretched film sample and it corresponded to a d -spacing of about 4.50 Å. From Table II, this dimension did not change significantly for the stretched films. In addition, there were also a few small diffraction peaks that appeared in the film samples stretched just in MD, and the intensity of all these diffraction peaks increased with increasing λ_{MD} . This result proves that stretching behavior also can induce crystallization of starch/PVA films.

Make a comparison between WAXD patterns of aged and stretched blend films combining with the diffraction data in Table II, we can find that peak positions of the aged film and the stretched film in WAXD pattern were almost similar and just peak height was different. This result confirms that the ordered crystalline structures resulted from aging and stretching is similar.

An interesting phenomenon was that there was an obvious difference between the X-ray diffractograms of the film uniaxially stretched and that of the film biaxially stretched. Except for the main crystalline diffraction described earlier, no new peaks appeared in the WAXD of the biaxially stretched film ($\lambda_{\text{MD}} \times \lambda_{\text{TD}} = 2.0 \times 2.0$) and the relative intensity of the only peak was fairly high.

In general, the change of diffraction peaks might result from orientation of crystalline structures. Therefore, to study the effect of the orientation of crystalline structures on diffraction peaks in X-ray diffractogram, WAXD experiments were done on the uniaxially stretched film ($\lambda_{\text{MD}} \times \lambda_{\text{TD}} = 3.0 \times 1.0$) in three orthogonal incidence directions showed in Figure 1. From Figure 8 we can see that the WAXD patterns obtained from (a) and (b) directions were almost superimposed, the possible reason is that the crystalline structure is planar orientated relative to

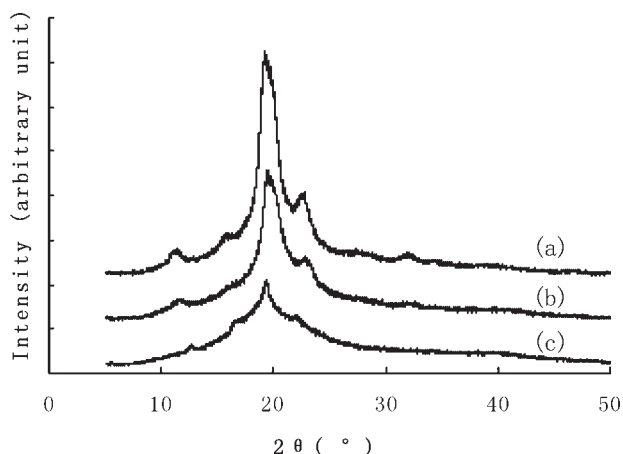


Figure 8 WAXD patterns of the stretched film sample ($\lambda_{MD} \times \lambda_{TD} = 3.0 \times 1.0$) in three orthogonal incidence directions.

the plane formed by MD and TD. However, the WAXD pattern obtained from (c) direction was different to those obtained from (a) and (b) directions,

and the peak height was obvious diverse. This result reflects that the orientation of crystalline structures during stretching result in the changes in diffraction peaks of WAXD patterns.

Mechanical properties

Figure 9 presented mechanical properties of the starch/PVA precursor film and the oriented films which were stretched at 60°C by various stretch ratios. As shown in Figure 9, the tensile strength for MD tests rose and the elongation at break for the same direction dropped rapidly with increasing λ_{MD} , and the mechanical properties in TD tests with increasing λ_{MD} behaved in an opposite manner to those of the MD tests. The earlier phenomenon shows that the molecular orientation in one direction would partly relax when the degree of orientation in the other direction increases.

To ascertain the effect of the orientation distribution in the plane of the film on mechanical properties of stretched films, four different directions (0,

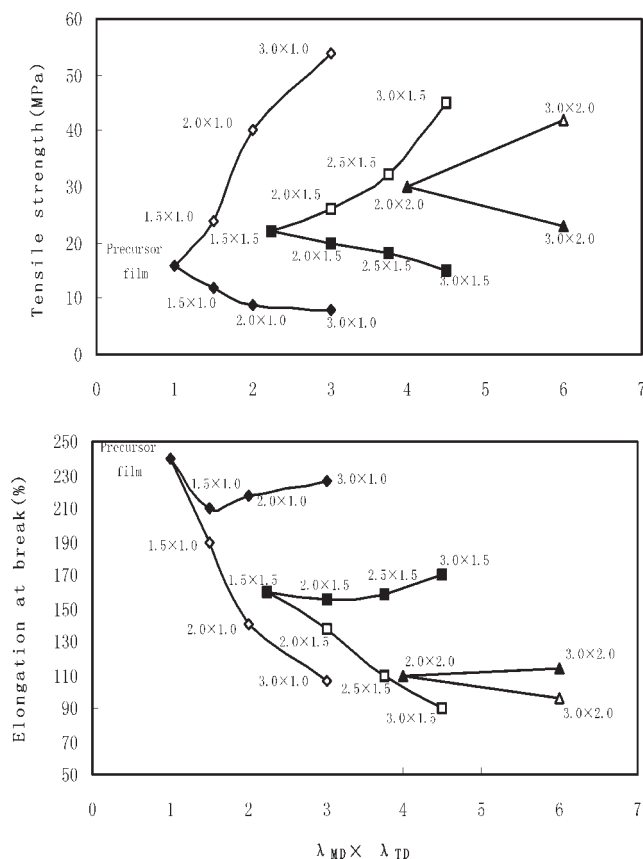


Figure 9 Mechanical properties (tensile strength (top) and elongation at break (bottom) in terms of stretch ratio ($\lambda_{MD} \times \lambda_{TD}$); open symbols are the test results along the MD while closed symbols are those along the TD) of starch/PVA films which are stretched at 60°C.

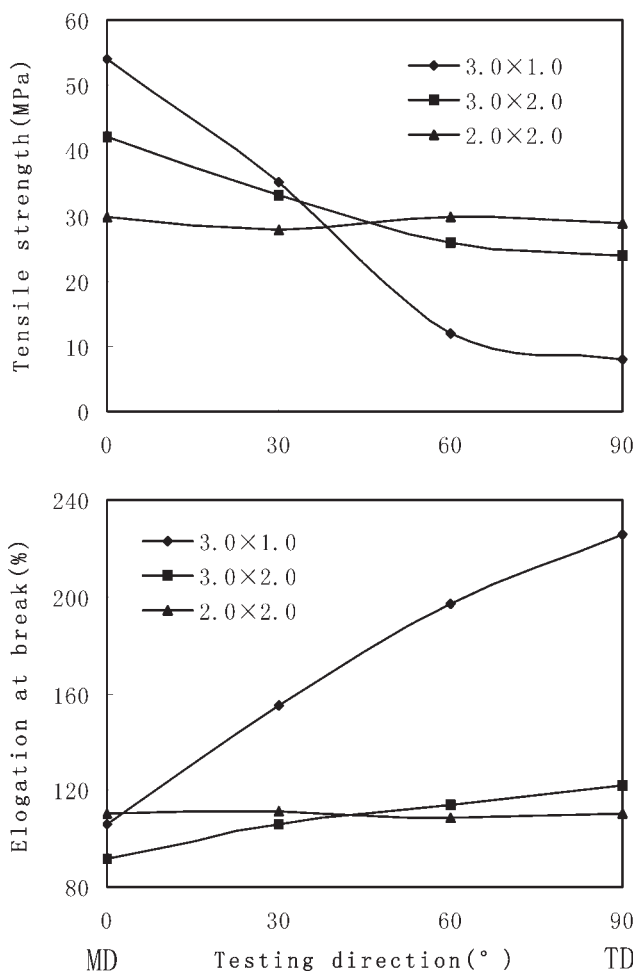


Figure 10 The development of in-plane tensile strength (top) and elongation at break (bottom) anisotropy in stretched starch/PVA films.

30, 60, and 90°) in the plane of the stretched film were chosen to perform tensile tests. Figure 10 shows the variety of tensile strength, and elongation at break in different directions. We can find that the tensile strength was decreasing and the elongation at break was increasing from MD to TD in 3.0×1.0 and 3.0×2.0 stretch condition. While in 2.0×2.0 condition, both tensile strength and elongation at break stayed almost constant in all directions. It indicates that the more different the stretch ratio between MD and TD is, the more obvious the in-plane anisotropy of stretched films is. If the film is stretched under equal biaxial conditions, the sample obtains balanced properties in all directions indicating in-plane isotropy.

CONCLUSIONS

The starch/PVA films are prepared by means of extrusion casting and biaxially orientation process and the crystallization, orientation morphology, and mechanical properties of films have been studied before and after biaxial stretching.

The unstretched extrusion-cast starch/PVA film can crystallize spontaneously during aging at room condition and this crystallization behavior significantly decreases the stretchability of aged films. The melt blending process makes the starch and PVA in precursor film disperse in molecular level and form a flexible and homogeneous film. No molecular orientation occurs along the MD during the extrusion-casting process, but the higher stretch ratio can lead to crystallization and a well-developed molecular orientation. Mechanical properties (tensile strength and elongation at break) are closely dependent upon the stretch ratio, and the anisotropy of orientation is also an important factor which would influence the mechanical properties of biaxially oriented starch/PVA films.

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