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Study on the properties of ethylenebisformamide plasticized corn starch (EPTPS) with various original water contents of corn starch

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Abstract

EPTPSs were prepared based on various original water contents of corn starch (10%, 13%, 16% and 19%). The structure and mechanical performance of resulting TPSs were studied in detail. The hydrogen bond between plasticizer and starch was detected by FT-IR. By scanning electron microscope (SEM), native corn starch granules were proved to transfer to a continuous phase. The crystallinity and retrogradation of EPTPSs were studied by X-ray diffraction (XRD). The effect of water on the mechanical properties of EPTPSs was also tested. The effect of moisture content on the glass–rubber transition temperature (T_g) was studied using dynamic thermal mechanical analysis (DMTA). It revealed that T_g of EPTPS decreased with increasing moisture content.

Keywords: Starch; Biodegradable; TPS; Ethylenebisformamide

1. Introduction

Much effort emphasized on the biodegradable plasticized polymers for the aim of the replacement of synthetic polymers derived from petroleum industry (Avérous, 2004). Starch was a well known polymer with some advantages of biodegradable, renewable characters. However, starch is a non-plasticized material because of it higher glass transition temperature than it decomposition temperature. In order to making native starch into plastic, it was important to decrease T_g of native starch. The addition of plasticizer was an effective way to resolve this problem. Plasticizers increased film flexibility due to their ability to reduce internal hydrogen bonding between polymer chains while increasing molecular space. In the former investigation, the most effective plasticizers were generally resemble most closely to the structure of the polymer they plasticize, thus, the most commonly plasticizers used in starch-based films were small substance with hydroxyl group, such as water, sorbitol and glycerol (Cheng, Karim, & Seow, 2006; Fishman, Coffin, Konstance, & Onwulata, 2000; Liu, Yi, & Feng, 2001). Recently, we have investigated the feasibility of small substance with acyl-amine group such as formamide to plasticize starch (Ma & Yu, 2004a, 2004b). The results revealed that formamide can form stronger hydrogen bond with starch than that of glycerol. Formamide could restrain the retrogradation of starch because of the stronger hydrogen bond interaction between formamide and starch. Subsequently, a small molecule contain two acyl-amine group named ethylenebisformamide was synthesized and used to the preparation of EPTPS (Yang, Yu, & Ma, 2006). The mechanical properties of this EPTPS were enhanced compared with the conventional glycerol plasticized starch (GPTPS), especially in it elongation at break.

Water was a good plasticizer for starch. However, pure water plasticized starch proved to be a fragile material due to the volatilization of water. On the other hand, if the dry starch was employed to the preparation of TPS, the dosage of plasticizer increased multiplied. Commonly, TPS was prepared using polyols or amides with starch containing

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a small quantity of water. Water represented an important role on TPS and the moisture content in starch affected significantly the properties of TPS. In this paper, we prepared EPTPS with various original water contents of the corn starch. The purpose was to investigate the variety of the EPTPS at different moisture content.

2. Experimental section

2.1. Materials

Corn starch was obtained from Langfang Starch Company (Langfang, Heibei, China). ethylenediamine and methyl formate were purchased from Tianjin Chemical Reagent Ltd. (Tianjin, China).

2.2. Ethylenebisformamide synthesis

As a general procedure, methyl formate (500 ml) was placed in a 1000 ml flask cooled by ice-bath and 250 ml ethylenediamine was slowly added. Subsequently, ice-bath was removed and the solution was refluxed for 10 h and after standing overnight the products were isolated by filtration. The solids obtained by filtration were recrystallized from anhydrous ethyl alcohol, m.p. 108–110°C of the product was consistent to the lit (Sidney, Clifford, & Harry, 1962).

2.3. Preparation of EPTPS

The plasticizers were blended (3000 rpm, 2 min) with various water contents of corn starch in the High Speed Mixer GH-100Y (Beijing Plastic Machinery Factory, Beijing, China), and then stored overnight. The ratio of plasticizers and corn starch (moisture weight, wt/wt) was 30:100. EPTPS was prepared as following: The mixtures were manually fed into the single screw Plastic Extruder SJ-25(s) (Screw Ratio L/D = 25:1, Beijing Plastic Industry Combine Corporation, Beijing, China) with a screw speed of 10 rpm. The temperature profile along the extruder barrel was 130, 135, 130, 130°C (from feed zone to die). The die was a round sheet with the diameter 3 mm holes. The extruded samples were conditioned in the sealed polyethylene bags at room temperature.

2.4. Fourier transform infrared (FT-IR) spectroscopy

The IR spectra were measured with Bio-Rad FTS3000 IR Spectrum Scanner. The conditioned samples were pressured to the transparent slices (0.5 mm) at 10 MPa and 100 °C using the Flat Sulfuration Machine (a compression molder), and tested by the reflection method.

2.5. Scanning electron microscopy (SEM)

The native corn starch and the fracture surfaces of the conditioned samples were performed with Scanning Electron Microscope Philips XL-3 (FEI Company, Hillsboro, Oregon, USA), operating at an acceleration voltage of 20 kV.

Native corn starch powders were suspended in acetone. The suspension drops were drawn on the glass flake, dried for removing the acetone, and then vacuum coated with gold for SEM. The conditioned EPTPS samples were cryo-fractured in liquid nitrogen. The fracture faces were vacuum coated with gold for SEM.

2.6. X-ray diffractometry

The native corn starch, ethylenebisformamide and conditioned EPTPS samples were carried out using a BDX3300 X-ray diffractometer (40 kV, 100 mA) equipped with a Ni-filtered Cu radiation and a curved graphite crystal monochromator at a scanning rate of 2°/min. The diffractometer was equipped with 1° divergence slit, a 0.16 mm beam bask, a 0.2 mm receiving slit and a 1° scatter slit. Radiation was detected with a proportional detector.

2.7. Mechanical testing

The Testometric AX M350-10KN Materials Testing Machine was operated and a crosshead speed of 10 mm/min was used for tensile testing (ISO 1184-1983 standard). The size of samples was $8 \times \Phi 3$ mm (length × diameter). The data was averages of 5–8 specimens.

2.8. Dynamic thermal mechanical analysis (DTMA)

The DTMA using a Mark NETZSCH DMA242 analyzer was performed on hot-pressed thick specimens ($40 \times 7 \times 2$ mm, prepared by Flat Sulfuration Machine, 5 MPa, 100 °C), in a single cantilever bending mode at a frequency of 3.33 Hz and a strain × 2N, corresponding to a maximum displacement amplitude of 30 μm. The analyzer compared the stress and strain signals and resolved the strain into the in-phase (storage) and out-of-phase (loss) components, from which storage or elastic (E') and loss (E'') moduli as well as the tan $\delta = E''/E'$ were obtained as functions of temperature. The range of temperature was from −100 to 100 °C. The standard heating rate used was 3.0 °C min^{-1}. For polymeric materials, a drop in storage modulus and a peak in tan δ were used as indicators of a glass transition.

3. Results and discussions

3.1. FT-IR analysis

The analysis of FT-IR spectra of the blends enabled the hydrogen bond interaction to be identified (Aoi, Takasu, & Okada, 1998). On the basis of the harmonic oscillator model the reduction in force constant Δf could be represented by Eq. (1).

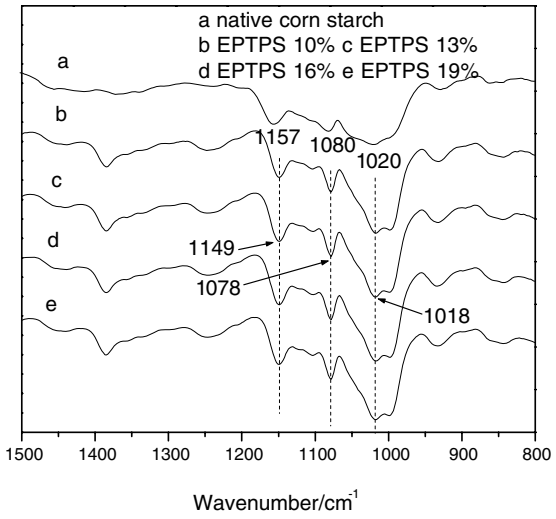


Fig. 1. FT-IR of native corn starch and EPTPS with various original water content of corn starch.

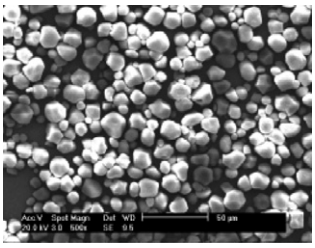
$$\Delta f = f_{np} - f_p = \frac{\mu(v_{np}^2 - v_p^2)}{4\pi^2} \quad (1)$$

where $\mu = m_1 m_2/(m_1 + m_2)$ corresponded to the reduced mass of the oscillator, v the oscillating frequency and f was the force constant. The subscripts np and p denoted non-plasticized and plasticized oscillators, respectively. In Eq. (1), v_{np} was a fixed value for native corn starch, and μ was invariable for the certain two oscillators. So, the reduction of force constant brought about by some interaction was directly related to the value of v_p. Thus, the lower the peak frequency the stronger was the interaction (Pawlak & Mucha, 2003).

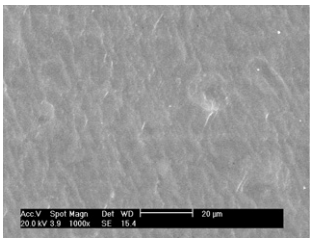
The frequency stretching shift of stretching vibration mode of native corn starch could be observed from Fig. 1. The characteristic peak 1080 and 1157 cm^{-1} (Fig. 1a) was ascribed to C–O bond stretching of C–O–H group, where the peak was shifted to 1078 and 1149 cm^{-1}, the 1020 cm^{-1} bond attributed to C–O bond stretching of C–O–C group in the anhydrous glucose ring (Fang, Fowler, Tomkinson, & Hill, 2002) shifted to 1018 cm^{-1}. From the analysis above, ethylenebisformamide could form stable hydrogen bond with starch. It was also found that the stretching shift of EPTPS at various original water contents of starch were the same to each other, which indicated that water could not affect the hydrogen bond between plasticizer and starch at the present water content.

3.2. Scanning electron microscopy (SEM)

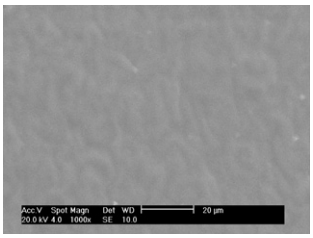
The microcosmic morphology of EPTPS was carried out using a scanning electron microscope two weeks after it preparation. Compared with native corn starch granules, TPS plasticized by ethylenebisformamide was a continuous phase. Form Fig. 2, it was found that with the original water content (10%) of native corn starch, the surface of



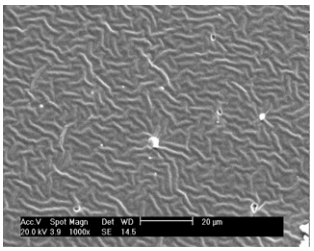
native corn starch granules



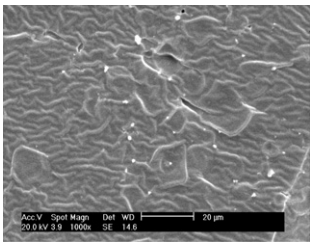
EPTPS (water content 10%)



EPTPS (water content 13%)



EPTPS (water content 16%)



EPTPS (water content 19%)

Fig. 2. SEM spectra of native corn starch and EPTPS with various original water contents of corn.

EPTPS is rather smooth. While the surface of EPTPS became rough with the increase of original water content of native corn starch, further more, a few crystallinities were observed at the original water content 16% and 19%. This phenomenon known as retrogradation was favored by the plasticization effect of water (Mathew & Dufresne, 2002). The mobility of amorphous chains increased with the water content in TPS, and the mobility of polymer chains favored the formation of crystalline domains of starch. As a result, the surface of EPTPS and it crystallinity transformed according to the amount of water in EPTPS.

3.3. Crystallization behavior and retrogradation of EPTPSs

The X-ray diffraction patterns of native corn starch and original TPS (newly prepared) materials were shown in Fig. 3. Compared with native corn starch, the crystal behavior of TPS plasticized by ethylenebisformamide changed much. In the processing, plasticizer molecules entered into starch particles, replaced starch intermolecular and intramolecular hydrogen bonds, and destructed the crystallinity of starch. According to the literatures reported formerly (Van Soest & Vliegenthart, 1997), there was typical

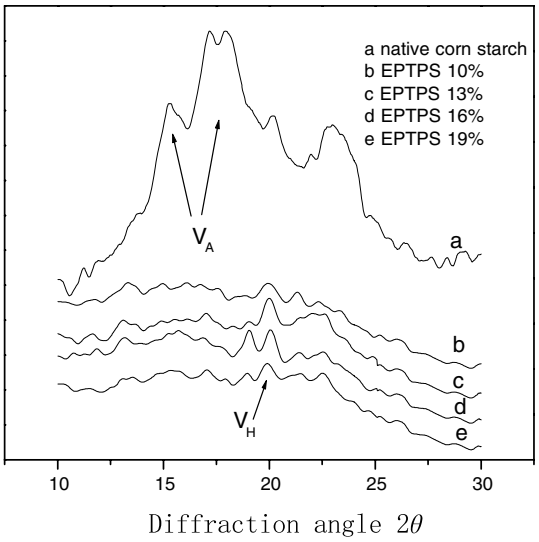


Fig. 3. X-ray spectra of native corn starch and EPTPS (newly prepared) at various original water contents.

A-type crystallinity in the native starch (Fig. 3a), but for EPTPS, A-type crystallinity disappeared and V_H-type crystallinity (the crystallinity between plasticizer and starch) was formed by the inductive of the thermal process.

Fig. 4 was the X-ray diffraction patterns of plasticizer and EPTPS (conditioned for 60 days at RH = 50% and RH = 100%) with various original water contents. Form Fig. 4, it was found that there was no A-type crystallinity of the native corn starch, which illustrated that ethylenebisformamide could restrain the retrogradation of starch. However, two crystallinities about 19° and 26° associated with plasticizer crytallinity were observed besides the existed V_H crystallinity. The possible explanation was that the melt point of ethylenebisformamide (108 °C) was high, i.e. the plasticizer was a solid at room temperature. So, it inclined to separate out of the EPTPS at the ambient atmosphere. On the other hand, when conditioned for 60 days at RH = 50%, the water uptake of EPTPS would equilibrium to each other, as a result, the area of crystallinity for individual EPTPS was equality basically. It was noticeable that there was no crystallinity of plasticizer when conditioned EPTPS (13%) in the RH 100% for two weeks (Fig. 4f). The reason must be that ethylenebisformamide was a hydrophilic material, and in a high moisture content ethylenebisformamide resolved in water, as a result, high moisture content restrained the separation of plasticizer from the EPTPS matrix.

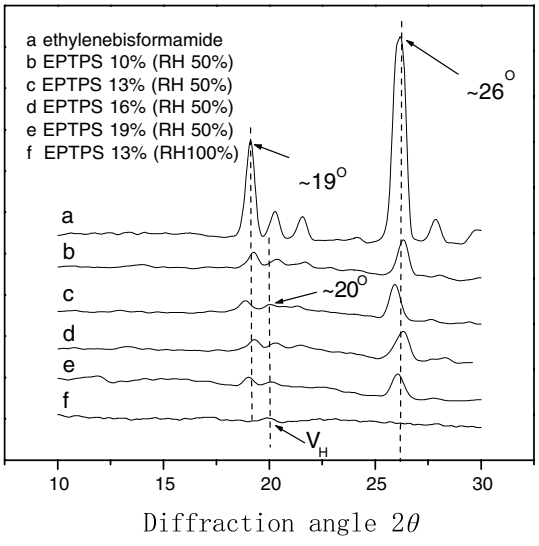


Fig. 4. X-ray spectra of ethylenebisformamide and EPTPS with various original water contents of corn starch.

3.4. Mechanical properties

The hydrophilic nature of thermoplastic starch made them susceptible to moisture attack and resultant changes in mechanical properties. The samples were exposed to a relative humidity level of 0% to 100% (Ma & Yu, 2004a) and the water uptake was determined. The stress and strain of EPTPSs at various moisture contents were shown in Figs. 5 and 6.

Form Fig. 5, it was indicated that the maximum elongation of EPTPSs (10%, 13%) related to the original water content of corn starch. However, the moisture content for the maximum elongation was similar at 15% for EPTPSs (16%, 19%). It was found that the elongation of all these EPTPSs decreased with the increase of moisture content after reaching the maximum. In the experimental section, we have mentioned that the process temperature of extruder was higher than 100 °C. Water would volatilize after the EPTPS was extruded. It was accepted that the volatilization of water occurred mainly on the surface of EPTPS. The prepared samples were subsequently conditioned in desiccators with different relative humidity. The water uptake of EPTPS in a higher relative humidity would mainly relate to the absorption of the surface of EPTPS, which would be equilibrium to the inner moisture content of the EPTPS, and the elongation of EPTPS would reach the maximum. The absorption of water continued after

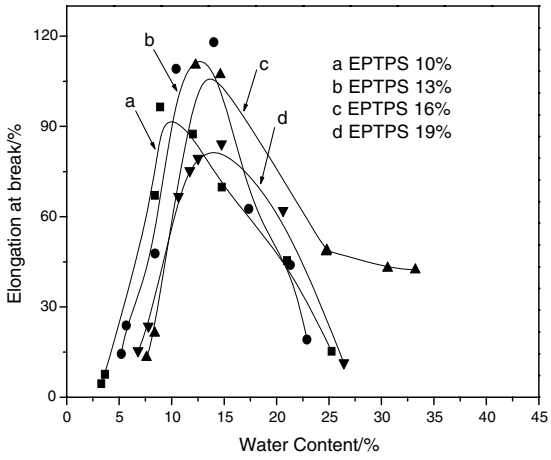


Fig. 5. Strain of EPTPS at various water contents.

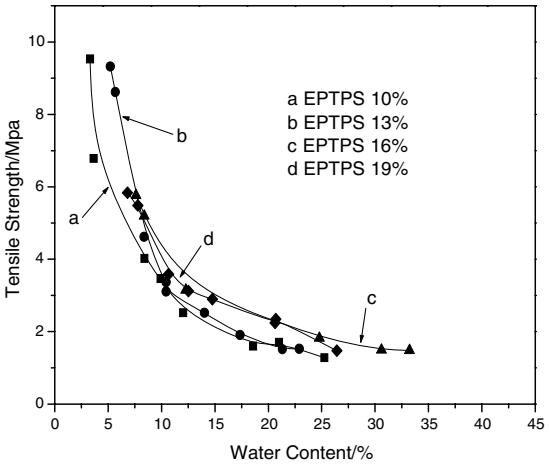


Fig. 6. Stress of EPTPS at various water contents.

equilibrium to it inner moisture content, which was mainly concentrated on the surface of the samples. The excesses water occupied the interspaces between starch and plasticizer, which leaded to the separation of starch and plasticizer, resulting in a decrease of the interaction between starch and plasticizer, therefore to a decrease of strain of EPTPSs.

For EPTPSs (16%, 19%), the elongation of which decreased with the moisture content higher than 15%. It was concluded that moisture content of EPTPSs more than 15% would destroyed the hydrogen bond between starch and plasticizer. It was indicated that proper moisture content of EPTPS was necessary to facilitate the formation of hydrogen bond between starch, plasticizer and/or water.

Another phenomenon was that the maximum of elongation of EPTPSs was not equal to each other. In the experimental results, the maximum of elongation of EPTPS (13%) was better than that of others. It could be explained by the reasons interpreted below. In order to process native starch, it was necessary to destruct its semi-crystalline granular structure, and during the procession, molecular structure of starch might be destroyed, e.g. depolymerization of starch, which would lead to the decrease of elongation of extruded EPTPSs. The depolymerization of starch in extruder has been shown to be accelerated under conditions of low moisture and high temperature (Chinnaswamy & Hanna, 1990; Myllymaki, Eerikainen, Forssell, Linko, & Poutanen, 1997). So, the EPTPS with low original water content of corn starch (10%) have the low elongation. In the preparation of EPTPS, we have attempted to process the blend of ethylenebisformamide (30%) and corn starch (original water content 8%), however, it was difficult to make the starch to plastic even raise the process temperature. Lin and Chang (2006) reported that the degradation of starch increased with the increasing concentration of plasticizer. With the increase of the original water content of corn starch, the concentration of plasticizer (including water and ethylenebisformamide) would increase in the blend. The increasing original water content would lead to the depolymerization of starch, resulting in the decrease of elongation of EPTPSs (16% and 19%, Fig. 5). It was concluded that proper water content should be combined with the blend of plasticizer and starch, thus, good mechanical properties of EPTPS would be obtained.

A sharp decrease in tensile stress and an increase in elongation at break were observed at water content below 15%. The material with water contents of 10–25% behaved in a rubbery fashion. EPTPS in the rubbery stare were soft and weak, having high elongations and low tensile stress. The stress of EPTPS decreased with the increase of water content as shown in Fig. 6, the final value of which was between 1 and 2 MPa.

3.5. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical experiment was a valuable technique to investigate the mechanical behavior of the materials, provide information about the relaxation mechanisms that might correlate with the composition and the microstructure of the materials. DMTA of EPTPS with the original water content (13%) of corn starch at three RHs conditioned ranging from 0 to 100% was shown in Fig. 7, and the detail about the storage modulus, dissipation factor tan δ and T_g were summarized in Table 1.

From Fig. 7, the evolution of tan δ showed two relaxations. They were ascribed to the existence of two phases in the plasticized matrix. The low temperature transition was assigned to T_g of plasticizer-rich domains and the high temperature one to T_g of starch-rich domains (Mathew & Dufresne, 2002). It could be seen that these two transitions of EPTPS shifted to lower temperatures with increasing moisture content (Table 1). The height of the tan δ peak was also took into consideration by Martin and Avérous (2001) formerly, which was ascribed to the degree of crystallinity: amorphous materials showed an intense peak because there was no restriction to the chain motion, whereas the crystal materials hinder the chain mobility, resulting in the reduction of height of tan δ. From Table 1,

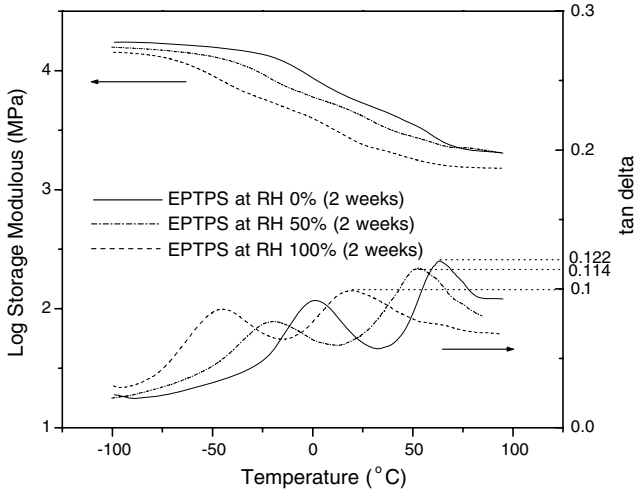


Fig. 7. Storage modulus and tanδ (DMTA) of EPTPS.

Table 1
DMTA behavior of EPTPS (13%) at different moisture content

	Log storage modulous (MPa)	$(\mathrm{Tan}\,\delta 1)_{max}$	T_{g1} (°C)	$(\mathrm{Tan}\,\delta 2)_{max}$	T_{g2} (°C)
EPTPS (RH = 0)	4.242	0.092	−45.1	0.122	64.2
EPTPS (RH = 50%)	4.194	0.077	−20.1	1.114	52.3
EPTPS (RH = 100%)	4.158	0.086	1.1	0.1	19.2

it indicated that at the starch-rich domains, the height of tan δ peak of EPTPS decreased with the increasing RH levels. It decreased from 0.112 for the 0% RH conditioned sample down to 0.1 for the 100% RH conditioned matrix. This phenomenon was ascribed to the formation of larger crystal domains with increasing water content, due to an increased mobility of the amorphous chains. The storage modulus value of EPTPS decreased with the increasing RH, i.e. a rigid material would be obtained at a lower RH, which was consisted to the results in Fig. 6.

4. Conclusions

EPTPSs were prepared based on various original water contents of corn starch. FT-IR of these EPTPSs was similar to each other at the present water content. SEM and DMTA analysis revealed that crystallinity of the EPTPSs matrix increased with the increase of water content due to the plasticizing effect of water. T_g of EPTPS decreased with the increasing moisture content. By the study on the mechanical properties of EPTPSs, it was testified that proper water content favored the formation of hydrogen bond of starch, plasticizer and/or water, resulting in the increase of elongation at break of EPTPSs.

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