

# The Possibility of Preparing Pseudo-thermoplastic Starch

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## Abstract

Starch is biodegradable polymer, its melting point is about 250°C, when the temperature is higher than 100°C, it begins to lose the equilibrium moisture inside the starch crumb and decomposes, so it is already degraded before melting. Therefore natural starch is not thermoplastic, melting process cannot be done. It could only possess thermoplasticity after using external plasticizers to make its molecular constitution become disordering. Therefore this study has used environment-protected plasticizer (glycerol and water) and corn starch to prepare the pseudo-thermoplastic starch. Its theory is to use glycerin and water as the plasticizer to plasticize the starch and reduce its melting point. First of all carry out gelatinization on the starch and then use the glycerol to plasticize it and prepare it as the pseudo-thermoplastic starch. Strength test, DSC, TGA and hot press test were used to analyze the properties of different pseudo-thermoplastic starches prepared by the plasticizers of difference ratios.

*Keywords:* biodegradable polymer, pseudo-thermoplastic starch

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## 1. Introduction

The traditional compound polymeric materials may cause great damage to the nature for it is hard to decompose. So the industrial community worked actively on developing the biodegradable polymer materials [1].

Starch is one of the biodegradable polymeric materials with the richest reserves, and it is very cheap so it has become the first choice for biodegradable plastic. Many newly developed compound biodegradable polymers have used starch as the rubber alloy or stuffing. And many other researches have worked on the upgrading of starch for application owing that it is difficult to process and lack of mechanical property.

The main ingredients of starch is C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>, it is a polymer generated by D-glucose. The particle structure of starch contains the inter part and epithelium two parts, the former is called α-Amylose, the latter is called β-Amylose (Amylopectin). Amylopectin is the main part to form epithelium of starch particle. Starch particle is composed of 20-25% of amylose and 75 - 80% of amylopectin. The amylose particle is smaller, it contains about 500—2,000 units of glucose, while amylopectin particle is larger than amylose, and it contains 10,000 — 600,000 units of glucose [3-7].

Polymeric materials usually use plasticizer to increase the movability of polymer long chain to improve its processability. Its theory is that the secondary bonds would be generated between plasticizer molecule and polymer molecule to reduce the binding strength of secondary bonds of the polymer long chain of the polymer so that it could provide more moving space for the polymer chains of the polymer, then we could get the soft and ductile material.[10-13]

The melting point of starch is about 250°C; it has already degraded before melting so machine-shaping on starch is hard to

be done. However its melting point and water contamination may be related to plasticizer content, and at proper temperature, pressure and shearing force, we may destroy the structure of microlite and then it becomes amorphous polymer, the amylose and amylopectin distribute evenly, then we could get the polymer with proper plasticity and excellent mechanical property.[14-16]

## 2. Experiment

### 2.1 Experimental materials

Cornstarch, (Sunlight foods CO., Ltd)

Glycerin: C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub> Mw=92 g/mol,(Fisher Co.,Ltd)

### 2.2 Preparation of Pseudo-thermoplastic Starch

Choosing glycerol as the plasticizer and adding different ratios of glycerol into the corn starch, and mix them in advance under room temperature. Using dispersing instruments to stir the starch after adding water, so that the whole stuff can be mixed evenly, raising the temperature to 70°C and conducting gelatinization. Then add glycerol and go on stirring so that we may destroy the starch crystal structure and the molecular chain also becomes disordering. The whole stuff forms more evenly colloid compound after natural drying, and it becomes the gel status pseudo-thermoplastic starch.

### 2.3 Experimental projects

Use the rotational viscometer, strength test, differential scanning calorimetry, TGA characterization, hot press test and so on to analyze the properties of pseudo-thermoplastic starch.

### 3. Results and Discussions

Table 3.1 The Appearance and Hand Feeling of Pseudo-thermoplastic Starch with Different Ratios of Plasticizers

Sample	Plasticizer	Content Appearance	Hand Feeling
Corn starch	0%	Yellow powder	powder
GTPS-0	0%	White, non-transparent	dry and inflexible
GTPS-5	5%	Yellow, transparent	dry and inflexible
GTPS-10	10%	Yellow, transparent	dry and inflexible
GTPS-15	15%	Yellow, transparent	ductile and flexible
GTPS-20	20%	Yellow, transparent	ductile and flexible
GTPS-30	30%	Yellow, transparent	ductile and flexible
GTPS-40	40%	Yellow, transparent	ductile and flexible
GTPS-50	50%	Yellow, transparent	ductile and flexible

As shown in Figure 3.1, the GTPS-0 without glycerol is white and non-transparent, this is mainly because the starch contains crystallite and this has made the stuff become dry and inflexible. As shown in Figure 3.2, the film of GTPS-5 with only 5% of plasticizer becomes transparent, and the transparent degree increases with the content of plasticizer. Secondary bonds are generated when plasticizer is added to the starch, it reduces the binding strength of secondary bonds of the polymer long chain to provide the polymer chains of the starch with more moving space, and this has made the starch film become soft and ductile, and the plasticization of starch film increases with the increase of plasticizer proportion. As shown in Figure 3.3, the film of GTPS-15 with 15% of plasticizer becomes ductile and flexible, the appearance and hand feeling of GTPS are shown in Table 3.1, the starch film and its mechanical property are examined in depth in Section 3.2.



Figure 3.2 Film Photo of GTPS-5

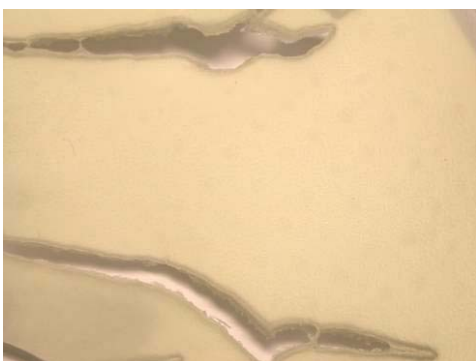


Figure 3.1 Film Photo of GTPS-0



Figure 3.3 Film Photo of GTPS-15



Figure 3.4 Film Photo of GTPS-50

### 3.2 Strength Test

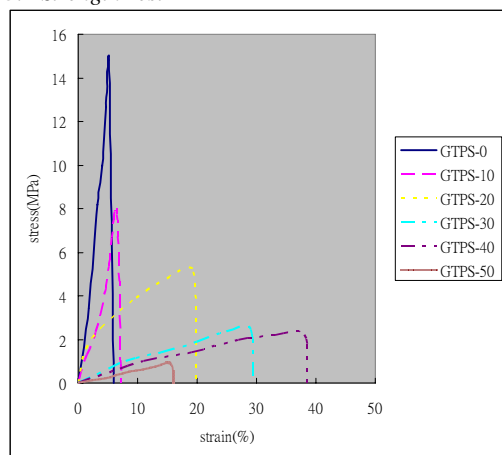


Figure 3.5 Stress-Strain Curve of Pseudo-thermoplastic Starch

As shown in Figure 3.5, GTPS-0 curve has low strain, high break strength and high modulus with the characteristics of hard and crisp, this is mainly because the crystallite of this starch is semi-crystalline. GTPS still has high strain, low break strength and low module after adding plasticizer. GTPS-10 curve still has low strain, high stress and high modulus with the characteristics of hard and crisp, its module and break strength reduces while strain increases a little compared with GTPS-0.

From the comparison of GTPS-20, GTPS-30 and GTPS-40, we could find out that the module and break strength reduces with the increase of plasticizer content, and strain increases with the increase of plasticizer content, they have shown the characteristics of soft and ductile, this is mainly because secondary bonds have been generated with the adding of plasticizer into starch, it has reduced the binding strength of secondary bonds of the polymer long chain within the starch to provide the polymer chains of the starch with more moving space, and this has made the starch film become soft and ductile. But the module and break strength of GTPS-50 reduces with the increase of plasticizer, and the strain reduces with the increase of plasticizer, it is soft and weak, therefore when the plasticizer content exceeds 40%, the ductibility of GTPS reduces largely.

### 3.3 The Influence of Shear Rate and Temperature on Pseudo-thermoplastic Starch Viscosity

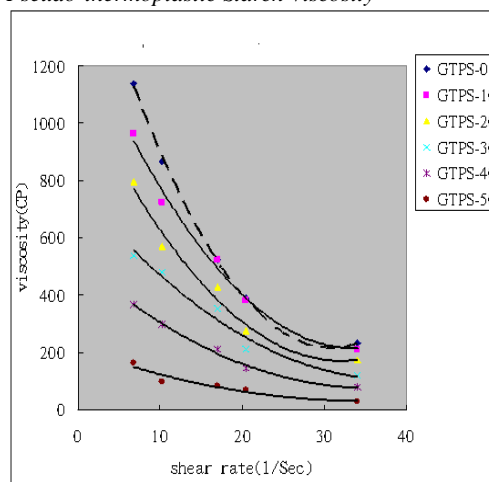


Figure 3.6 GTPS Viscosity versus Shear Rate at 70°C with Different Plasticizer Ratios

As shown in Figure 3.6, the movability of polymer long chain increases with the adding of plasticizer into the starch. The secondary bonds are generated between plasticizer and starch molecule; it reduces the binding strength of secondary bonds among the polymer long chains of starch and promotes the starch mobility. It is evident that the viscosity of GTPS-50 with plasticizer is far lower than GTPS-0 without plasticizer. The descending degree of viscosity increases with the increase of plasticizer content, so the viscosity of GTPS-50 is far lower than GTPS-10.

When the starch suffers the shearing force, the entanglement degree of molecular chain is damaged. With the increase of shear rate, the collapsing scope of entanglement phenomena caused by shearing action reduces largely, and the adding of plasticizer also makes the entanglement degree of molecular chain reduce, therefore the descending degree caused by shear rate of GTPS-0 viscosity without plasticizer is higher than the GTPS-50 with plasticizer. With the increase of plasticizer content, the descending degree of viscosity caused by shear rate reduces, therefore the descending degree of GTPS-10 viscosity caused by shear rate is far higher than GTPS-50 with high plasticizer content. And all samples show the shear-thinning flow behavior, the viscosity descends with the increase of shear rate and the non-Newtonians fluid flow behavior.

### 3.4 Differential Scanning Calorimetry

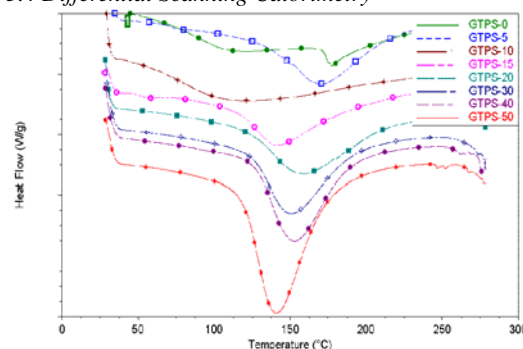


Figure 3.7 DSC Figure of GTPS with Different Plasticizer Ratios

As shown in Figure 3.7, GTPS-0 has endothermic peak around 178°C, while GTPS-50 has endothermic peak around 141.34°C. It is obvious that the melting point of the starch after adding the plasticizer descends because the plasticizer has filtrated into the starch and weakened the hydrogen bonding of the starch polymer chains, this has destroyed the crystal structure of the starch, the molecular chain becomes disordered and the melting point of starch descends.

GTPS-10 has endothermic peak around 123.33°C, but the peak value is not obvious, while GTPS-50 has obvious endothermic peak around 141.34°C. With the increase of plasticizer content, the GTPS and its melting point becomes more obvious, that is its peak value becomes larger.

When the plasticizer content exceeds 10%, the descending degree of melting-point reduces, the descending degree of GTPS-15 melting point begins to reduces, so the overabundant plasticizer content would blocks the descending degree of melting point. This is mainly because the excessive plasticizer has made the glycerol produce the hydrogen bonding and this weakens the hydrogen bonding between glycerol and starch.

### 3.5 TGA characterization

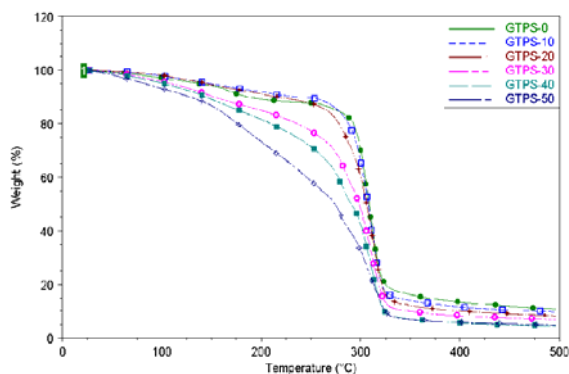


Figure 3.8 TGA Figure of GTPS with Different Plasticizer Ratios

As shown in Figure 3.8, GTPS-0 has few weight losses within 100°C, and a few around 100°C, which is the loss of the water. We could observe from GTPS-10 that it has large amount of weight losses around 290.0°C for the adding of glycerol, it is the weight loss of glycerol.

Then we compare TGA curves of GTPS-10 and GTPS-50, the curves show that the weight loss increases with the increase of glycerol content, this shows that thermostability reduces with the increase of plasticizer content for the plasticizer may clear up the microlite inside the starch and destroy the tight coupling hydrogen bond.

### 3.6 Hot Press Test



Figure 3.9 Thermo-compression Photo of GTPS-30 at 170°C

Use hot press bed to test the possibility of thermoplastic, and use GTPS-30 to carry out the test, its melting point is at 151.4°C. As shown in Figure 3.9, when the temperature is 170°C, the GTPS-30 may be softened after heating and become distorted, this proves that the glycerol has obvious plasticize effect.

## 4. Conclusions

The natural starch begins to loss the equilibrium moisture of the starch crumb when the temperature is higher than 100°C, and it begins to decompose, its fusing temperature is about 250°C, so it degrades before melting. Therefore natural starch is not thermoplastic, melting process cannot be done, and therefore it only possesses thermoplasticity when using external plasticizers to make its molecular constitution become disordering.

The increase of plasticizer content in the starch may increase the transparent degree of GTPS, and its ductibility increases too.

It is learnt from GTPS strength test that the module and break strength reduces with the increase of plasticizer, and the strain increase with the increase of plasticizer, but the strain of GTPS-50 reduces with the increase of plasticizer, the ductibility of GTPS reduces largely.

At 70°C, GTPS shows the shear thinning flow behavior; its viscosity reduces with the increase of shear rate. It is observed from the higher plasticizer content that appearance shear viscosity is lower.

In DSC picture, GTPS has obvious melting endothermic peak between 130°C and 170°C. Although GTPS-10 has melting endothermic peak around 123.33°C, its peak value is large and wide and this has made the GTPS melting point become unobvious. The increase of plasticizer content makes the GTPS melting point become more obvious, but the overabundant plasticizer content may block the descending degree of melting point.

In TGA figure, the weight loss of GTPS increases with the higher plasticizer content, and its thermostability reduces.

Natural starch is the natural macromolecule with fractional crystallization and double helix structure, when we use the external plasticizer to change the double helix structure into random coil structure, we clear up its microlite and destroy the tight coupling hydrogen bond, so that thermoplastic processing becomes possible. And the property analysis of GTPS could be the reference for future thermoplastic processing.

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