

NOTE

Biodegradable Thermoplastic Starch

INTRODUCTION

Starch, as a recycled natural polymer resource, has many special properties in comparison with synthetic polymers, of which its biodegradability appears even more outstanding and important in the current world in which attention has been drawn to the protection of the ecological environment.^{1,2}

Thousands of tons of plastic litter are dumped or discarded onto the earth each year, which harms and encroaches on the existing living space of human beings and forces scientists to pay even more attention to studying and developing environment biodegradable plastics in order to retard or eradicate plastic pollution.³⁻⁵

Natural macromolecules such as starch, although showing high environmental biodegradability, are difficult to be processed into articles because thermal degradation occurs before they enter the melting stage. This hinders the use of natural polymers as plastics. Taking starch as an example, there exist many hydrogen bonds among the starch macromolecules. These hydrogen bonds hamper the movement of the starch molecules, so it is impossible to process starch into common synthetic plastic products. If the processing ability of starch is improved, its practical value will increase significantly. Recently, some researchers have been engaged in this study; they have changed native starch into thermoplastic starch through some treatments. The produced thermoplastic starch can be processed into ordinary plastic equipment. The Warner-Lambert Co. and others have made great process in this area.⁶⁻¹⁰ They first mixed starch with some additives; then the mixture was extruded in a specially designed extruder with the suitable temperature, pressure, and moisture. The extruded starch showed a melting stage during extrusion. We have been studying thermoplastic starch since 1991. The mechanical properties, rheological properties, the glass transition temperature of the materials, the crystal structure, and the granular structure were studied. The present article focuses on the effect of additives on the mechanical and rheological properties of the extruded starch.

EXPERIMENTAL

Materials

Starch was provided by Red-flag Starch Plant; other chemicals all came from the Tianjin Chemical Co.

Preparation of the Thermoplastic Starch

A weighed amount of starch and other additives were mixed under room temperature in a GH-DY high-speed kneader; then, the mixture was put into the hopper of the SJ-25 extruder and extruded into rod samples under a controlled screw rotation.

Analysis of the Samples

The tensile test was carried out with a WD-5 electron multipurpose tensometer. The rheological properties of the samples were tested with an XLY-II capillary rheometer. The SEM photo and X-ray diagrams were tested with a KYKY-100B scanning electron microscope and a Regaku D/Max-100 X-ray diffractometer.

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties of the thermoplastic starch relied on the temperature under which it was produced, the amount of water contained, and the properties of the additives as well as their amount added in the starch composite. Of the above additives, some were even more important in determining the mechanical properties of the thermoplastic starch. Polyhydric alcohols have the same hydroxide radicals as does starch, so they are compatible with starch macromolecules. Figure 1 shows the effect of glycol, glycerol, and hexylene glycol on the mechanical properties. It indicates that the tensile strength of the thermoplastic starch decreased as the amount of polyhydric alcohol added increased, while the percentage elongation increased.

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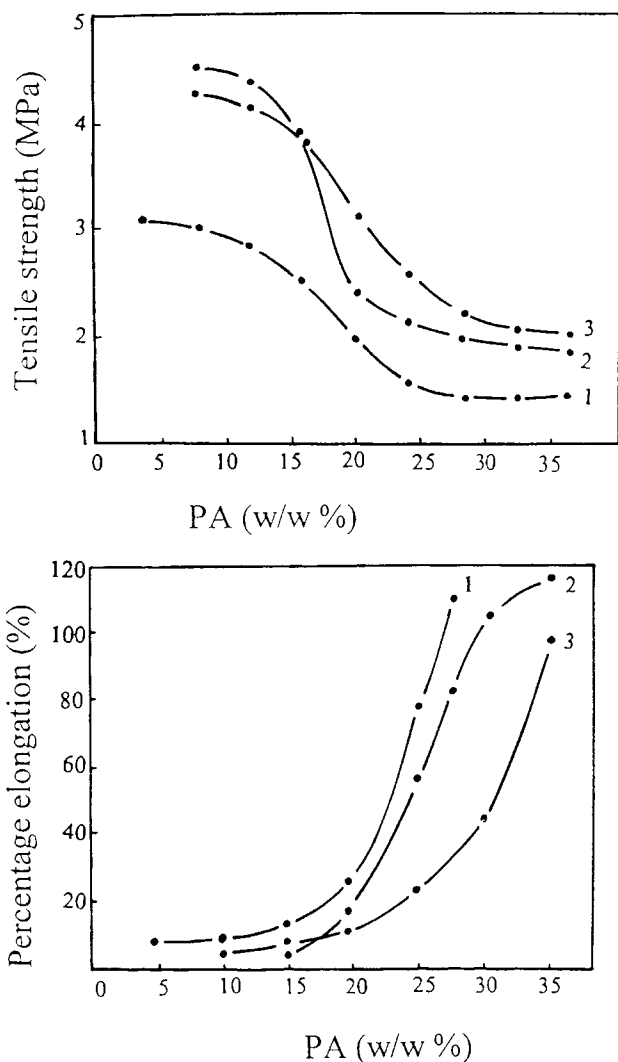


Figure 1 Effect of polyhydric alcohol on the mechanical properties of thermoplastic starch: (1) glycol; (2) glycerol; (3) hexylene glycol.

It is well known that starch is a kind of natural polymer containing many hydrogen bonds among the hydroxide radicals of the starch macromolecules; therefore, it shows higher tensile strength. When the polyhydric alcohols are added, they act as a dilutor and lower the interaction of the molecules; thus, the tensile strength falls. At the same time, they also act as a plasticizer that improves the movement of the segments and macromolecules, which leads to the increase of the percent elongation. This is testified to by the comparison of the glass temperature of the thermoplastic starch and native starch.

Rheological Properties

The effect of polyhydric alcohol on the rheological properties of the thermoplastic starch is shown in Figure 2. It

tells us that the thermoplastic starches all behaved as a pseudoplastic liquid, although the polyhydric alcohols and their amount are different. The curves indicated that the viscosity was not a constant value and depended on the shear rate.

The apparent viscosity fell with the increasing amount of polyhydric alcohols, because they widen the distance between the macromolecules and weaken the molecular interaction. The apparent viscosity of the system also relied on the temperature. The apparent activation energies for two different systems were calculated according to the Arrhenius equation. System one contains additive glycol, and system two, glycerol:

$$E_{g1} = 46.4 \text{ kJ/mol}; \quad E_{g2} = 38.41 \text{ kJ/mol}$$

The additives can evidently change the glass transition

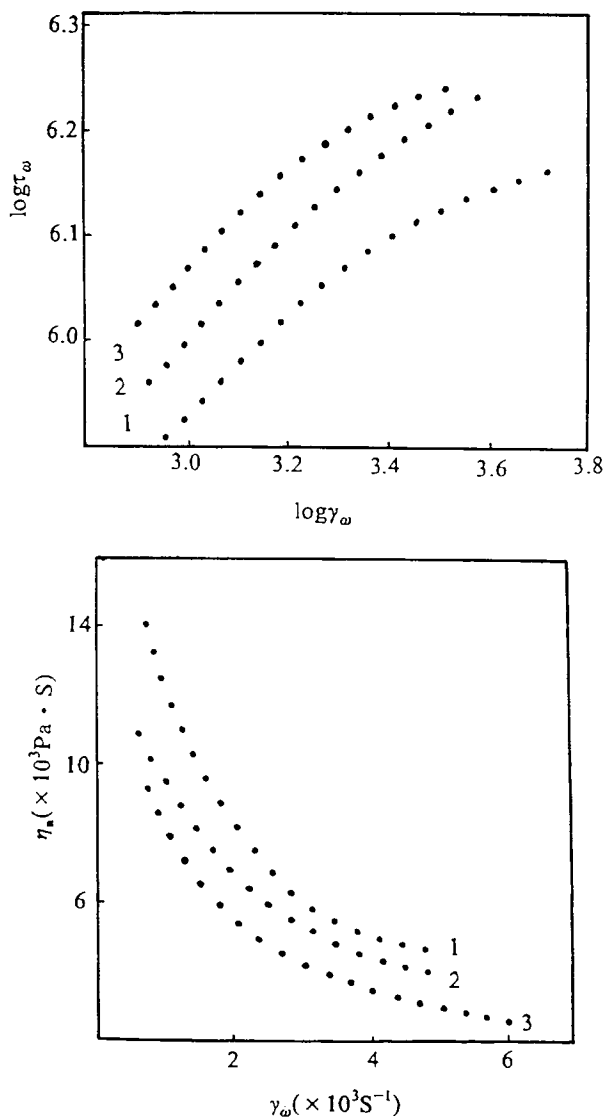


Figure 2 Rheological properties: (1) glycol; (2) glycerol; (3) hexylene glycol.

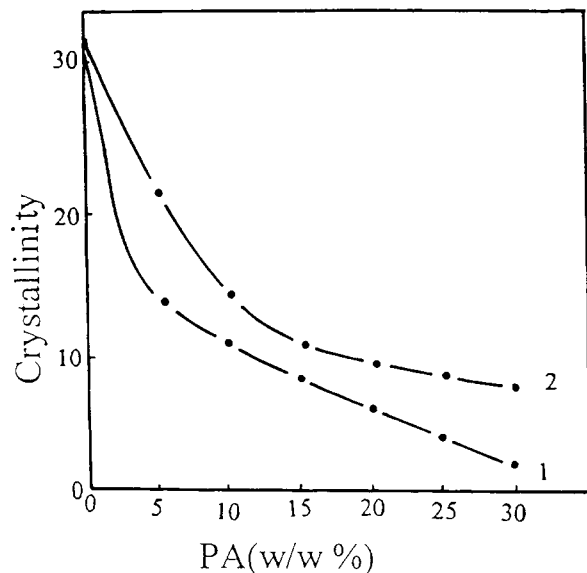


Figure 3 Crystallinity of the thermoplastic starch: (1) glycol; (2) glycerol.

temperature (T_g) of the starch. The experimental results showed that the T_g shifted to the low-temperature region as the additive amount increased. This explains why polyhydric alcohol can promote the movement of the segments.

Crystallinity and Softening Temperature

Figures 3 and 4 demonstrate that the crystallinity and softening temperature (ST) of the thermoplastic starch both showed a declining trend when the amount of polyhydric alcohol increased. The addition of polyhydric al-

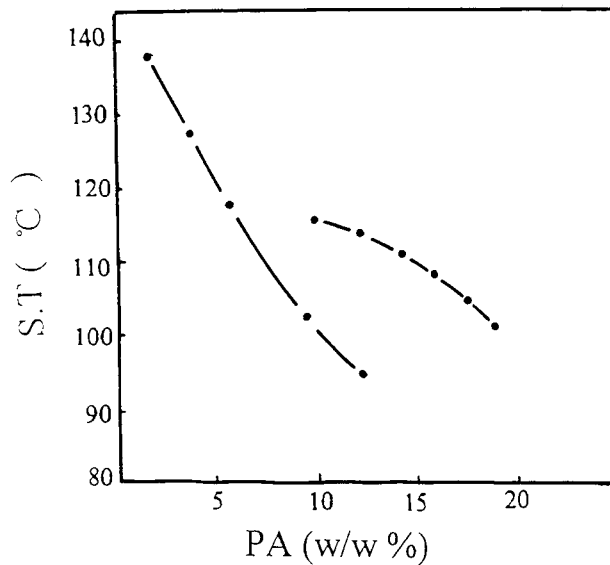
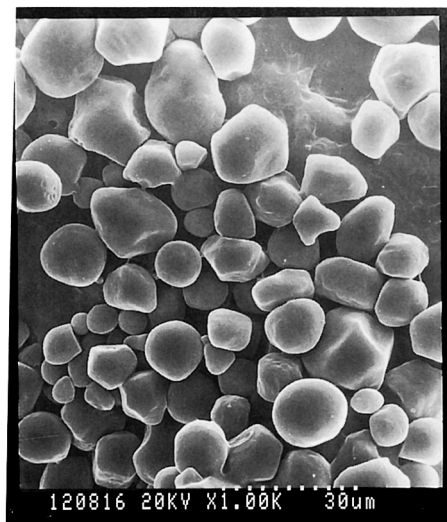


Figure 4 Softening temperature of the thermoplastic starch: (1) glycol; (2) glycerol.

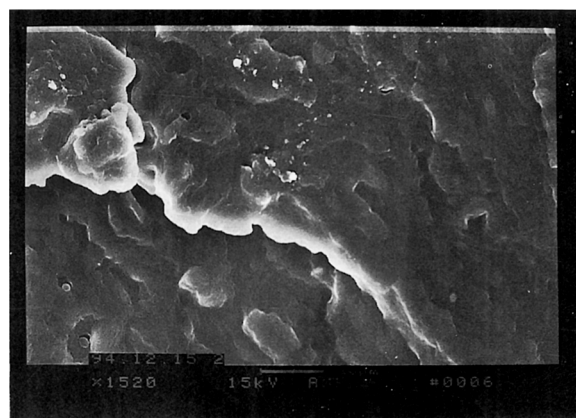
cohol could not only decrease the interaction of the macromolecules, but also destroy the crystal structure of the starch during the extrusion. So, it is possible for starch to melt in the extruder and maintain the amorphous state after extrusion.

Scanning Electron Photomicroscope

The shape of the thermoplastic starch containing glycerol, glycol, and hexylene glycol is shown in Figure 5. The starch granules that are partially built up by the spherical crystal



A



B

Figure 5 SEM photos: (A) native starch; (B) thermoplastic starch.

almost disappear after extrusion, with only a few crystalline pieces dispersing in the continuous amorphous phase. This accords with the X-ray results.

CONCLUSION

1. Polyhydric alcohol can change the mechanical properties of the thermoplastic starch significantly.
2. The addition of the polyhydric alcohol can decrease the apparent viscosity of the thermoplastic starch.
3. Polyhydric alcohol can decrease the interaction of the macromolecule, destroy the crystalline structure of the starch during extrusion, and lead to the decreasing of the crystallinity, glass temperature, and softening temperature.

The project was supported by National Natural Science Foundation of China.

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Received May 17, 1996

Accepted May 23, 1996