

Biodegradable Extruded Starch Blends

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ABSTRACT: We prepared biodegradable extruded starch blends by first mixing starch with additives and then processing the mixture in an extruder. The mechanical properties, including tensile strength and elongation at break, solubility, biodegradability, rheological properties, molecular weight, and glass-transition temperature of the extruded blends were studied. Glycerol and urea, to some extent, could both decrease the tensile strength and increase the percentage elongation at break because the former acts as a plasticizer and the latter can break down interactions among

starch macromolecules. The extruded starch blends showed thermoplasticity, and their melts behaved as pseudoplastic liquids at a comparatively low shear rate. The biodegradability of the extruded starch was slightly higher than that of native starch. The molecular weight of starch displayed a decreasing tendency after extruding modification. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 627–635, 2003

Key words: extrusion; biodegradable; rheology

INTRODUCTION

Interest in environmentally degradable plastics has increased enormously with the increasing volume of industrial waste^{1,2} and municipal solid waste because plastics products are among the most visible forms of this trash. The impacts of global litter have exerted additional pressure for degradable plastics, especially in packing and other disposable applications, as a quick-fix solution to the complex problem. At present, many degradable materials and products, mainly biodegradable and/or photodegradable polymers, have been developed. Polyhydroxybutyrate and polyhydroxybutyratevalerate copolymer, targeting the products in personal hygiene and special packing,³ are well-known biodegradable materials produced by bacteria from carbohydrates. A process for producing the biodegradable polymers polylactide and polycaprolactone has also been developed. Such materials closely match the characteristics of existing nondegradable plastics and should compete in properties. However, these materials are too expensive to be used in the common disposable applications such as packing, bottles, and containers for foods, which are the main articles causing the plastics pollution. Thus, attention is focused on the development of cheap biodegradable plastics that can be substituted for commonly used plastic materials. Some researchers have made films from amylose because it is biodegradable in the environment.⁴ Because dry granular starch is

unprocessable with ordinary plastics procession equipment, such as ordinary synthetic polymers such as polyethylene, it is usually added to synthetic polymers as a filler to produce biodegradable plastics. However, starch is a hydrophilic polymer, and it is not compatible with synthetic hydrophobic polymers, so the surface treatment of starch granules with surfactants⁵ or the graft copolymerization of starch with hydrophobic monomers has been used to improve compatibility^{6–9} because graft copolymerization is one of the effective ways to modify natural polymers.^{10,11} However, these kinds of plastics are actually partially biodegradable. The biodegradation of starch in the environment causes deterioration of the matrix, leading to the formation of a polymer mesh, which finally breaks down into small pieces.^{12,13} St. Lawrence Starch markets master batch products that produce films or mold articles containing about 6% cornstarch and what they call *prooxidant* or *autooxidant* additives, which are claimed to continue breaking down the percentage elongation at break (PE) once the starch granules have been consumed by microorganisms. We developed master batch materials containing up to 60% starch, so the starch component in the final plastics articles can reach 30%. The bags as a pioneer product made from the starch/PE composite materials have been used in supermarkets in some cities of China.

Dry starch does not show a glass-transition temperature (T_g) on the differential scanning calorimetry (DSC) diagram, unless it contains excess water over equilibrium moisture content.¹⁴ Russell et al.¹⁵ reported a DSC study of waxy maize starch at various moisture levels and found three distinct endotherms that were referred to as MI, Z (melting), and G (gelatinization). The G endotherm was observed only at

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50% moisture or above. Biliaderis et al.¹⁶ proposed a three-phase model to account for the observed thermal behavior. Actually, the dry starch already decomposes before the temperature reaches the T_g of 500 K¹⁷ because the strong interactions between starch macromolecules obstruct the movement of segments or whole molecules, leading to a high T_g , so starch as a kind of polymer does not show thermoplasticity before decomposition.

In recent years, a type of modified starch, or a biodegradable extruded starch composite or blend, has been reported. The material can be reprocessed into various end products in common plastics equipment and has become a hopeful alternative for biodegradable plastic materials.^{18–20} It has been used for making toothpicks and chopsticks in China. In an earlier article, we discussed the processing of the extruded starch.²¹ This article discusses the properties of the extruded starch blends.

EXPERIMENTAL

Materials

Corn starch was obtained from Tianjin Redflag Starch Plant and contained 12% water. Urea, glycerol, alcohol, dimethyl sulfoxide, and other chemicals all came from Tianjin Chemical Company, and α -amylase was provided by the Tianjin Microorganism Institute.

Preparation of the extruded starch blends

To investigate the key points in determining the thermoplasticity of starch, we added as few components as possible. The native starch was changed in the range of 40–75 wt %, glycerol was 25–55 wt %, urea was 0–5 wt %, moisture content of starch was about 18 wt %, and no additional water was added. A weighed amount of starch, glycerol, and urea were first mixed, and then, the mixtures were extruded and pelletized in a 25/1 L/D twin-screw extruder at 60 rpm.²¹ The temperature profile during the extrusion was 140/160/150/120°C, measured from the feed section to the die.

Mechanical properties and rheological properties

The starch blends were first extruded and pelletized as described previously, and rheology measurements were carried out with a XLY-II capillary rheometer. The extruded starch blends were allowed to equilibrate for 12 h in an environmental chamber with a relative humidity of 50% and at a temperature of 25°C, and then, the samples were preheated for 1 h before being tested in the rheometer, in which the L/D was 25/1 and the diameter of the die was 2 mm. The temperature profile was 150/150/155/155°C. The ap-

parent shear rate (γ_a) was calculated from the following equation:

$$\gamma_a = 4Q / \pi R^3 \quad (1)$$

where Q is the output and R is the capillary radius. Shear stress (τ) was calculated with the following relationship:

$$\tau = \Delta P / 2(L/R) \quad (2)$$

where ΔP is the pressure difference, L is the capillary length, and R is the capillary radius.

For most thermoplastics, the following power law is followed:

$$\tau = K \gamma^m \quad (3)$$

where K is the consistency, γ is the shear rate, and m is the index in the power law.

Substituting eq. (3) into the Newtonian relationship between τ and γ yields the following expression, by which viscosity (η) and γ values can be obtained:

$$\eta = K \gamma^{m-1} \quad (4)$$

Similar prepared samples were tested with a WD-5 multipurpose electron tensometer to obtain the tensile strength (TS) of the extruded starch blends.

Molecular weight of the extruded starch

The extruded starch blend was first weighed and dissolved in dimethyl sulfoxide and then filtered to get the liquid, which was consequently added to alcohol to precipitate the dissolved starch. The precipitated starch was centrifuged to obtain pure starch. The molecular weight changes of the purified starch were represented by intrinsic viscosity ($[\eta]$) change, which was calculated from flowing times of the purified starch in 1 mol of KOH aqueous solution determined with a Ubbelohde viscometer at 25°C.²²

Biodegradability of thermoplastic starch

Starch molecules are composed of glucoses bonded by α -1,4 linkages and α -1,6 linkages. Aldehyde groups —CHO are produced when the starch molecules are attacked by α -amylase, and the produced concentration of aldehyde groups (—CHO) can represent the biodegradability of starch. The specific procedure of this test was described in detail elsewhere.²³

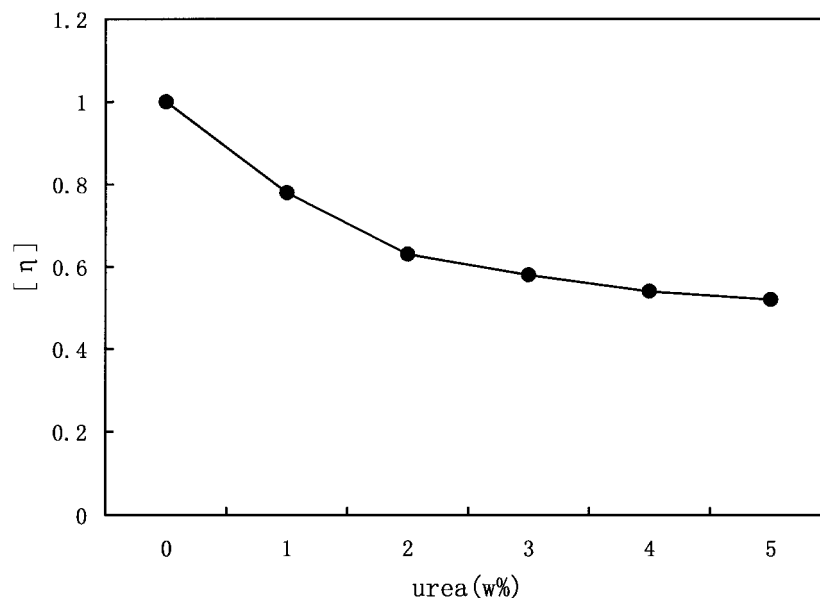


Figure 1 Solution relative $[\eta]$ of starch.

RESULTS AND DISCUSSION

Molecular weight of the extruded starch

Starch extrusion has been widely used in food processing. Several articles about starch η and the effects of various factors such as screw speed, moisture content, extrusion temperature, and additives have been reported elsewhere.^{24–26} The degradation in the molecular weight occurring during extrusion is a common trend because of various variables, especially shear force and high temperature. Here, we only discuss the effect of urea on the molecular degradation during the extrusion when other conditions were fixed.

It was difficult to test the molecular weight of starch macromolecules with the Ubbelohde viscometer because of the existence of the branched chains, but we could use $[\eta]$ changes to reflect the molecular changes of starch during the extrusion, which was calculated by the following equation:

$$[\eta] = [\eta]_{\alpha} / [\eta]_0$$

where $[\eta]_{\alpha}$ and $[\eta]_0$ are the intrinsic viscosity values of the extruded starch and native starch, respectively, obtained from the experiment. Figure 1 gives the effect of urea on the η of the extruded starch. The $[\eta]$ of the extruded starch steadily decreased with the increasing amount of urea added in the starch blend. This implied the breakdown of starch molecules under the action of shear force and a high temperature during the extrusion. Urea could aggravate the degradation by disrupting the hydrogen bonds existing among starch macromolecules and, consequently, destroying the crystal and granular structure of the starch.

Mechanical properties

Mechanical properties such as TS and PE are basic and important parameters for the evaluation of polymeric materials or end products. Figures 2 and 3 show that the PE steadily rose and reached a nearly constant value with the increasing urea content, but the TS of the extruded starch blend decreased, which showed that the action of the urea was complex during the extrusion.

Urea can easily evaporate at a comparatively high temperature. When starch was added and mixed with urea, the starch granules were soaked with urea. At high temperatures, the vaporizing of the urea penetrated inside the starch granules and could initiate the disruption of starch granules and the disorder of the compact arrangement of the starch macromolecules under the help of high temperature and shear force, leading to a decrease of the interaction among the starch macromolecules. As a result, the TS fell, and the PE rose.

Also, urea is an effective agent in breaking down hydrogen bonds. The nitrogen atoms in urea molecules have a high electron negativity and can form hydrogen bonds more easily with hydroxide groups in starch macromolecules. In native starch, there are many hydrogen bonds between starch macromolecules directly or indirectly through water molecules. These hydrogen bonds play an important role in maintaining the stability of the helix structure and are one of the main reasons why a starch melt is hard to flow when it is heated. Under the action of shear force, pressure, and additives, the orderly arrangement of the starch molecules is destroyed, leading to the breakdown of hydrogen bonds between starch macro-

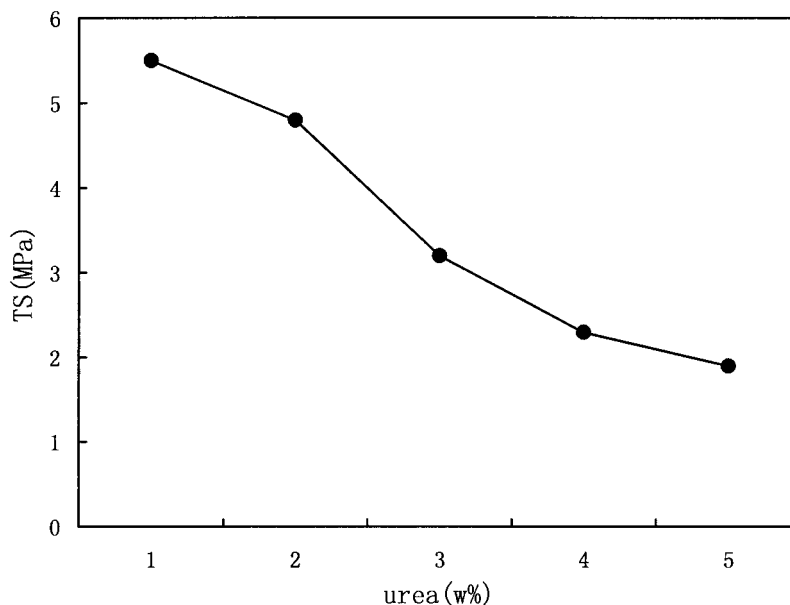


Figure 2 PE of the extruded starch blends: starch = 80% (w/w), glycerol = 15–19% (w/w), and urea = 1–5% (w/w).

molecules. This gives urea an opportunity to form new hydrogen bonds with starch, which results in a reduction in interactions among starch macromolecules.

Finally, urea can help decompose starch macromolecules, as discussed previously. The previous factors bring about the phenomena on the mechanical properties of the extruded starch, decreasing the TS and increasing the PE.

T_g

The T_g of the extruded starch blend was investigated by positron annihilation spectroscopy.^{27,28} Figure 4

gives the relationship between lifetime (τ_1 , τ_2 , and τ_3) and temperature. The lifetimes τ_2 and τ_3 are related to the free volume in the crystal and amorphous phase, respectively, whereas τ_1 is related to the molecules themselves. It is clear that τ_2 and τ_3 both existed in a transition area in the temperature range of 60–80°C, and this temperature range could be considered to be the T_g of the extruded starch blend.

Rheological properties

The rheological properties of the extruded starch blend were tested with a capillary rheometer, and the results are shown in Figure 5. The melts of the ex-

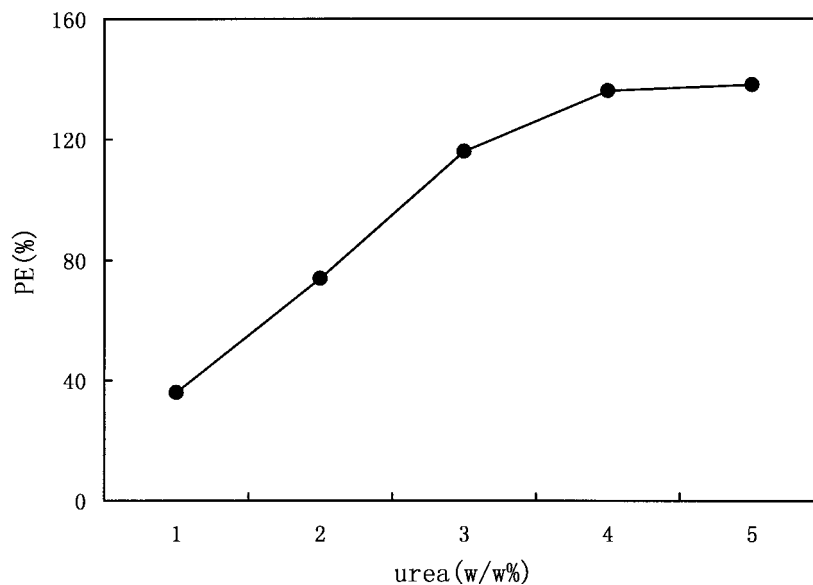


Figure 3 TS of the extruded starch: starch = 80% (w/w), glycerol = 15–19% (w/w), and urea: 1–5% (w/w).

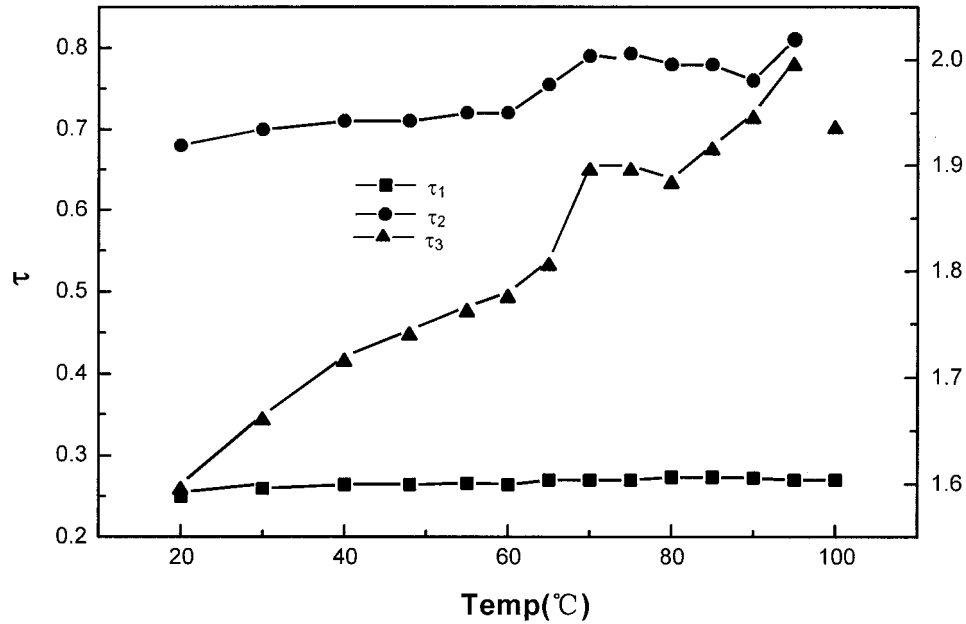


Figure 4 Positron annihilation spectra of the extruded starch.

truded starch blends behaved as a pseudoplastic fluid. The apparent η decreased significantly in the low shear scope and reached a constant value when γ was further increased, which no longer followed the power law.

As discussed previously, glycerol and water both acted as plasticizers. However, urea could also act as a plasticizer by reducing the interaction between starch macromolecules by breaking down hydrogen bonds that originally existed in the starch macromolecules. So the interactions among macromolecules, or seg-

ments within a macromolecule, decreased sharply. Therefore, starch macromolecules regained their flowing ability, and the segments recovered movement. It is important for polymer materials to have an adequate flowing ability during the procession from materials to end products.

Brabender η of the extruded starch

When starch was dispersed and heated in the water, a starch paste was formed. The Brabender η curve

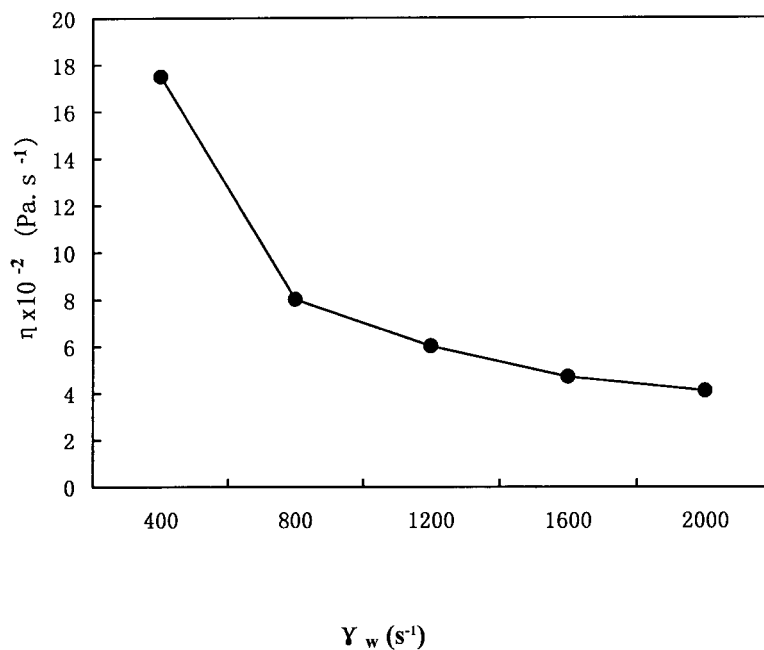


Figure 5 Rheological characteristics of the extruded starch: starch = 80% (w/w), glycerol = 18.5% (w/w), and urea = 1.5% (w/w).

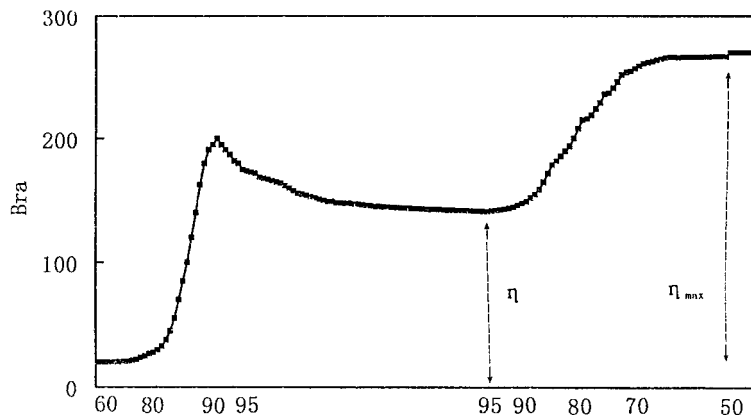


Figure 6 Schematic Brabender η curve.

shows the η change of the paste during the programmed heating and then cooling as shown in Figure 6, in which η represents the viscosity of the paste when it started to cooled down and η_{\max} represents the maximum viscosity during the cooling stage. The viscosity difference ($\Delta\eta$) and rising percentage of viscosity (δ) are defined and calculated according the following equations:

$$\Delta\eta = \eta_{\max} - \eta$$

$$\delta = \Delta\eta / \eta \times 100\%$$

δ reflects the formation of the starch hydrogel caused by physical crosslinkage through hydrogen bonds during the cooling stage. To examine the effect of extrusion on the Brabender η of the starch, we comparatively tested extruded starch samples with different glycerol contents against corresponding nonextruded starch blends that

had the same compositions. Although the makeup of the samples was different, the absolute solid starch amount in each of the samples was the same. The Brabender η was calculated per the standard procedure and conditions. Figure 7 gives the relationship between δ and the content of glycerol in the extruded starch/glycerol composite, whereas Figure 8 is the δ values of the starch/glycerol blends without extrusion. Obviously, the δ value of the extruded starch was much lower than that of starch blend, indicating that the original hydrogen bonds among starch macromolecules had been recombined and that glycerol molecules participated in the breakdown and formation of new hydrogen bonds with starch macromolecules during extrusion. So the hydrogel network of the starch macromolecules was partly discontinued by the glycerol molecules, and the η certainly decreased. Naturally, the degradation of starch molecules and the addition of glycerol may have caused some decrease in η .

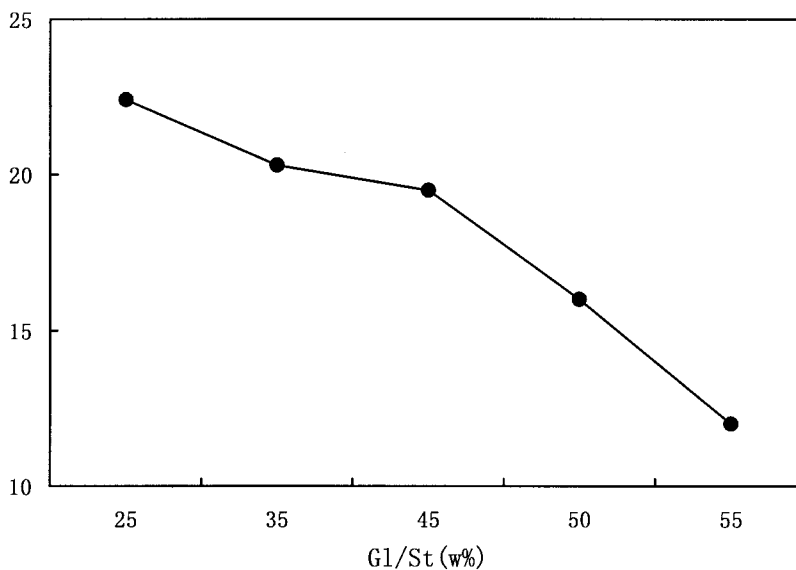


Figure 7 δ of the extruded starch/glycerol blends versus glycerol content (St = native starch; St/Gl = extruded starch/glycerol blend).

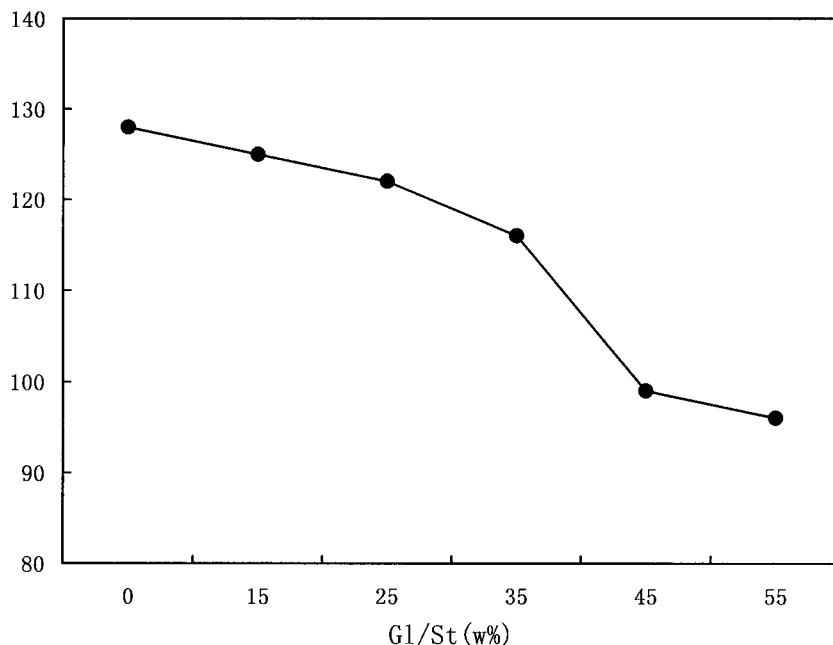


Figure 8 δ of the nonextruded starch/glycerol blend versus glycerol content (St = native starch; St/Gl = extruded starch/glycerol blend).

As we all know, for a polymer solution, the more the polymer is dissolved in solvent, the higher η is obtained. When the starch granules are destroyed, the η of the aqueous solution should be increased if the crosslinkage is not considered. For the nonextruded starch, the high Brabender η was due to the physical crosslinkage by hydrogen bonds that existed between the starch macromolecules with the help of the granular and crystal structure. The decrease in Brabender η for the extruded starch just showed that some changes happened in the physical crosslinkage during the extrusion.

Solubility of the extruded starch

The solubility of polymer materials depends on the polarity of macromolecules and phase structure. Starch samples (glycerol content = 25 wt %) were added into the water and left standing for 30 min. The moist starch was separated from the solution by centrifugation and was weighed after it was dried at 110°C for 3 h.²⁹ Native starch was slightly dissolved in the water although starch molecules contain a lot of hydrophilic groups (hydroxide). After extrusion, the granular and crystal structures were destroyed, and

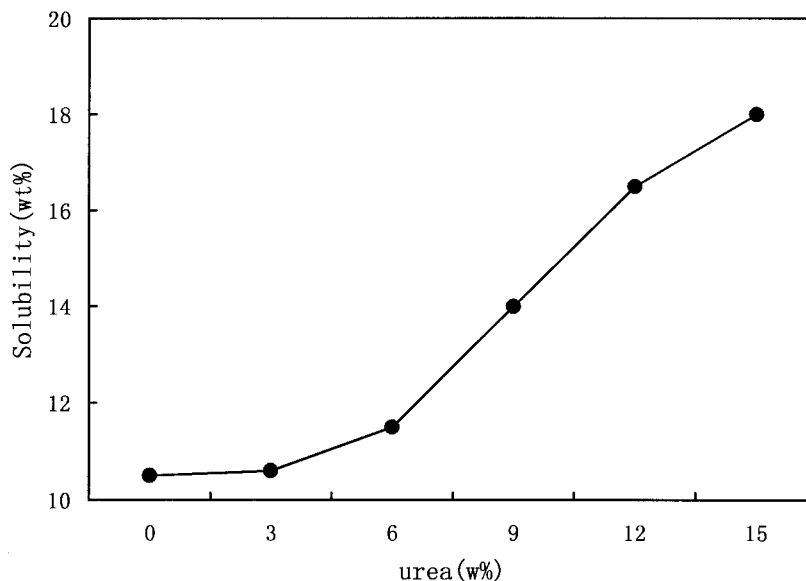


Figure 9 Solubility of the extruded starch blend.

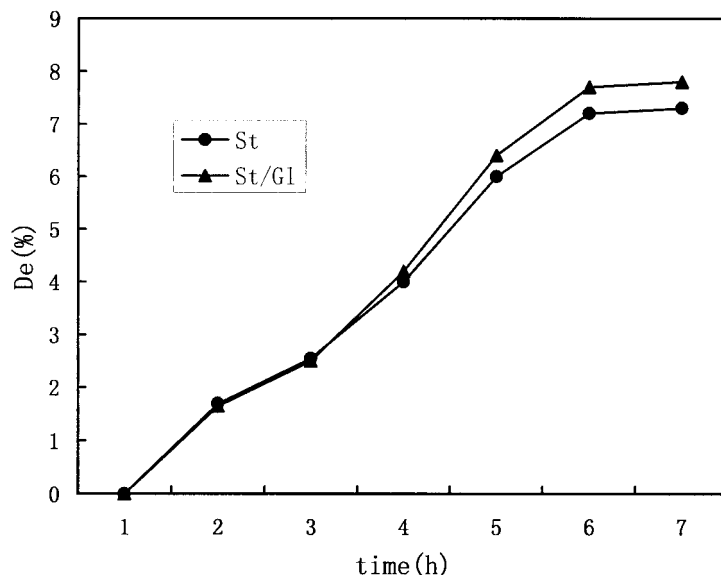


Figure 10 Biodegradability of the starches.

the average molecular weight was also lowered because of degradation, so the solubility was increased. Figure 9 gives the changes of solubility of the extruded starch as the urea content of the extruded starch blends varied. Obviously, the solubility of the extruded starch grew drastically when the urea content was beyond 6%, which may be attributed to the soluble small molecules (urea and glycerol; glycerol content = 25 wt %), the degradation of the starch molecular weight, and the structure changes of starch granules.

Biodegradability of the extruded starch

Native starch is biodegradable in the environment because amylase can attack the macromolecules and cause the breakdown of molecules. Human beings can obtain energy by metabolizing starch, the main component in grains, because we can find amylase in the body. Figure 10 indicates that the biodegradability of the extruded starch was slightly better than that of native starch. Native starch is a partially crystallized natural polymer, and there are numerous hydrogen bonds among the macromolecules, so starch molecules even retain their stable helix configuration in solution because of the existing hydrogen bonds. After extrusion, the hydrogen bonds that stabilized the structure, including the configuration and crystal structure, were destroyed, so amylase could comparatively easily locate and disrupt the linkages between the glucose units. Also, the addition of hydrophilic small molecules and the decrease of molecular weight during the extrusion were favorable to the attack of amylase because more hydrophilic end groups —OH were exposed to the amylase.

CONCLUSIONS

1. The extruded starch resumed thermoplasticity through the extrusion process in an extruder. The melt of the extruded starch behaved as a pseudoplastic fluid.
2. The molecular weight of the starch decreased slightly because of the action of shear force, additives, and high temperature during the extrusion.
3. Extrusion caused the crystal and granular destruction of starch, leading to changes in mechanical properties and η .
4. The extruded starch showed similar biodegradability to native starch under the attack of amylase.
5. The solubility of the extruded starch grew drastically when the urea content was beyond 6%.

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