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Study on the properties of ethylenebisformamide and sorbitol plasticized corn starch (ESPTPS)

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Abstract

A mixed plasticizer (ethylenebisformamide and sorbitol) was used to the preparation of thermoplastic starch (TPS). And the other three TPSs were prepared as a contradistinction, including glycerol plasticized starch (GPTPS), ethylenebisformamide plasticized starch (EPTPS), and sorbitol plasticized starch (SPTPS). FT-IR expressed that the microcosmic chemical environments of the group in all these TPSs mentioned above shifted to lower frequency compared with the native corn starch, which indicated that, the strong and stable hydrogen bond had been formed between plasticizers and starch. By scanning electron microscope (SEM) native corn starch granules were proved to transfer to a continuous phase. After being stored for 2 weeks at ambient atmosphere, the mechanical properties of these TPSs were investigated and a comprehensive tensile stress and elongation at break of ESPTPS was obtained better than that of EPTPS, SPTPS, and GPTPS. X-ray diffraction (XRD) showed that the typical A-style crystallinity in the native corn starch has been destructed. On the other hand, water resistance of ESPTPS was better than the conventional GPTPS. ESPTPSs proved to be having good thermal stability by thermogravimetric analysis (TGA), and the decomposition temperature was increased with the increase of the sorbitol content. T_g (detected by dynamic thermal mechanical analysis (DTMA)) of ESPTPSs was lower than that of EPTPS and SPTPS.

Keywords: Thermoplastic starch; Ethylenebisformamide; Sorbitol; Mechanical properties

1. Introduction

It was well known that starch was an inexpensive and abundant natural resource. Many efforts had been made to develop biodegradable materials based on starch because of the worldwide environment and resource problems resulting from the petroleum-derived plastics (Avérous, 2004). Native starch was a non-plasticized material because of the intra- and inter-molecular hydrogen bonds between hydroxyl groups of starch molecules, which leaded to the crystallinity in the native starch. Thermoplastic process was the transformation of the semi-crystalline granule into a homogeneous material with the destruction of hydrogen bonds between the macromolecules under shear and pressure. In this process, some small molecular substances commonly named plasticizer were added to the native starch and blended thoroughly previously, and then plasticized under shear and pressure, new hydrogen bonds between plasticizer and starch were formed synchronously with the destruction of hydrogen bonds between starch molecular, thus starch was plasticized.

Traditional plasticizers were polyols such as glycerol, glycol, xylitol, sorbitol, and sugars (Avérous, 2004; Fishman, Coffin, Konstance, & Onwulata, 2000; Forssell, Mikkilä, Moates, & Parker, 1998; Liu, Yi, & Feng, 2001; Wang, Shogren, & Carriere, 2000; Barret, Kaletunc, Rosenburg, & Breslauer, 1995). Some small molecules contain –CO-NH– functional group like urea (Kazuo et al., 1998) was also proved to be as plasticizer for the native starch. It was, however, a solid with little internal flexibility and hence urea-plasticized TPS became rigid

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and brittle. In our previous work (Ma & Yu, 2004a, 2004b, 2004c), we investigated the formamide or formamide/urea as plasticizers to produce TPSs. The elongation at break was enhanced and water resistant was ameliorated to some extent. Recently, we utilized a novel plasticizer ethylenebisfomamide (Yang, Yu, & Ma, 2006) to prepare thermoplasticized starch (EPTPS), the result indicated that EPTPS was a water resistance material and the elongation at break was enhanced extremely compared with TPSs mentioned above, while the tensile stress was rather low. Sorbitol plasticized starch (SPTPS) was known to be a material of high tensile stress and low elongation at break. So the combination of ethylenebisformamide and sorbitol as a mixed plasticizer was expected to improve the mechanical properties of TPS. From all of the results, this mixed plasticizer plasticized starch (ESPTPS) was considered to be a better material on its mechanical properties and water resistance than the conventional TPSs.

2. Experimental section

2.1. Materials

Corn starch (12% moisture) was obtained from Langfang Starch Company (Langfang, Heibei, China). Glycerol, ethylenediamine and methyl formate were purchased from Tianjin Chemical Reagent Ltd. (Tianjin, China) and sorbitol from KRS Fine Chemical Co. 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, 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 was consistent to the literature (Sidney, Clifford, & Harry, 1962).

2.3. Preparation of TPSs

The plasticizers were blended (3000 rpm, 2 min) with 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 (wt/wt) was 30:100. TPSs were 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 135–140–140–135 °C (from feed zone to die) for the preparation of EPTPS and ESPTPS, 110–120–120–110 °C for GPTPS and 153–158–153–150 °C for SPTPS. The die was a round sheet with the diameter 3 mm holes. The extruded samples were conditioned in the sealed polyethylene bags at ambient atmosphere for 2 weeks.

2.4. Fourier transform infrared (FT-IR) spectroscopy

The IR spectra were measured with Bio-Rad FTS3000 IR Spectrum Scanner. The conditioned TPSs 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, OR, 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 TPSs 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, conditioned TPSs 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. Water absorption

The bars of samples were cut into small pieces, and weighed immediately, then put into the oven, dried at 105 °C for 24 h. These small pieces of sample were weighed immediately after being taken out. The water content rate (K) took the following formulation:

$$K = \frac{w_2 - w_1}{w_1} \times 100\%,$$

in which, w_2 was the real mass of the sample, g; w_1 was the mass of the drying sample, g.

The samples were stored at different relative humidity conditions for a period of time, then taken out and weighed immediately. The water content rates (K) at different relative humidity were calculated.

2.8. 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 cm × 3 mm (length × diameter). The data were average of 5–8 specimens.

2.9. Thermogravimetric analysis (TGA)

TPS was cut into small crumb, which were tested by ZRY-ZP thermal analysis instrument (Beijing Plastic Machinery Factory, Beijing, China). The experiments were carried out in the air. The samples were about 5–10 mg, the scope of testing temperature was from the room temperature to 510 °C and the heating rate was 15 °C/min.

2.10. Dynamic thermal mechanical analysis (DTMA)

The dynamic thermal mechanical analysis (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)

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

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 variation 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 from 1150 cm^{-1} to 1148 cm^{-1} (Figs. 1b–d), the 1020 cm^{-1} bond attributed to C–O bond stretching of C–O–C group in the anhydroglucose ring (Fang, Fowler, Tomkinson, & Hill, 2002) shifted from 1018 to 1016 cm^{-1} and the band at 3395 cm^{-1} associated with O–H group shifted from 3304 to 3294 cm^{-1}.

As shown in Fig. 1, the frequency stretching shift of both in C–O–H group and C–O–C group were similar to each other for different TPSs, which indicated that strong and stable hydrogen-bonds were formed between plasticizer and O atom in C–O bond of starch. It was found that the O–H bond stretching were variation for these TPSs. For the reason of lower peak frequency related to the stronger interaction of plasticizer and starch, it could be deduced that the order of the hydrogen-bond-forming ability for plasticizers was ethylenebisformamide > sobitol > glycerol. For the mixed plasticizer, stronger hydrogen bond was formed with the increase of ethylenebisformamide.

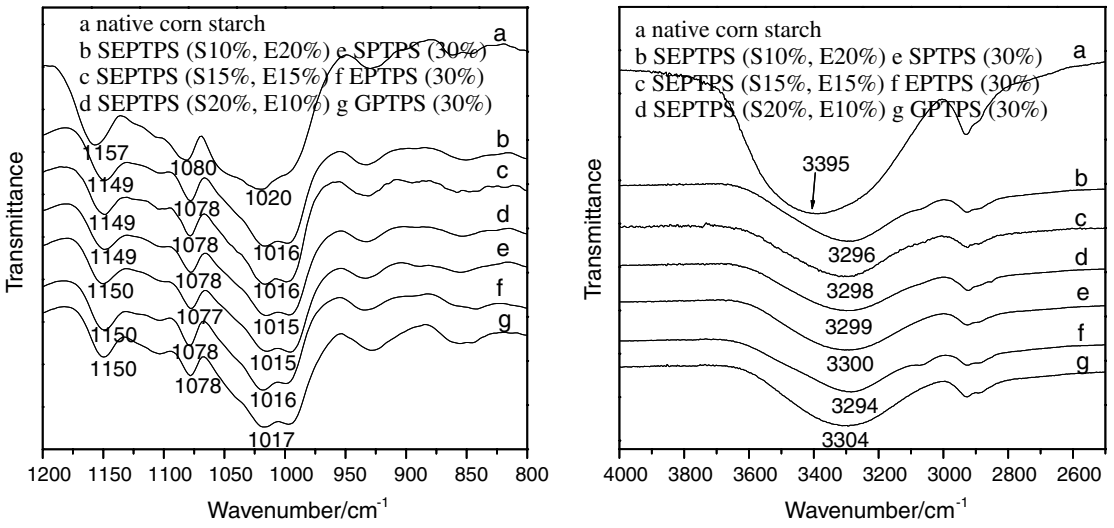


Fig. 1. FT-IR spectra of ethylenebisformaide plasticized TPS (S: Sorbitol, E: ethylenebisformamide, plasticizer content: wt %).

3.2. Scanning electron microscopy (SEM)

Stable hydrogen bond formed between plasticizer and starch by the analysis of FT-IR spectra. A continuous phase was predicated to be formed under shear and pressure as a result. The microcosmic morphology of native corn starch granules and the extruded TPS was shown in Fig. 2. Compared with native corn starch granules, the microcosmic morphology of TPSs prepared using single or mixed plasticizer was a continuous phase. Due to the high shear and temperature conditions with the action of plasticizer, native corn starch granules were molten or physically broken up into small fragments. These plasticizers were tested to disrupt intermolecular and intramolecular hydrogen bonds of native corn starch and made it plastic.

3.3. Crystallization behavior

The crystallization behavior of native corn starch and original TPSs (newly prepared) could be detected by the X-ray experiment. As shown in Fig. 3, the crystallization behavior of TPS plasticized by single or mixed plasticizers changed much compared with native corn starch. 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 earlier literatures (Van Soest & Vliegenthart, 1997), there was typical an A-type crystallinity

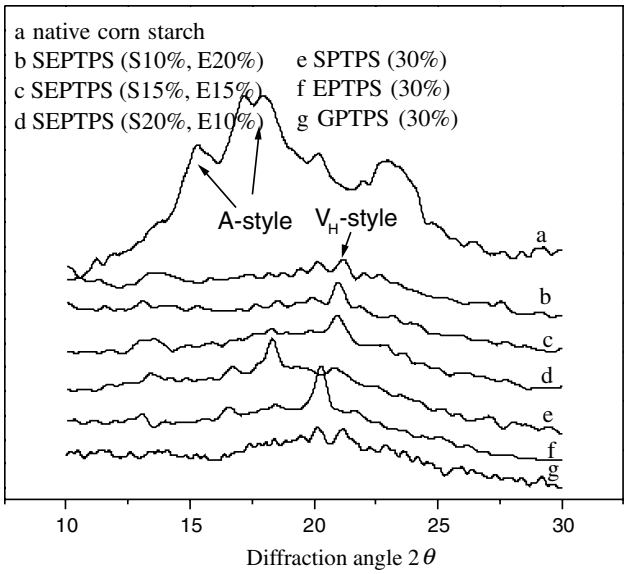
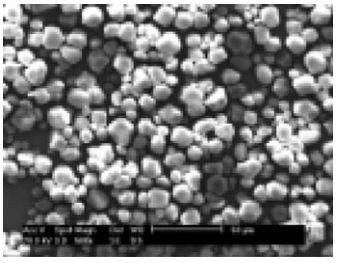
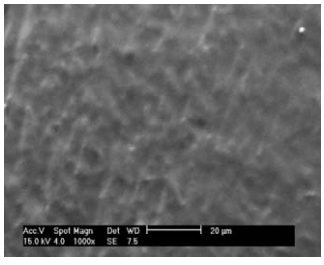


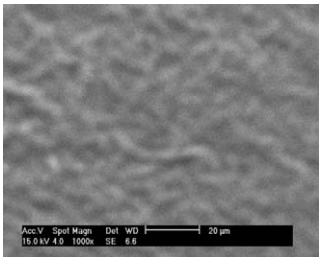
Fig. 3. The diffractograms of native cornstarch and different TPSs.



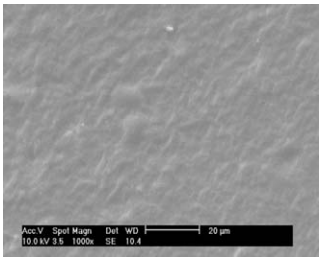
native cornstarch granules



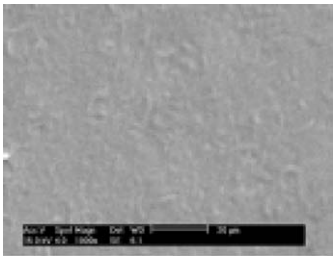
ESPTPS (S 10%, E 20%)



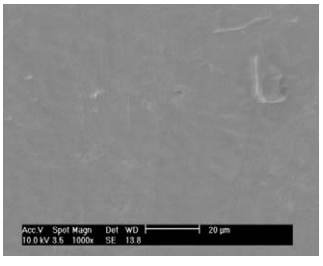
ESPTPS (S 15%, E 15%)



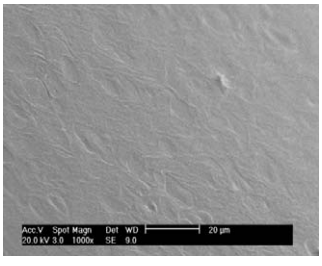
ESPTPS (S 20%, E 10%)



SPTPS (30%)



EPTPS (30%)



GPTPS (30%)

Fig. 2. SEM micropgraph of native corn starch and several TPSs.

in the native starch (Fig. 3a), after the thermal process of the mixture of corn starch and plasticizer, A-type crystallinity of native corn starch disappeared and a V_H-type crystallinity (the crystallinity between plasticizer and starch) was formed due to the inductive of the thermal process with the destroy of native corn starch crystallinity.

3.4. Water absorption

Water absorption of the prepared TPSs at RH 100% was shown in Fig. 4. From the curve of Fig. 4, we found that the balance water content of SPTPS, EPTPS and ESPTPS was evident lower than that of GPTPS. After 35 days equilibrium, the utmost balance water content of these TPSs were 30.9%, 35.2%, 38.8%, 38.2%, 40.5%, and 53.0% (from a to f), respectively. The drastically decrease of the water content of SPTPS, EPTPS, and SPTPS compared with that of GPTPS indicated that these TPSs were better water resistant materials. The causation of this phenomenon must be that ethylenebisformamide and sorbitol could form stronger hydrogen bonds with corn starch than that glycerol with corn starch, which restrained the water molecule to combine with the plasticizer or the corn starch. As a result, TPSs prepared by ethylenebisformamide, sorbitol or the mixture of them presented good water resistance.

3.5. Mechanical properties

The effects of various mixture of ethylenebisformamide and sobitol (maintaining a constant total content of 30%) on the mechanical properties of TPSs were shown in Fig. 5. For SPTPS, the peak stress was 9.1 MPa, and the peak strain was only 69.2%. On the contrary, EPTPS showed a higher elongation at break (176.2) and a lower tensile stress (3.5 MPa). The tensile stress of ESPTPS incresed with the increase of sorbitol content, and the elongation at break reached the maximum value of 117.5% when the ratio of sobitol:ethylenebisformamide was 15:15. Compared with the conventional GPTPS, the present ESPTPS have better mechanical properties on the tensile stress and elongation at break. From the discussion above, the mixed plasticizer (ethylenebisformamide and sorbitol) plasticized starch possessed a comprehensive mechanical properties better than the single plasticizer (including glycerol, ethylenebisformamide, and sorbitol) plasticized ones.

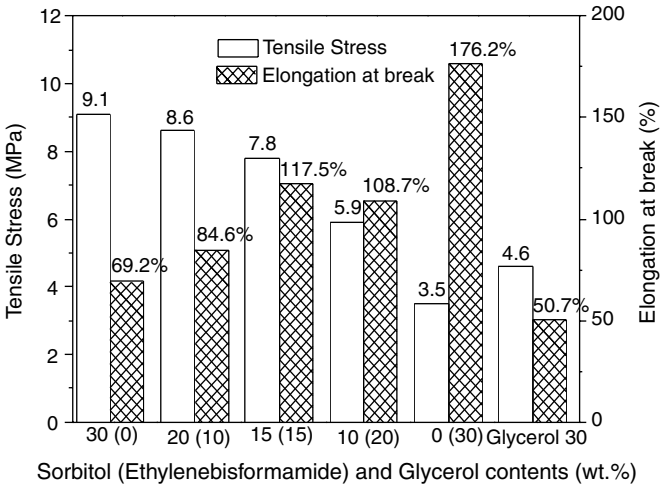


Fig. 5. Effect of different plasticizer on the mechanical properties.

3.6. Thermal stability

Fig. 6 presented the TGA experimental results. The forms of the mass loss curves were similar for these TPSs. Since the boiling points of the plasticizers were above 100 °C, the mass loss below 100 °C was mainly ascribed to water loss and from 100 °C to the decomposition onset

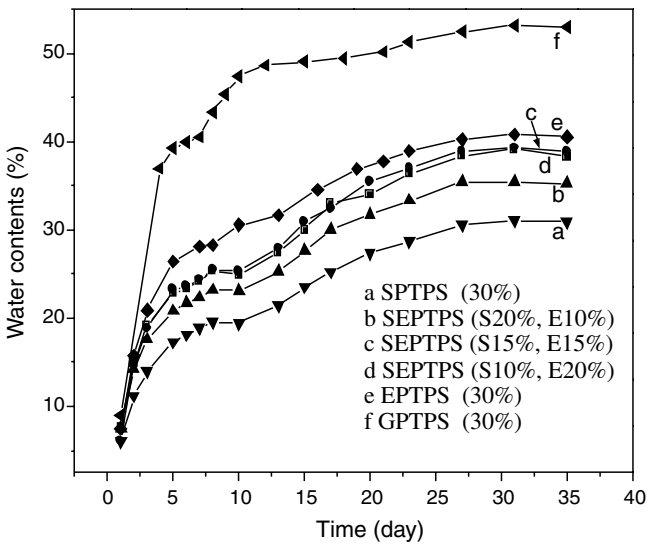


Fig. 4. Water contents of several TPSs at RH100%.

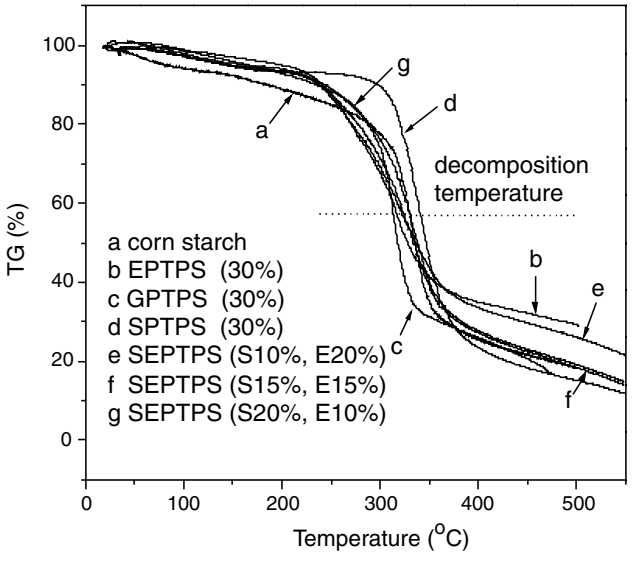


Fig. 6. TGA curves of native corn starch and different TPSs.

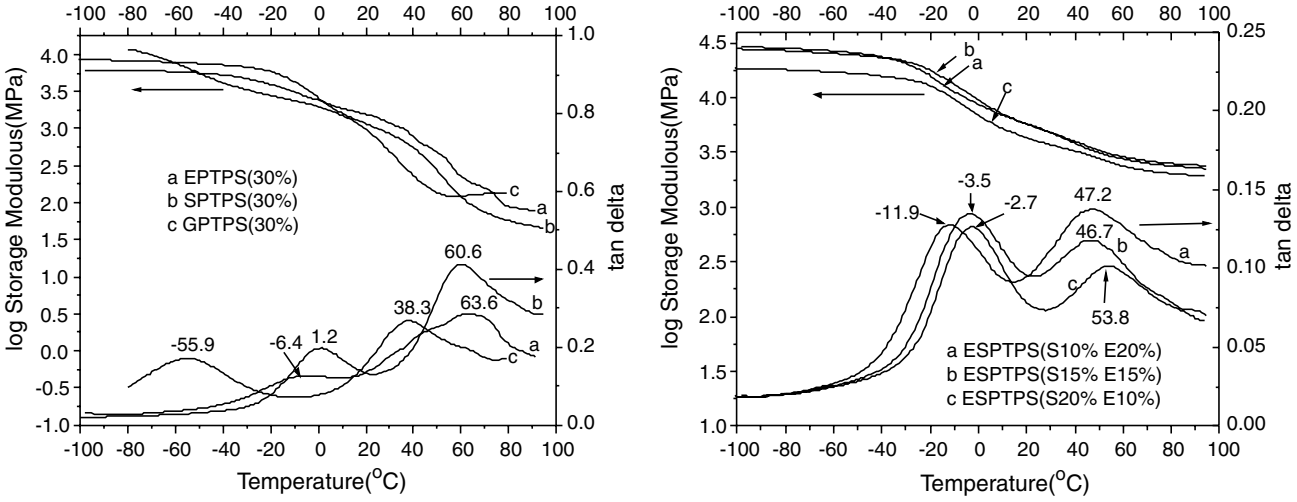


Fig. 7. Storage modulus and tan δ (DMTA) of several TPSs.

temperature was related to the volatilization of both water and plasticizers. Compared with native corn starch, all these TPSs could restrain the water loss below 100 °C because of the interaction between water and TPSs. As shown in Fig. 6, the decomposition temperature was lined out by the dot line and the residual weight for the dotted line was 58% or so. It was proved that the decomposition temperature of EPTPS, SPTPS, and ESPTPS was higher than that of GPTPS, the reason must be that stronger hydrogen bond was formed between ethylenebisformamide/sorbitol and starch than that glycerol and starch, which made its possess better thermal stability than the conventional GPTPS.

3.7. Dynamic mechanical thermal analysis

Dynamic mechanical experiment was a valuable technique to investigate the mechanical behavior of the materials, provide information about the relaxation mechanisms that correlated with the composition. Dynamic mechanical thermal analysis (DMTA) of several TPSs was shown in Fig. 7.

From Fig. 7, the evolution of tan δ showed two relaxations. The higher relaxation associated with an important decrease of the storage modulus attributed to the TPS glass relaxation which decreased drastically compared with that of the native starch (Bikiaris & Panayiotou, 1998). As reported elsewhere (Lourdin, Bizot, & Colonna, 1997), the lower relaxation could be consistent with the plasticizer glass transition and independence of the plasticizer content. During the plasticized process, intermolecular and intramolecular hydrogen bonds of the native starch were substituted by the hydrogen bonds between starch and plasticizer, as a result, T_g of the starch decreased. T_g of GPTPS, SPTPS, and EPTPS was 38.3, 60.6, and 63.6 °C, respectively. This evolution could be ascribed to the strong action between the starch and plasticizer, as we have discussed in FT-IR section, the order of hydrogen-bond-forming ability was ethylenebisformamide > sorbitol > glycerol, and the stronger hydrogen bonds could decrease starch chain mobility and consequently increased the matrix glass transition. The lower relaxation of ESPTPS correlated with the plasticizer showed a regular change, it increased with the increase content of sorbitol, however, T_g of the mixed plasticizer was not predicated in the range of two T_g of ethylenebisformamide and of sorbitol. Furthermore, T_g of ESPTPSs was all lower than that both EPTPS and SPTPS. It was hypothesized that during the thermoplasticized process, a certain hydrogen bond was formed between ethylenebisformamide and sorbitol, as a result the amount of hydrogen bond between plasticizer and starch decreased, which resulted in the decrease of T_g of the mixed plasticizer and EPTPSs.

4. Conclusion

The properties of several TPSs had been detected by means of different technology. The analysis of FT-IR, X-ray, and SEM indicated that intra- and intermolecular hydrogen bonds of starch had been destructed, and the microcosmic morphology of TPSs was predicated to be a continuous phase. From the result of water absorption curve and stress–strain curve, TPSs prepared by glycerol, ethylenebisformamide or sorbitol revealed some disadvantages on its water resistance or mechanical properties. Mixture of ethylenebisformamide and sorbitol was proved to be a good plasticizer for the corn starch. Compared with the single plasticizer (glycerol, ethylenebisformamide or sorbitol) plasticized starch, ESPTPS possessed the characteristics of good water resistance and mechanical properties, which illuminated that ESPTPS was a good material. T_g of ESPTPS was lower than that of EPTPS and SPTPS, which indicated the interaction between ethylenebisformamide and sorbitol.

References

Aoi, K., Takasu, A., & Okada, M. (1998). New chitin-based polymerhybrids, 3. Miscibility of chintin-graft-poly (2-ethyl-2-oxazoline) with poly (vinyl alcohol). *Macromolecular Chemistry and Physics, 199*, 2805–2811.

Avérous, L. (2004). Biodegradable multiphase systems based on plasticized starch: A review. *Journal of Macromolecular Science: Part C–Polymer Reviews, 44*(3), 231–274.

Barret, A., Kaletunc, G., Rosenburg, S., & Breslauer, K. (1995). Effect of sucrose on the structure, mechanical strength and thermal properties of corn extrudates. *Carbohydrate Polymer, 26*, 261–269.

Bikiaris, D., & Panayiotou, C. (1998). LDPE/starch blends compatibilized with PE-g-MA copolymers. *Journal of Applied Polymer Science, 70*(8), 1503–1521.

Fang, J. M., Fowler, P. A., Tomkinson, J. C., & Hill, A. S. (2002). The preparation and characterisation of a series of chemically modified potato starches. *Carbohydrate Polymer, 47*, 245–252.

Fishman, M. L., Coffin, D. R., Konstance, R. P., & Onwulata, C. I. (2000). Extrusion of pectin/starch blends plasticized with glycerol. *Carbohydrate Polymer, 41*, 317–325.

Forssell, P. M., Mikkilä, J. M., Moates, G. K., & Parker, R. (1998). Phase and glass transition behavior of concentrated barley starch-glycerol-water mixtures, a model for thermoplastic starch. *Carbohydrate Polymer, 34*, 275–282.

Kazuo, O., Isao, Y., Toshiaki, Y., Shin, O., Seichi, R., Yuuko, N., et al. (1998). Studies on the retrogradation and structural properties of waxy potato starch. *Bulletin of Chemical Society in Japanese, 71*, 1095–1100.

Liu, Z. Q., Yi, X. S., & Feng, Y. (2001). Effects of glycerin and glycerol monstearate on performance of thermoplastic starch. *Journal of Material Science, 36*, 1809–1815.

Lourdin, D., Bizot, H., & Colonna, P. (1997). ''Antiplasticization'' in starch-glycerol films. *Journal of Applied Polymer Science, 63*(8), 1047–1053.

Ma, X. F., & Yu, J. G. (2004a). Studies on the properties of formamide plasticized-thermoplastic starch. *Acta Polymerica Sinica, 2*, 240–245.

Ma, X. F., & Yu, J. G. (2004b). The plasticizers containing amide groups for thermoplastic starch. *Carbohydrate Polymer, 57*, 197–203.

Ma, X. F., & Yu, J. G. (2004c). Urea and formamide as a mixed plasticizer for thermoplastic starch. *Polymer International, 53*, 1780–1785.

Pawlak, A., & Mucha, M. (2003). Thermogravimetric and FTIR studies of chitosan blends. *Thermochimica Acta, 396*(1–2), 153–166.

Sidney, V. L., Clifford, M. M., & Harry, M. B. (1962). Extent of formaldehyde reaction with selected amides. *Journal of Organic Chemistry, 27*, 2067–2070.

Van Soest, J. J. G., & Vliegenthart, J. F. G. (1997). Crystallinity in starch plastics: consequences for material properties. *Trends in Biotechnology, 15*, 208–213.

Wang, L., Shogren, R. L., & Carriere, C. (2000). Preparation and properties of thermoplastic starch-polyester laminate sheets by coextrusion. *Polymer Engineering and Science, 40*, 499–506.

Yang, J., Yu, J., & Ma, X. (2006). Preparation and properties of ethylenebisformamide plasticized potato starch (EPTPS). *Carbohydrate Polymers, 63*, 218–223.