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Microstructure and mechanical properties of orientated thermoplastic starches

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Effect of orientation on microstructure and mechanical properties of thermoplastic starches with different amylose/amylopectin ratios was studied to understand the relationship between structure and properties in starch-based materials. Hydrogen bonds and the highly branched microstructure in amylopectin resist the orientation of the polymer chains. The unique microstructures of amylopectin form gel-balls and super-globes after gelatinization. A gel-ball contains mainly the chains from same sub-main chain in amylopectin, and remains in regular pattern and keeps a certain "memory". The gel-balls and super-globes can be deformed under shear stress. However, the deformation does not alter the orientation ofthe polymer chains inside the gel-balls significantly. Orientation increases both modulus and yield stress but decreases the elongation, which is mainly contributed to by the orientation of amorphous phase. The oriented super-globe has large interior stress after retrogradation (crystallization) that results in micro-cracks and poor mechanical properties. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

The development and production of biodegradable thermoplastic starches have been spurred by a growing interest in a solution of the environmental problems and application of renewable resources. Furthermore, the unique microstructures of different starches can be used as an outstanding model system to add our conceptual approach of understanding the relationship between structure and properties in polymers.

Synthetic polymers have been developed to the point that you can design microstructures and control molecular weight and molecular weight distribution. However, the mesoscopic structure within the starch granule has evolved to suit the plant's own needs and is much more complex [1]. The starch granule is a heterogeneous material. Chemically, it contains both amylose and amylopectin. Physically, it has both amorphous and crystalline regions. Most granular native starches are a mixture of amylose, a linear structure of alpha-1,4 linked glucose units and amylopectin, a highly branched structure of short alpha-1,4 chains linked by alpha-1,6 bonds. Most native starches are semi-crystalline with a crystallinity about 20–45% [1, 2]. Amylose and the branching points of amylopectin form the amorphous regions. The short branching chains in the amylopectin are the main crystalline component in granular starch. The crystalline regions are present in the form of double helices with a length of approximately 5 nm [3]. The amylopectin segments in the crystalline regions are all parallel to the axis of the large helix. The molecular weight of amylopectin is about 100 times larger than that of amylose. The ratio of amylose/amylopectin depends upon the source of the starch and also can be controlled by extraction processing. Starch granules also contain small amounts of lipids and proteins.

The orientation of polymer materials acts an important role in determining their performance, ranging from mechanical to optical characteristics. Products with "designed-in" orientation are increasingly important in the polymer industry. They include filaments with uniaxial orientation and films and bottles with biaxial orientation. Uniaxial orientation has a strong influence on mechanical properties. For example, the tensile stress of polypropylene could increase more than 10 times after orientation [4].

In this work the effect of orientation on the microstructure and mechanical properties of thermoplastic starches with different amylose/amylopectin ratios has been studied. Tensile properties of extruded sheets in different directions with various degrees of orientation were measured. Microstructure, in particular the orientation and crystallization of the materials were studied using WAXS, DSC and ESEM. A super-globe model was established to explain the relationship between the microstructure and mechanical properties.

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TABLE I List of materials and their characterization

Starches	Water content (%)	Amylose content (%)	Molecules weight (MW)
Waxy	12.9	0	20,787,000
Corn	12.7	26	13,000,000
G50	12.3	50	5,115,000
G80	12.2	80	673,000

2. Experimental

2.1. Materials and orientation control

Corn starch with different amylose/amylopectin ratios was used in the experimental work as model materials. All the starches are commercially available and were kindly supplied by Goodman Fielding (Australia). Table I lists the starches and their characterization. G50 and G80 are both corn starches with amylose content of 50 and 80 respectively. In all the formulations, weights of starch were corrected for moisture and given on a dry weight basis.

Starch and water were pre-mixed in a ratio of 77:23 (w:w) using a 10 liter laboratory scale high speed mixer (HSM-10) for 5 min, then extruded using a twin extruder (Theysohn 30) at the highest setting up temperature 175°C. A die width at 300 mm was used. The temperature of the die was set at 110°C. The sheets were pulled out of the die using a three roller system with positive tension. The degree of orientation of the sheets was controlled by the speed of drawing of the rollers in front of the die. The thickness of the sheets varied from 0.15–0.35 mm depending on drawing speed. The moisture content in the extruded sheets is about 13–14% after loosing some water during extrusion.

2.2. Specimen preparation and mechanical properties measurement

Specimens were cut from the extruded sheets according to ASTM method D638-86 (5 mm width of narrow section, and 25 mm gauge length) from two directions: parallel and cross extrusion direction. The cut specimens were equilibrated and stored under 62% humidity conditions and 23°C for 48 h. Mass variation of the specimens during storage was also recorded.

Tensile tests were performed in accordance with ASTM standard on an Instron 100 apparatus using a crosshead speed of 10 mm/min. All data was recorded and processed through a computer with Instron Instrument software.

The size variation of the sheets equilibrated under the same conditions was recorded. The ratio of the variation was calculated on the base of measuring 20 × 20 cm sheets.

2.3. Microstructure characterization and thermal behavior

Wide-angle X-ray scattering (WAXS) was used to study the orientation and crystallinity of materials. WAXS patterns of the materials were detected using a Siemens D500 diffractometer, with Cu K_α radiation monochromatised with a graphite diffracted beam monochromator. The generator was operated at 45 KV and 30 mA.

A Perkin-Elmer Pyris-1 DSC apparatus was used to study the thermal behavior such as gelatinization and melting temperature. Measurements were made on approximately the same mass of starch (about 3 mg on dry base) which was equilibrated with an approximate amount of distilled water in a stainless steel high-pressure DSC pan, result in a starch/water ratio of 30/70. The detailed method of sample preparation has been described in a previous paper [5].

To investigate the failure micromechanisms of the materials, the fracture surfaces of the broken samples after tensile testing were examined using an environmental scanning electron microscope (ESEM) (Philips, The ElectroScan ESEM 20A). The environmental scanning electron microscope has the ability to image both dry and hydrated materials, without the need for a conductive coating as required in a conventional SEM [6].

3. Results and discussion

Table II provides some indications of processing behavior. It is seen that both torque and die pressure were increased with increasing amylose content. Similar results were also observed by van Soest and Essers [7]. The sheets of amylopectin materials are transparent suggesting that the granular structures were completely destroyed during extrusion. The materials became less transparent with increasing amylose content indicating more heterogeneous or crystalline parts in the materials. As mentioned before, the degree of orientation is controlled by the drawing speed in the front of the die. Since the viscosity of starch-based materials is much higher but melting stress is much lower than that of conventional polymers (e.g., polyolefin), the achievable drawing speed for the starch-based materials is not as high as for the polyolefins (such as PP and PE). The starch sheet will break if the speed is not reduced.

The shear and extensional flows in polymer processing have an effect on the microstructure of the melt. This, at the molecular level, may result in the entanglements between molecules, elongation of parts of the molecules occurs, gives rise to tensile stress in the melt. The orientation is greatest in the products where the polymer solidifies while the stresses that shape the melt are still acting. During the extrusion the die temperature was controlled at 110°C which is below the melting temperature of starches [5, 7]. That could create large shear stress and orientation.

Table III lists the mechanical properties of various extruded sheets under different drawing speeds. The mechanical properties of the sheets cut from parallel and cross-extrusion were measured respectively. The

TABLE II Effect of amylose/amylopectin ratio on processing behavior

Materials	Waxy	Corn	G50	G80
Die pressure (Bar)	65	78	88	97
Torque (%)	36	42	73	87

TABLE III Effect of orientation on mechanical properties

Materials	Speed (cm/min)	Thickness (mm)	Direction (extrusion)	Modulus (Mpa)	Yield st. (Mpa)	Elongation (%)
Waxy	50	0.33	Parallel	1251 ± 72	10.6 ± 0.87	10.3 ± 1.14
			Cross	1172 ± 68	10.5 ± 0.43	2.5 ± 0.56
	90	0.27	Parallel	2111 ± 58	14.3 ± 0.53	8.1 ± 0.71
			Cross	2062 ± 81	13.7 ± 0.79	1.7 ± 0.23
	120	0.21	Parallel	2332 ± 132	17.2 ± 0.88	4.6 ± 0.62
			Cross	2222 ± 121	16.5 ± 1.10	2.0 ± 0.19
	150	0.17	Parallel	2404 ± 146	19.8 ± 1.31	3.9 ± 0.31
			Cross	2320 ± 142	19.6 ± 1.27	1.9 ± 0.19
Corn	50	0.32	Parallel	1305 ± 52	11.1 ± 0.54	12.8 ± 0.98
			Cross	1290 ± 61	10.8 ± 0.62	7.5 ± 0.67
	90	0.27	Parallel	2245 ± 88	19.2 ± 0.97	8.6 ± 0.34
			Cross	2125 ± 67	18.8 ± 1.32	2.1 ± 0.11
	120	0.22	Parallel	2245 ± 89	19.2 ± 1.71	5.2 ± 0.29
			Cross	2125 ± 94	18.8 ± 2.11	2.2 ± 0.38
	150	0.17	Parallel	2249 ± 178	19.3 ± 2.81	3.9 ± 0.52
			Cross	2119 ± 290	18.7 ± 2.99	1.7 ± 0.33
G50	50	0.32	Parallel	1814 ± 92	10.9 ± 1.29	12.6 ± 0.49
			Cross	1332 ± 87	10.6 ± 1.12	12.0 ± 0.62
	90	0.26	Parallel	2322 ± 172	11.8 ± 1.35	11.6 ± 1.25
			Cross	2023 ± 224	10.9 ± 1.51	7.5 ± 1.32
	120	0.21	Parallel	2558 ± 541	18.1 ± 1.22	7.5 ± 2.13
			Cross	2246 ± 394	17.5 ± 1.94	7.2 ± 1.92
G80	50	0.33	Parallel	1881 ± 139	14.5 ± 2.30	15.2 ± 1.73
			Cross	1200 ± 119	7.3 ± 2.81	11.9 ± 1.39
	90	0.26	Parallel	2550 ± 392	17.1 ± 3.47	11.8 ± 2.20
			Cross	1503 ± 620	10.6 ± 2.78	7.9 ± 2.28

mechanical testing was carried out after equilibration for 48 h under 62% relative humidity condition. The effect of aging time and conditions on the mechanical properties will be discussed in a separate paper. It is seen that the higher the amylose content, the better the mechanical properties: modulus, yield stress and elongation are increased with increasing amylose content. Similar results have been reported by previous researchers [8–10].

Orientation increased both modulus and yield stress but decreased the elongation. In particular, the elongation on the cross-extrusion direction is decreased significantly for amylopectin rich materials. The interesting phenomena are the effect of orientation on the modulus; yield stress and elongation are dependent on amylose/amylopectin ratio. The differences in modulus and yield stress between the two directions are higher for amylose rich materials; the differences in elongation are higher for amylopectin rich materials. The higher the amylopectin content, the lower the elongation is on the cross-extrusion direction.

The increase in modulus and yield stress by orientation has been observed for many polymer materials. Typical applications are fiber and orientated films. It can be simply explained by the orientation of polymer chain along the drawing direction. The energy of break of polymer chains is much higher than that of deformation. The difference of tensile properties between parallel and cross-extrusion direction in polypropylene (PP) could be as high as 10 times [4]. However, the starch-based materials have not achieved as great a difference as PP. In particular, the difference between the two directions for amylopectin materials is much lower than for most conventional polymers. It needs mentioning that some of increases in the modulus and yield stress is contributed to by the reducing thickness. The effect of thickness on the mechanical properties will not be discussed in this paper, but it is safe to discuss the differences between the two directions.

Table IV shows the size variation of extruded sheets in two directions after aging at 62% relative humidity and 23°C for six weeks at room temperature. It is seen that the sheets have shrunk in two dimensions. The degree of shrinkage is higher in the parallel direction than that in the cross-extrusion direction. The degree of shrinkage increased with increasing degree of orientation. In Comparison with polyolefins, the shrinkage is significant. The degree of shrinkage is slightly higher for the amylopectin rich materials with the same degree of orientation.

It is well known that polymers have high thermal expansion or shrinkage coefficients because the increase in the thermal vibrations with increased temperature

TABLE IV Size variation (%) of extruded sheets with different drawing speeds after aging under 62% relative humidity for 6 weeks at room temperature

		Drawing speed			
Materials	Direction	50 cm/ min	90 cm/ min	120 cm/ min	150 cm/ min
Waxy	Parallel	−1.8	−2.0	−2.5	−2.5
	Cross-section	−1.5	−1.5	−1.7	−2.0
Corn	Parallel	−1.6	−2.1	−2.1	−2.3
	Cross-section	−1.3	−1.7	−1.6	−1.8
G50	Parallel	−1.6	−1.9	−1.9	
	Cross-section	−1.4	−1.6	−1.7	
G80	Parallel	−1.5	−1.9		
	Cross-section	−1.4	−1.7		

is only weakly resisted by the van der Waals bonding between the polymer chains [11]. If the polymer is partly crystalline there is a decrease in the specific volume when the crystallinity increases. The significant shrinkage of starch-based materials was contributed to by two factors: loss of moisture and recrystallization. The degree of recrystallization of amylopectin rich materials increases with increasing time, which results in the creation of significant interior stress during shrinkage. The shrinkage of polymer material is unisotropic if there is molecular orientation present, with the shrinkage coefficient being smaller in the direction that has the greatest fraction of covalent bonding.

The magnitude of the relaxation time depends on the molecular mass and the melt temperature, both of which affect the viscosity. In reality the stress relaxation behavior is more complex. The molecular orientation in the extruded sheet will be greater near the surfaces than at the center because the shear stress and molecular orientation were initially greater and there was less time for relaxation before solidification occurred. The difference in polymer chain orientation between surface and center developed micro-cracks on the surface (see Fig. 1). Similar cracks develop in the less tough glassy plastics (PS and PMMA) have been observed [11]. In the amylopectin rich materials the increase in crystallization with time increases the stress between surface and interior, clearly enhancing the crack development.

The orientation of polymer chain and recystallization were studied by WAXS. Figs 2 and 3 show the various WAXS patterns of waxy and G80 starches under different drawing speeds respectively. In Fig. 2 it is seen that the pure amylopectin materials were amorphous directly after extrusion. The crystallization of the amylopectin was observed after aging the materials for 48 h under 62% relative humidity and achieved constancy after 4 weeks. The B-type crystal structure [1, 12], with a maximum at 16.8° (2θ), indicated they are preferably formed by crystallization of the short outchains of amylopectin. The important point is that the orientation did not make amylopectin chains crystallize and that there is no significant difference between the two directions.

Figure 1 Micro-cracks on the surface of amylopectin rich materials (observed by ESEM).

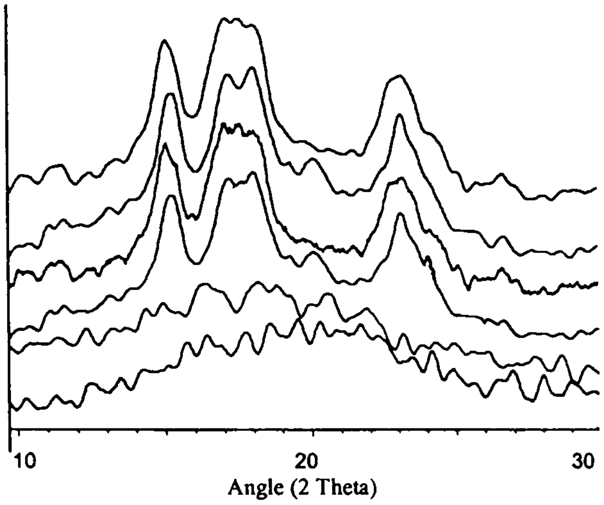

Figure 2 X-ray diffractograms of amylopectin rich materials (waxy) after extrusion with different drawing speeds. From top to bottom:

No.	Drawing speed	Direction	Aging time
1	150 cm/min	parallel	4 weeks
2	150 cm/min	cross	4 weeks
3	50 cm/min	parallel	4 weeks
4	50 cm/min	cross	4 weeks
5	150 cm/min	parallel	quenched
6	150 cm/min	cross	quenched

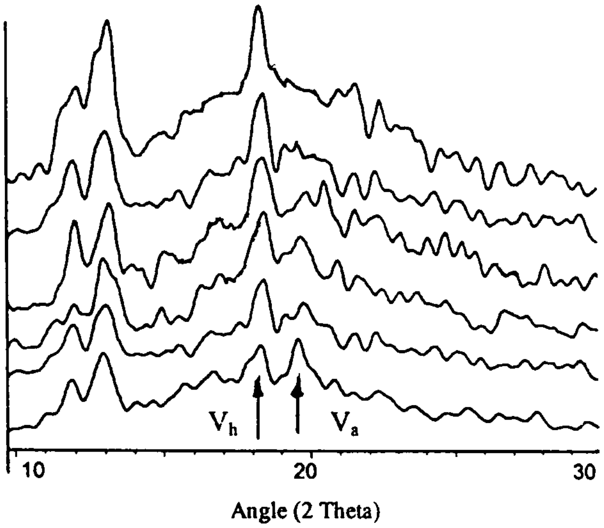

Figure 3 X-ray diffractograms of amylose rich materials (G80) after extrusion with different drawing speeds. From top to bottom:

No.	Drawing speed	Direction	Aging time
1	120 cm/min	parallel	4 weeks
2	120 cm/min	cross	4 weeks
3	50 cm/min	parallel	4 weeks
4	50 cm/min	cross	4 weeks
5	120 cm/min	parallel	quenched
6	120 cm/min	cross	quenched

Fig. 3 shows the diffractogram of amylose rich materials. Three crystal structures [1, 12] identified as B-type, Va-type (13.2° and 20.6°) and Vh-type (12.6°

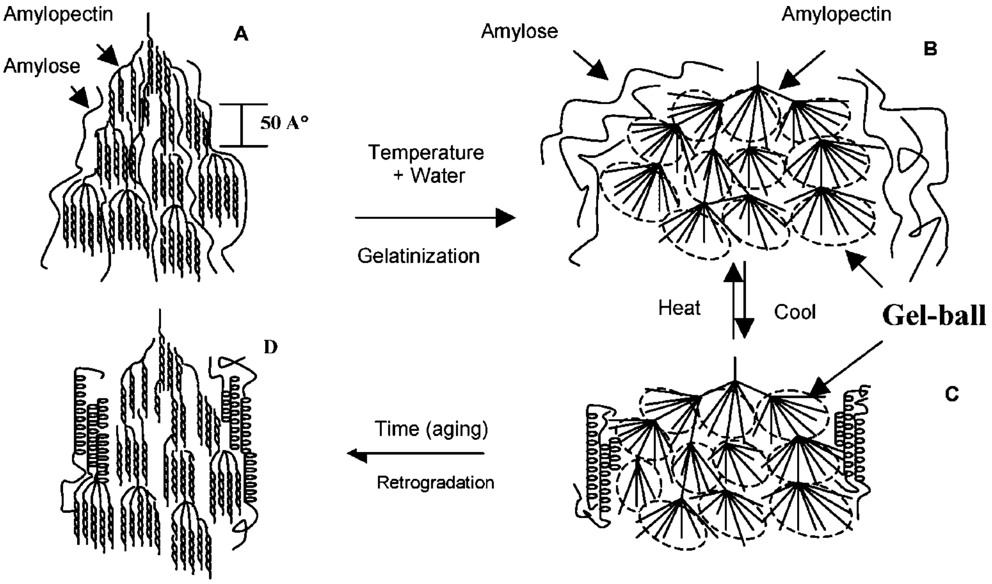

Figure 4 Schematic representation of phase transition for starch during gelatinization and retrogradation.

and 19.4°) were observed. The formation of the Va-type structure was only observed directly after extrusion or in the materials stored at low humidity and below their glass transition temperature. Similar results have been reported by previous researchers [8, 13]. The crystallinity is slightly higher in the parallel direction than in the cross-extrusion direction. The peaks 12.6 and 19.4° slightly increased with increasing drawing speed.

Fig. 4 shows a schematic representation of the phase transition for starch during gelatinization and retrogradation. The well accepted concept of "gelatinization" means destroying the crystalline structure in starch granules (see part a and b in Fig. 4). Previous research on starch suspension (starch/water: 30 w/70 w) has shown that amylose and amylopectin were partly separated during gelatinization [3, 14] because they are incompatible [15, 16]. Less water in the thermoplastic starch systems may disadvantage this separation. On the other hand the shear stress during extrusion may enhance the separation. Due to separation, amylose may be partly leached out of amylopectin. However, most of the amylose will still be present in the amylopectin even in a 10% starch system [17].

After gelatinization through extrusion, the gelatinized amylopectin remains in an amorphous state, initially even though there are still small amounts of ungelatinized parts. The double helix crystalline structure formed by short branch chains in amylopectin has been torn apart during gelatinization. However, these short branch chains still remain in a regular pattern and keep a certain "memory". We consider these short branch chains form gel-balls. A gel-ball contains mainly the chains from same sub-main chain (see part b in Fig. 4). One amylopectin molecule may form a relatively separated super-globe. The molecular entanglements between the gel-balls and super-globes are much less than those between linear polymer chains due to their size and length of the chains (only 4-6 glucose). The V-type single helix crystal was formed directly after extrusion (see part c in Fig. 4), which results in higher modulus and yield stress for amylose rich materials initially. The crystallinity of B-type crystal increases with time (see part d in Fig. 4). D. French [18] has reported that the thickness of crystalline lamellae in native amylopectin and recrystallized amylopectin were the same (about 50 Å), which supports the "memory" existing. This "memory" tends to bring polymer chains back to their original position.

The movement of these gel-balls requires less energy than that of long linear chains, especially when these balls are lubricated by plasticizer (water). The gel-balls and super-globes can be lubricated more efficiently with the same amount of plasticizer as linear amylose. This explains why the amylopectin rich materials have lower viscosity during extrusion (see Table III), and lower modulus and higher elongation initially.

The crystallinity, in particular for the amylopectin rich material, increases with time, which results in an increase in the modulus and decrease in the elongation. The crystallinity of the linear amylose rich material is relatively stable, so the mechanical properties are also stable. During aging the amylose and amylopectin also cocrystallize to form (physical) cross-links between amylopectin and/or amylose [19, 20]. These cross-links can also increase the modulus.

Orientation does not affect the crystallization rate of amylopectin due to the gel-ball and super-globe structures. The gel-balls and super-globes can be deformed under shear stress, orientated along the extrusion (drawing) direction. However, the deformation of the gel-balls and super-globes did not make the polymer chains inside the gel-balls orientated significantly. The recrystallized segments in amylopectin are only parallel to the axis of the large helix. This explains there is no significant difference measured by WAXR. The effect of orientation on the mechanical properties for amylopectin rich materials is mainly contributed to by the orientation of the amorphous parts.

Because of the highly branched microstructure and forming of the gel-ball and super-globe after gelatinization the entanglement of polymer chains in amylopectin-rich materials is much less than that in amylose-rich linear materials. The orientation reduces further the entanglement between the short branches. That can be used to explain the poor mechanical properties, particularly the lower elongation in cross-direction.

4. Conclusion

The degree of orientation for starch-based materials can not be achieved to the same extent as conventional polymers, such as polyolefin due to the physical crosslinks by hydrogen bonds and a higher molecular weight. The gelatinized amylopectin forms unique microstructures: gel-ball and super-globe. Orientation does not affect the crystallization rate of amylopectin because of the gel-ball and super-globe structures. The gel-balls and super-globes can be deformed under shear stress, orientated along the extrusion (drawing) direction. However, the deformation of the gel-balls and super-globes did not make the polymer chains inside the globe orientate significantly.

Orientation increased both modulus and yield stress but decreased the elongation. The effect of orientation on the modulus, yield stress and elongation were dependent on the amylose/amylopectin ratio. The differences of modulus and yield tress between the two directions are higher for amylose rich materials; the differences of elongation are higher for amylopectin rich materials. The higher the amylopectin content, the lower the elongation in the cross-s extrusion direction.

The model of gel-ball and super-globe has been used to explain the relationship between microstructures and mechanical properties. The model can also be used to explain other properties for starch-based materials, such as processing behavior and relaxation time.

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