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Studies on the properties of natural fibers-reinforced thermoplastic starch composites

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Abstract

As the matrix of natural fiber, thermoplastic starch (TPS) was prepared with urea and formamide as the mixed plasticizer. This TPS could effectively restrain starch retrogradation. SEM micrographs showed good dispersion and adhesion between starch and fiber. Studies in the dependence of mechanical properties of reinforced TPS on the contents of fiber and water demonstrated that with increasing fiber content from 0 to 20%, the initial tensile strength was trebled up to 15.16 MPa, while the elongation was reduced from 105 to 19%. The reinforcement effect was gradually weakened with the increasing of water contents, but at the high water contents (>30%) both the fiber and water contents had no effect on the tensile strength. The thermal stability and water resistance of TPS reinforced by fiber were obviously improved. X-ray diffractograms illustrated that this matrix still restrained the retrogradation of starch when the fiber content was below 20%.
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1. Introduction

In recent years, great progress has been achieved in the development of biodegradable products based on agricultural materials (Curvelo, de Carvalho, & Agnelli, 2001; Herrmann et al., 1998). One of the most studied and promising raw materials for the production of biodegradable plastics is starch, which is a natural renewable carbohydrate polymer obtained from a great variety of crops. Starch is a low cost material in comparison to most synthetic plastics and is readily available. Starch has been investigated widely for the potential manufacture of products such as water-soluble pouches for detergents and insecticides, flushable liners and bags, and medical delivery systems and devices (Fishman et al., 2000). Native starch commonly exists in a granular structure with about 15–45% crystallinity. Under the action of high temperature and shear, starch can be processed into thermoplastic starch (TPS) (Forssell et al., 1997). During the thermoplastic process, water and other plasticizers play an indispensable role (Hulleman et al., 1998), because the plasticizers can form hydrogen bonds with the starch. This is because starch is a multi-hydroxyl polymer with three hydroxyl groups per monomer. There are vast intermolecular and intramolecular hydrogen bonds in starch. When the plasticizers form hydrogen bonds with the starch, the original hydrogen bonds between hydroxyl groups of starch molecules are destroyed, thus enabling the starch to display the plasticization.

As the matrix, the conventional TPS materials are susceptible to aging and starch retrogradation. TPS, in which usually the plasticizer is glycerol, was thought to tend to retrogradation after being stored for a period of time. Starch retrogradation is re-crystallization of its molecules, which makes TPS fragile (Van Soest & Knooren, 1997). Urea was proven to prevent retrogradation. It is, however, a high melting solid with little internal flexibility and hence urea-plasticized TPS becomes rigid and brittle (Stein & Greene, 1997). Preliminary studies in our laboratory have shown that a combination of urea and formamide does effectively restrain TPS retrogradation and make thermoplastic starch flexible (Ma & Yu, 2004; Ma et al., 2004).

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Unfortunately, the properties of TPS are not satisfactory for some applications such as packaging materials. TPS has two main disadvantages when compared to most plastics currently in use, i.e. it is mostly water-soluble and has poor mechanical properties. Its water resistance may be improved by mixing it with biodegradable polymers (Averous et al., 2000), adding crosslinking agents such as tri-sodium tri-meta phosphate, $Na_3P_3O_9$ (Demirgöz et al., 2000) or adopting the multilayer technique. Multilayer films based on plasticized wheat starch (PWS) and various biodegradable aliphatic polyesters have been prepared through flat film coextrusion and compression molding. Biodegradable aliphatic polyesters are chosen as the outer layers of the stratified 'polyester/PWS/polyester' film structure (Martin et al., 2001).

Another approach is the use of fibers as reinforcement for TPS. The fibers described in the literature for this intention are cellulose micro-fibers (Dufresne & Vignon, 1998), natural fibers (Wollerdorfer & Bader, 1998) and commercial regenerated cellulose fibers (Funke et al., 1998). Unlike biodegradable polyester, when natural fibers are mixed TPS their mechanical properties are obviously improved, the chemical similarities of starch and of plant fibers providing a good compatibility. A significant improvement in water resistance is obtained by adding commercial cellulose fibers (Funke et al., 1998) or micro-fiber (Dufresne et al., 2000). This behavior is related to the highly crystalline 'hydrophobic' character of the cellulose fibers in comparison to starch hydrophilic property. Besides, these authors (Curvelo et al., 2001; Dufresne & Vignon, 1998) demonstrated an improved thermal stability due to a higher and longer thermal resistance of cellulose fibers.

This paper reported on the properties of TPS composites firstly prepared with urea (20 wt% of starch) and formamide (10 wt% of starch) as the mixed plasticizer and micro winceyette fiber as reinforcement. The mechanical properties, water resistance, thermal stability and starch retrogradation of the product materials were studied as a function of the fiber contents.

2. Experimental

2.1. Materials

Cornstarch (11% moisture) was obtained from Langfang Starch Company (Langfang, Heibei, China). The micro winceyette fiber with a fiber length of about 12 mm was obtained from Tianjin Textile Industry University. The plasticizers, glycerol, formamide, and urea, were purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. Plasticization

The plasticizers were blended (3000 rpm, 2 min) with cornstarch and fiber by use of a High Speed Mixer GH-100Y (made in China), and then stored overnight. The ratio of plasticizers and cornstarch (wt/wt) was 30:100. When two plasticizers were used together, another step for the premixture of them was required. Urea/formamide-plasticized TPS (UFPTPS) were prepared as following: The mixtures were manually fed into a single screw Plastic Extruder SJ-25(s) (Screw ratio $L/D = 25:1$, made in China). Operating at 20 rpm. The temperature profile along the extruder barrel was based on four heating zones, which are 120, 130, 130 and 110 °C from feed zone to die. The die was a round sheet with the diameter 3 mm holes.

2.3. Scanning electron microscope (SEM)

The fracture surfaces of extruded TPS strips were examined using Scanning Electron Microscope Philips XL-3, operating at an acceleration voltage of 20 kV. TPS strip samples were cooled in liquid nitrogen, and then broken. The fracture faces were vacuum coated with gold for SEM.

2.4. Storage conditions and water contents

In order to analyze the effect of environmental humidity on tensile properties and TPS retrogradation, the specimen is extruded through 3 mm holes, so the specimen is a columned strip, which is used for mechanical testing. Strips were stored in closed chambers over several aqueous mixtures at 20 °C for 5 or 10 days. The materials used are dried silica gel, $MgCl_2$ saturated solution, substantive 35.64% $CaCl_2$ solution, NaCl saturated solution and distilled water, providing relative humidities (RH) 0, 33, 50, 75 and 100%, respectively. The slices for X-ray diffractometry were stored at 50% RH and tested very few days.

Water contents were determined gravimetrically by drying small pieces of TPS at 105 °C overnight. At this temperature, evaporation of the plasticizers was negligible.

2.5. Mechanical testing

Samples of 8 cm diameter, 3 mm in size were cut from the extruded strips, and pressed with the Flat Sulfuration Machine into the sheet. Testometric AX M350-10KN Materials Testing Machine was operated at a crosshead speed of 10 mm/min for tensile testing (ISO 1184-1983 standard). The data was averaged over 5–8 specimens.

2.6. X-ray diffractometry

The extruded TPS strips were pressured at 10 MPa with the Flat Sulfuration Machine. After some storage time at several RHs (Relative Humidity), the slices were placed in a sample holder for X-ray diffractometry; Powders were packed tightly in the sample holder. X-ray diffraction patterns were recorded in the reflection mode in angular range 10–30°(2θ) at ambient temperature using a BDX3300 diffractometer, equipped with 1° divergence slit, a 16 mm beam bask, a 0.2 mm receiving slit and a 1° scatter slit operated at the Cu K(wavelength of 1.542 Å. The radiation from the anode, operating at 36 kV and 20 mA, monochromized with a 15 μm nickel foil. The diffractometer was. Radiation was detected with a proportional detector.

2.7. Thermal analysis (TG)

TPS was cut into small pieces (5–10 mg), which were tested using a ZRY-ZP thermal analysis instrument (Beijing Plastic Machinery Factory, Beijing, China). in the temperature range from room temperature to 450 °C using a heating rate of 15 °C/min.

3. Results and discussion

3.1. Microscopy

SEM micrograph at 500× magnification of fragile fractured surface of TPS filled with different fiber contents were shown in Fig. 1, which revealed the dispersion of fiber in TPS matrix. The fiber's surface appeared to be covered by TPS and fiber breakage was clear. This was attributed to strong interaction between the fiber and TPS.

However, a spot of starch granular figures, pointed out by the arrows in Fig. 1c and d, existed in TPS containing 15 or 20% fiber contents, while there was no obvious starch granular figures in TPS with low fiber content (as shown in Fig. 1a and b). This inferred that with increase of the fiber content, the starch granular fusion was affected by the fiber during the thermoplastic processing of TPS. The fiber content was limited by high viscosity or insufficient dispersion during processing. TPS with below 15% fiber content could be processed quite well without the additional plasticizer, when the weight ratio of the gross plasticizer and cornstarch (0.3:1) was kept constant.

3.2. Mechanical properties

The stress–strain curves (Fig. 2) of TPS, which had been immediately enveloped after thermoplastic processing and stored for 1 week in the plastic bags before the testing, showed that for TPS with low fiber contents (0 and 5%) represented the typical pattern of rubbery starch plastic materials reported previously (Van Soest & Knooren, 1997). The plots were essentially linear at low strain and curved towards the strain axis at higher strains. It was clear that with the increase in fiber contents, the height of the rubber plateau was increased although the length was shortened.

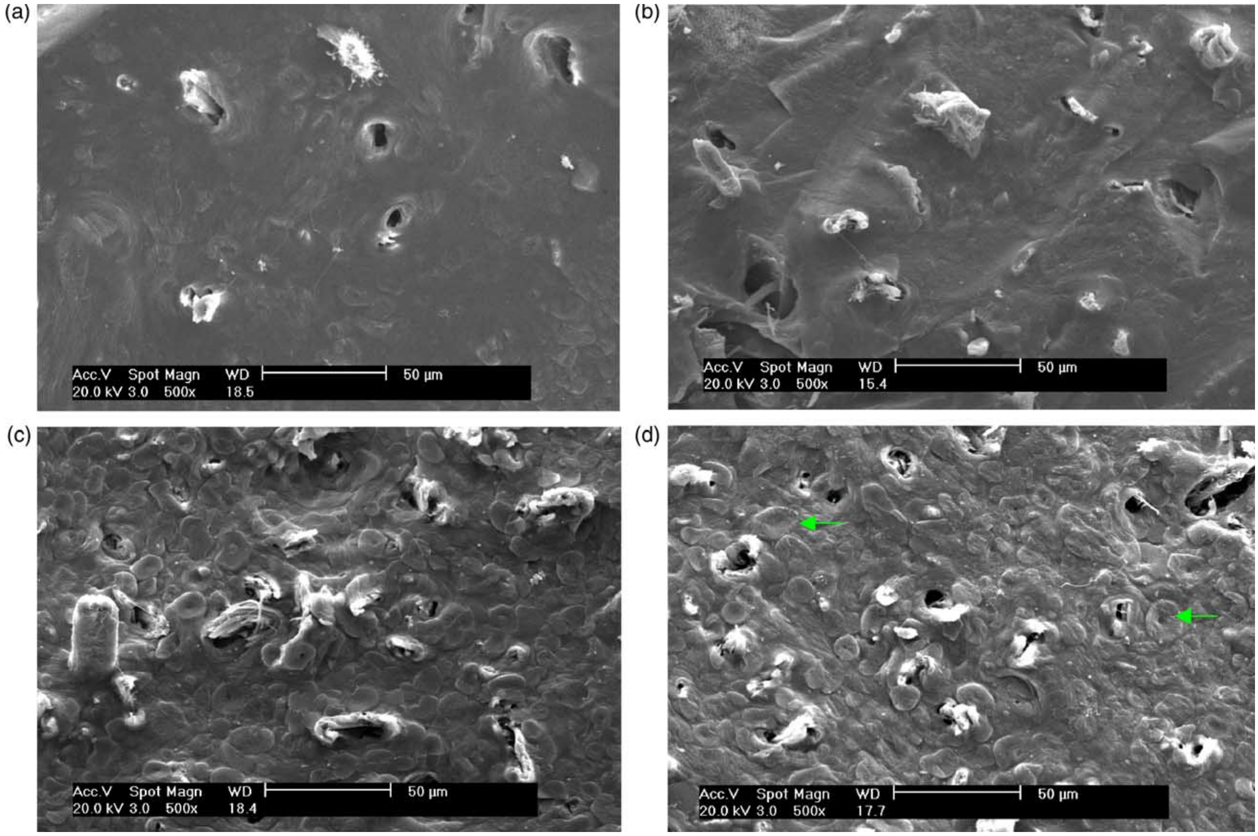

Fig. 1. SEM micrograph at 500× magnification of fragile fractured surface of TPS filled with different fiber contents. (a) 5% Fiber contents, (b) 10% fiber contents, (c) 15% fiber contents, and (d) 20% fiber contents.

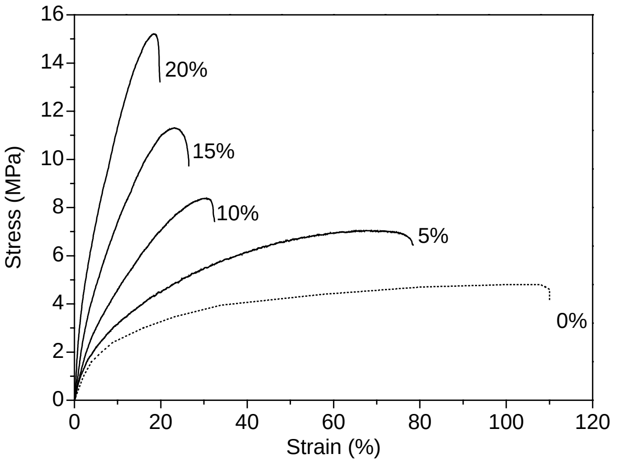

Fig. 2. The effect of the fiber contents on the stress–strain curves of TPS.

A comparison of the tensile strength, elongation, Youngs modulus and Energy Break for the fiber reinforced TPS with several different fiber contents to those of the pure TPS matrix (Fig. 3). showed that for increasing fiber content, the initial tensile strength was trebled up to 15.16 MPa, while the application of the fiber made the elongation fall from 105 to 19%. The Youngs modulus of TPS behaved analogous to the tensile strength as a consequent of introducing fibers. Energy Break, visually expressed as the areas below the stress–strain curves of TPS (in Fig. 2) had the similar behavior with the elongation. A considerable increase of tensile strength indicated that TPS was suited as the matrix for natural cellulose fibers. This was due to the remarkable intrinsic adhesion of the fiber–matrix interface caused by the chemical similarity of starch and the cellulose fiber.

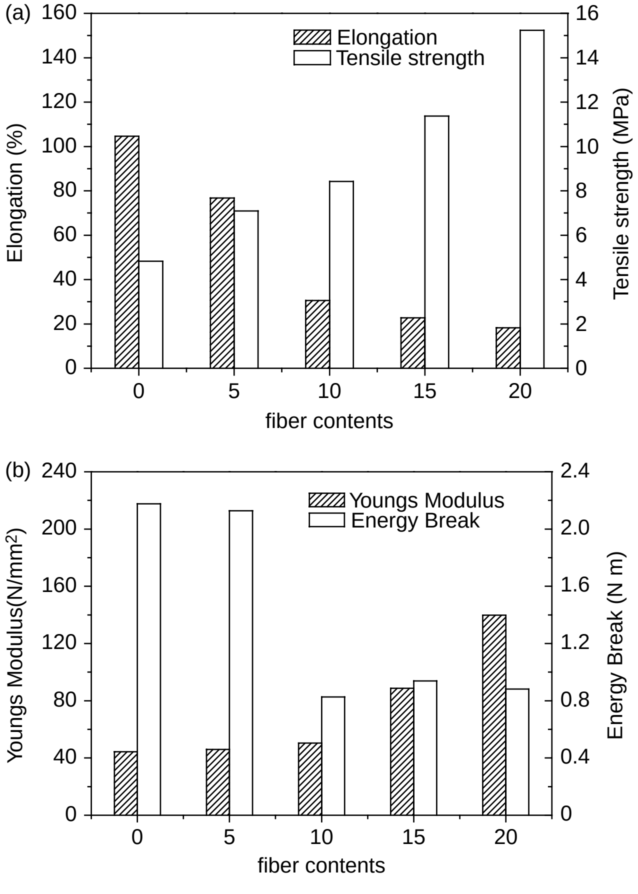

Fig. 3. The effect of the fiber contents on the mechanical properties of TPS.

TPS with different fiber contents were conditioned at different RHs. Changes in the environmental humidity and storage time greatly affected the water contents of TPS, which, in turn, induced large changes in the tensile strength (as shown in Fig. 4). The materials gradually lost mechanical strength with increase of water contents. The greater the fiber contents, the more the tensile strength of TPS was for almost the whole range of water contents. This evolution could be linked to strong fiber–TPS matrix interaction between the two carbohydrate products. The existence of such interaction, related to the fiber contents, had already been confirmed by Avérous et al. (2001). The Reinforcement effect increased with the fiber contents at the same water contents. However, this reinforcement effect was gradually weakened the increase of water content; since water could separately form hydrogen bond with starch and fiber, and then substitute original interaction between starch and fiber. At the high water contents (>20%) the fiber contents would have no effect on the tensile strength, and at even higher water contents (>30%) both the fiber and water contents would have no effect on the tensile strength.

The elongation of TPS with the different fiber contents changed with increasing water contents similarly (Fig. 4), i.e. the elongation of all samples decreased when the water contents deviated from a certain value. The more the fiber content was, the less the change of the curve. With increase of fiber contents, TPS basically had a reducing elongation over the whole range of water contents. For any individual TPS with different fiber content, water content could not obviously affect the elongation at high water contents (>25%).

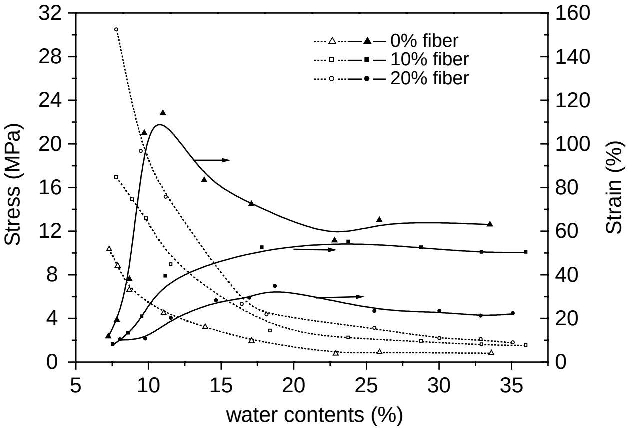

Fig. 4. The effect of water contents on the stress and strain of TPS with the different fiber contents.

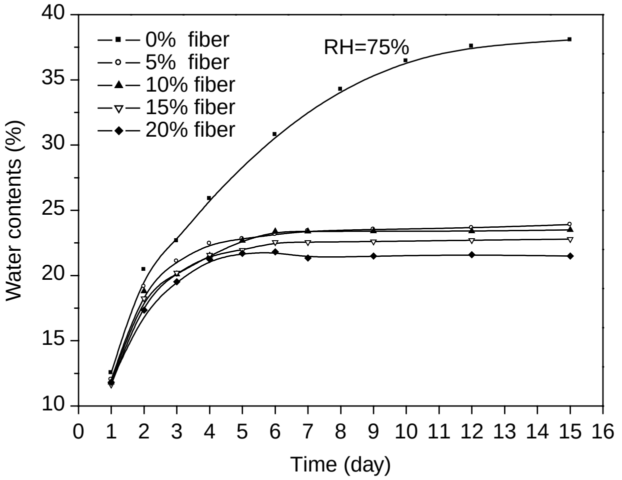

Fig. 5. The relation of water contents in TPS with different fiber and storage time at RH = 75%.

3.3. Water absorption

Water sensitivity is another important criterion for many practical applications of starch products. Fig. 5 showed the relation of water contents in TPS with different fiber and storage time at RH = 75%. It took only 6 days for TPS containing fiber to reach absorption equilibrium, and about 15 days for TPS without fiber component. The equilibrium water content for pure TPS was about 37%, while the one for TPS containing fiber from 21 to 24% varied with fiber contents variation.

As a whole, at high humidities the fiber component could effectively restrain the water absorption of TPS matrix, and reduced the water sensitivity of TPS. This behavior was related to the hydrophobic character of the fibers in comparison to starch hydrophilic property. However, the effect of fiber contents on the equilibrium water content or water sensitivity of the materials was not obvious, although basically the greater the fiber content was, the less the water absorption was.

3.4. Thermal stability

The behavior of the TG mass loss curves was similar in the composites (Fig. 6). The fiber, even at low content (5%, as shown in Fig. 6b), could improve thermal stability, while the effects of fiber contents (Fig. 6b–d) on mass loss at the onset temperature was not obvious. Mass loss at the onset temperature was 15 and 10% for pure TPS and the composites, respectively. For the composites, the moisture content mainly contributed to mass loss at the onset temperature (Curvelo et al., 2001), while for pure TPS the moisture content and the addition of plasticizer resulted in the mass loss. This difference was due to the good adhesion between TPS and fiber. The fiber component decreased the mass loss of plasticizer, therefore, the thermal stability of TPS materials was improved.

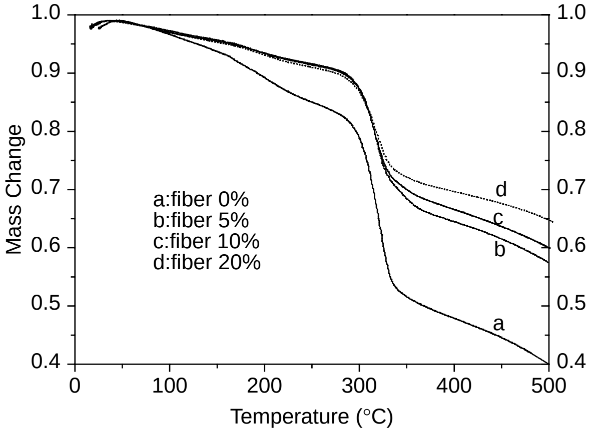

Fig. 6. The effect of fiber contents on thermal stability of TPS.

3.5. X-ray diffractometry

The X-ray diffractograms of TPS with different fiber contents and which had been stored at RH = 50% for two months (Fig. 7) showed that with increasing fiber content, the peak which was attributed to cellulose crystallinity at 22.5° (Vijay & Sanjeev, 1999), gradually got stronger. According a report (Amash & Zugenmaier, 2000), the addition of fiber would improve the crystallinity of the matrix. However, as the matrix, TPS plasticized by the mixture of urea and formamide did not show the obvious starch crystallinity peak at any of the different fiber contents (below 20%). This illustrated that this matrix still restrained the retrogradation of starch when fiber was added into the matrix. But as indicated by the arrows in Fig. 7d, the unobvious starch crystallinity peaks had appeared. Here obvious peak at 22.5° was ascribed to cellulose crystallinity. It meant that TPS with above 20% fibers could hardly resist starch re-crystallization without the additional plasticizer, which was similar to the result from SEM (Fig. 1d).

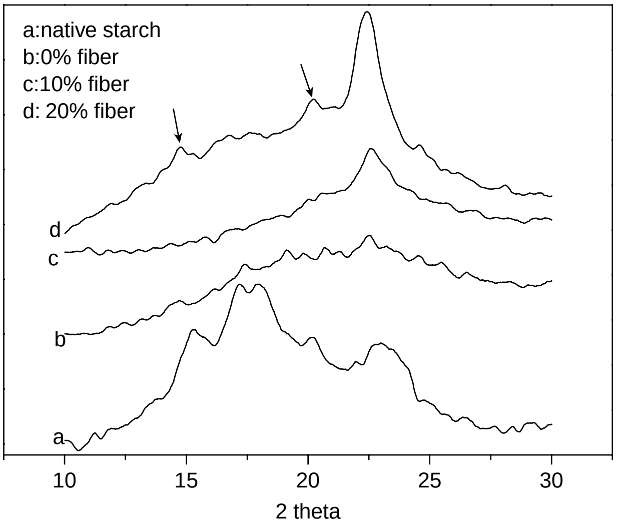

Fig. 7. The X-ray diffractograms of TPS with different fiber contents.

4. Conclusions

The introduction of micro winceyette fiber could effectively improve the tensile strength, water resistance and thermal stability of TPS because of the good adhesion between starch and fiber. With the increase of fiber content from 0 to 20%, the initial tensile strength was trebled up to 15.16 MPa, while the elongation was reduced from 105 to 19%. The reinforcement effect was gradually weakened with the increase of water content, but at the high water contents (>30%) both the fiber and water content had no effect on the tensile strength. When the weight ratio of the gross plasticizer and cornstarch (0.3:1) was kept constantly, TPS with below 15% fiber content could be processed quite well and TPS with below 20% fiber content could effectively restrain the starch retrogradation without the additional plasticizer.

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