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Effect of carbonyl content on the properties of thermoplastic oxidized starch

Yu-Rong Zhang, Shui-Dong Zhang, Xiu-Li Wang, Rong-Yi Chen, Yu-Zhong Wang *

Center for Degradable and Flame-Retardant Polymeric Materials (ERCEPM-MoE), College of Chemistry, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610064, China

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ABSTRACT

In order to improve the properties of starch, oxidized starches (OS) with different carbonyl contents were prepared by hydroxyl peroxide under mild conditions. Glycerol as a plasticizer was added into OS to produce thermoplastic oxidized starches (TPOS). It was found that the content of carbonyl and carboxyl had a great effect on the thermal properties, mechanical properties and moisture resistance of TPOS. TPOS with 38.5% carbonyl content (TPOS38.5) showed the lowest glass transition temperature (T_g) and moisture absorption, as well as the best mechanical properties. The effects of plasticizer content on the properties of TPOS38.5 were also investigated. All the results indicated that the oxidation could improve the properties of TPOS.

1. Introduction

Starch is a renewable and biodegradable macromolecule. Its low cost, availability and non-toxic degradation products have made it an important raw material for the production of biodegradable plastics. To prepare thermoplastic starch (TPS) materials, plasticizers such as polyols (Ma & Yu, 2004; Shi et al., 2007; Singh, Singh, & Saxena, 2002; Yang, Yu, & Ma, 2006) must be added. The presence of a large number of hydroxyl groups gives TPS poor water resistance (Müller, Yamashita, & Laurindo, 2008). To improve the property, other synthetic biodegradable polymers may be blended with TPS (Chang, 2000; Maliger, McGlashan, Halley, & Matthew, 2006; Wang, Shogren, & Carriere, 2000; Wang, Yu, & Ma, 2007), and the starch can be chemically modified (Biswas et al., 2008; Bodil & Bengt, 2002; Hank, Ewan, Marianne, Roper, & Robert, 2007; Kapusnia & Siemion, 2006).

Oxidation can introduce the carbonyl groups into starch chains. Many kinds of oxidizing reagents can be used to oxidize starch, such as periodate (Kanth et al., 2006; Tang, Du, & Fan, 2003; Zhang et al., 2007), hypochlorite (Forssell, Hamunen, Autio, Suortti, & Poutanen, 1995; Kuakpetoon & Wang, 2001; Kuakpetoon & Wang, 2008; Wang & Wang, 2003) and hydroxyl peroxide (Wang, Yu et al., 2007). Although dialdehyde starch is the most valuable OS (Kanth et al., 2006; Para & Karolczyk-Kostuch, 2002; Zhang et al., 2007), its application in industry is limited due to its high price. OS prepared by hypochlorite has a low degree of oxidation and yield (Forssell et al., 1995; Kuakpetoon & Wang, 2001; Wang & Wang, 2003). Hydroxyl peroxide is an inexpensive and effective oxidizing reagent to prepare OS with high carbonyl content (Wang, Yu et al., 2007). Moreover, starches oxidized by hydroxyl peroxide can be prepared under mild conditions, which could limit the decrease in molecular weight. During oxidation, starch loses its original crystallization, and the hydroxyl groups in the glucose ring are partially oxidized to aldehyde or ketone groups, which weaken the hydrogen bonds between the starch chains, resulting in strengthening thermoplastic behavior and hydrophobicity (Wang, Yu et al., 2007). Although starch oxidized by hydroxyl peroxide has many merits, the properties of OS with high oxidation degree have not been investigated yet, therefore, it is necessary to research the properties of OS prepared with hydroxyl peroxide.

Starch does not dissolve in water at room temperature, but the physical properties of starch will change significantly when the water temperature rises above to 53 °C. Starch swells at high temperature to form uniform paste; the process is referred as starch gelatinization (Liu et al., 2009). When starch was gelatinized, its intermolecular and intramolecular hydrogen bonds were destroyed and some chemical reactions are easier to conduct. In this context, starch was gelatinized and oxidized under a mild condition by hydroxyl peroxide (Wang, Zhang, Zhang, & Wang, 2007). TPOS was prepared by mixing OS with glycerol. The thermal properties, moisture resistance and mechanical properties of TPOS were investigated. Moreover, the effect of the contents of water and glycerol on the mechanical properties of TPOS was also considered.

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* Corresponding author. Tel./fax: +86 28 85410259.
E-mail address: yzwang@email.scu.edu.cn (Y.-Z. Wang).

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2. Materials and methods

2.1. Materials

Corn starch (11.6% moisture) was obtained from Langfang Starch Company (technical grade, Langfang, Heibei, China). Hydroxyl peroxide (H_2O_2, 30%), analytical grade (99.5%), was purchased from KeLong Chemical Reagent (Chengdu, China). The other chemicals were used as received without further purification.

2.2. Oxidation of starch by hydroxyl peroxide

OS was prepared according to the following procedure: 50.0 g starch and 250.0 mL distilled water were added in a 1000 mL three-necked round-bottomed flask, and the mixtures were heated at 80 °C for an hour with mild stirring. Then, 200.0 mL distilled water was added in the mixture with 24.6 mL of hydroxyl peroxide (in a 0.7 molar ratio of hydroxyl peroxide to the glucose unit in starch molecule) after the temperature dropped to 20 °C, and continued to react for 1 h. During oxidation, the mixture was stirred vigorously with a mechanical stir to ensure the hydroxyl peroxide uniformly dispersed in the gelatinized starch. The reaction temperature was kept at 25 °C with pH of 7.0. After 24 h, the slurry was separated by centrifugation and the product was washed five times with 200 mL distilled water. The product was dried for 24 h at 50 °C in the vacuum oven then at 120 °C for 24 h. The IR spectrum of OS had a characteristic absorption peak at 1735 cm^{-1}. The broad band at 1735 cm^{-1} was the characteristic band of C=O due to the oxidation of hydroxyl groups to carbonyl groups (Kweon, Choi, Kim, & Lim, 2001; Para, 2004). And it was also confirmed by HNMR: in OS38.5 peaks at 9.7 ppm and 10.2 ppm were assigned to the aldehyde groups (Marsman, Pieters, Janssen, & Beenackers, 1990; Zhang et al., 2007). The significant difference of the ^1H NMR spectroscopy of OS55.4 is that there is a peak at 12.6 ppm which was assigned to the hydroxyl protons of carboxylic group, and the peaks at 10.2 ppm can hardly be seen because the aldehyde group was oxidized to a carboxylic group. From the above discussion, it can be concluded that when the carbonyl content was lower than 38.5%, the products of the oxidation was ketone starch; while the carbonyl content was as high as 54%, the product was carboxylic starch. The determination of carbonyl content had been investigated in details in our previous report (Wang, Yu et al., 2007). In order to prepare oxidized starches with different carbonyl contents, we changed reaction time, amounts of peroxide and temperature. Oxidized starches with carbonyl contents of 17.6%, 38.5%, 49.3% and 55.4% (OS17.6, OS38.5, OS49.3 and OS55.4) were prepared in this paper, respectively.

2.3. Determination of the carbonyl contents

The carbonyl contents of the oxidized starches were determined according to references (Kuakpetoon & Wang, 2001; Wing & Willett, 1997).

A dry sample (1.0 g) was slurried in distilled water (300 mL) and heated to boiling to complete solubilization. The cooled solutions were adjusted to pH 3.2 with 0.15 M aqueous HCl, and 60.0 mL of a hydroxylamine hydrochloride solution (hydroxylamine hydrochloride, 25 g; 100 mL 0.5 M NaOH diluted to 500 mL) was added. The solutions were heated to 40 °C in an oven for 4 h and titrated rapidly to pH 3.2 with 0.15 M HCl. A water sample was used as a control. The carbonyl content, which reflects the extent of oxidation, was expressed as the number of carbonyl groups per 100 glucose units.

2.4. Preparation of thermoplastic oxidized starch (TPOS)

Thermoplastic gelatinized starch (TPGS) and TPOS with carbonyl contents of 17.6%, 38.5%, 49.3% and 55.4% were prepared according to the following procedure: 15% weight ratio of glycerol based on gelatinized starch or OS was mixed with them, respectively, under a high-speed stirring and maintained in a polyethylene bag at 35 °C for 12 h, then the mixtures were pressed at 120 °C to get 0.5 mm thick films.

In order to study the effect of water content on mechanical properties of TPOS38.5, water and glycerol as plasticizers were added to prepare TPOS38.5 according to the same procedure above.

2.5. Differential scanning calorimeter (DSC)

Thermal properties of the samples were studied using a German NETZSCH 204DSC under nitrogen purge. The samples (5–8 mg) were heated from room temperature to 120 °C within 10 min to eliminate any residual water, and then cooled to 0 °C at a cooling rate of 10 °C min^{-1}. After that the samples were heated again up to 200 °C at the same heating rate. An empty capsule was used as a reference.

2.6. Moisture absorption

Samples were dried at 110 °C for 36 h and cooled to 25 °C in a desiccator, then weighed immediately (M_0). The samples were conditioned in 100% relative humidity at 25 ± 1 °C until a constant weight was obtained and then were weighed again (M_1). The 100% relative humidity was obtained by using closed vessel containing water inside (Kapusnia & Siemion, 2006). The amount of water absorbed by the samples was calculated by the following formula:

$$\text{water absorbtion } (\%) = (M_1 - M_0)/M_0 \times 100$$

2.7. Mechanical property testing

Tensile testing of the samples was done by the Universal Electricity Control Testing machine (Changchun, China) at a crosshead speed of 10 mm/min (ISO 1184-1983 standard). All the measurements were performed for five specimens and averaged (Kanth et al., 2006).

3. Results and discussions

3.1. Thermal behaviors of TPOS

Fig. 1 showed the DSC curves of TPGS and TPOS with 15 wt% of glycerol. The glass transition temperatures (T_g) determined from DSC curves were listed in Table 1. It could be seen clearly that T_g of TPGS was 72 °C, and T_g of TPOS decreased from 63 to 52 °C with increasing the carbonyl content from 17.6% to 38.5%. When the gelatinized starch was oxidized, the hydroxyl group of starch was transformed to ketone or aldehyde group. As a result, the hydrogen bonds among starch molecules weakened, leading to lower T_g. As the degree of oxidation increased, that is, more hydroxyl groups of starch were oxidized to carboxyl groups, and the hydrogen bonds increased again, T_g of TPOS49.3 and TPOS55.4 increased to 66 and 78 °C, respectively.

3.2. Moisture absorption of TPOS

In theory, the hydrophobility of starch would increase as its hydroxyl groups were oxidized to aldehyde or ketone groups. In this

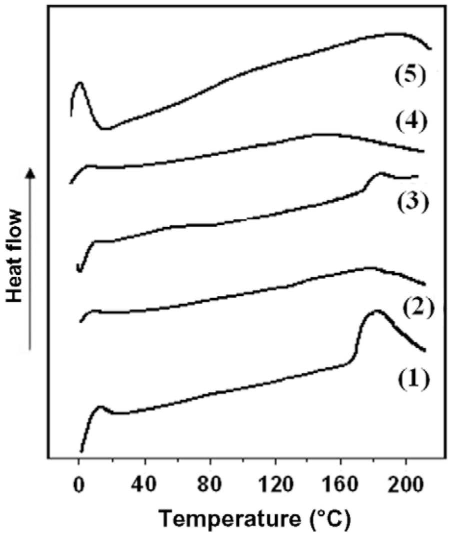

Fig. 1. DSC curves of TPGS and TPOS: (1) TPGS; (2) TPOS17.6; (3) TPOS38.5; (4) TPOS49.3; (5) TPOS55.4.

Table 1
T_g and moisture absorption of TPGS and TPOS.

Sample	T_g (°C)	Moisture absorption (%)
TPGS	72	30.7 ± 2.85
TPOS17.6	63	23.3 ± 2.04
TPOS38.5	52	19.8 ± 1.52
TPOS49.3	66	22.9 ± 1.89
TPOS55.4	78	32.1 ± 1.45

paper, the water absorption of TPOS with different carbonyl contents in 100% relative humidity was studied. The results were shown in Table 1. When the carbonyl content of TPOS was 38.5%, its moisture absorption was lowered significantly to 19.8% compared with pure gelatinized starch (30.7%). The result demonstrated that the oxidation of gelatinized starch by hydroxyl peroxide could improve its hydrophobility, that is, the water resistance properties of TPOS could be enhanced by oxidation. However, when the carbonyl content of OS was more than 38.5%, the water absorption of TPOS increased obviously. As TPOS55.4 was concerned, its water absorption reached 32.1%, even higher than that of TPGS. The main reason is that when the carbonyl content of OS is more than 38.5%, it mainly exits in carboxyl form.

3.3. Mechanical properties of TPOS

Table 2 showed that the mechanical properties of TPGS and TPOS with different carbonyl contents varied with moisture absorption. Before water absorption, the tensile strength of TPGS was 24.1 MPa, while the tensile strength of TPOS decreased greatly as the carbonyl content increased from 17.6% to 55.4%. The tensile strengths of TPOS17.6, TPOS38.5 and TPOS49.3 were 16.1 MPa, 12.4 MPa and 2.8 MPa, respectively. TPOS55.4 had the poorest mechanical property and its tensile strength was only 1.1 MPa. All the samples had very low elongations at break. This phenomenon could be ascribed to the breakage of hydrogen bond and the decrease in molecular weight of the starch molecules.

Table 2
Effect of water on mechanical properties of TPGS and TPOS.

Sample	Before moisture absorption		After moisture absorption	
	TS (MPa)	Elongation (%)	TS (MPa)	Elongation (%)
TPGS	24.1 ± 1.23	1.2 ± 0.09	2.1 ± 0.15	16.2 ± 1.23
TPOS17.6	16.1 ± 1.15	1.5 ± 0.07	2.6 ± 0.20	21.5 ± 1.52
TPOS38.5	12.4 ± 0.85	2.1 ± 0.12	6.1 ± 0.52	20.4 ± 1.23
TPOS49.3	2.8 ± 0.14	1.1 ± 0.08	0.9 ± 0.06	30.1 ± 2.12
TPOS55.4	1.1 ± 0.08	0.2 ± 0.01	–	–

When TPGS and TPOS with different carbonyl contents reached an water-absorbing equilibrium in 100% relative humidity, their mechanical properties were distinctly changed. All the samples showed lower tensile strengths and higher elongations at break than those before water absorption. The tensile strength of TPGS decreased to 2.1 MPa and at the same time, the tensile strengths of TPOS17.6, TPOS38.5 and TPOS49.5 decreased to 2.6 MPa, 6.1 MPa, and 0.9 MPa, respectively. Due to its poor mechanical properties, the tensile strength of TPOS55.4 could not be measured. After water absorption, the tensile strengths and elongations at break of TPOS17.6 and TPOS38.5 were both higher than those of TPGS, which may be ascribed to the fact that their hydroxyl groups were partially oxidized to aldehyde or ketone groups, enhancing their hydrophobility.

Though the absorbed water reduced the tensile strengths of the samples, it played a role of plasticizer for TPGS and TPOS, resulting in the increase of the elongations at break effectively.

3.4. Properties of TPOS38.5

The above discussion showed that TPOS with suitable carbonyl contents would have better water resistance and mechanical properties. For all the samples, TPOS38.5 has the best comprehensive properties. In order to prepare TPOS with the optimal properties, the effect of plasticizer on the properties of TPOS38.5 was carefully studied.

3.4.1. Effect of glycerol on the mechanical properties of TPOS38.5

Glycerol is a good plasticizer for TPS, and had a great influence on the mechanical properties of TPS. The effect of glycerol content on the mechanical properties of TPOS38.5 was shown in Figs. 2 and 3. The mechanical properties of TPOS38.5 was similar to those of thermoplastic dialdehyde starches (Tang et al., 2003). The tensile strength of TPOS38.5 decreased with the increase of glycerol content, while the elongation at break increased. The tensile strength of TPOS38.5 had the highest value (22 MPa) when the content of glycerol was 5%. Its tensile strength dropped to 5.6 MPa as the

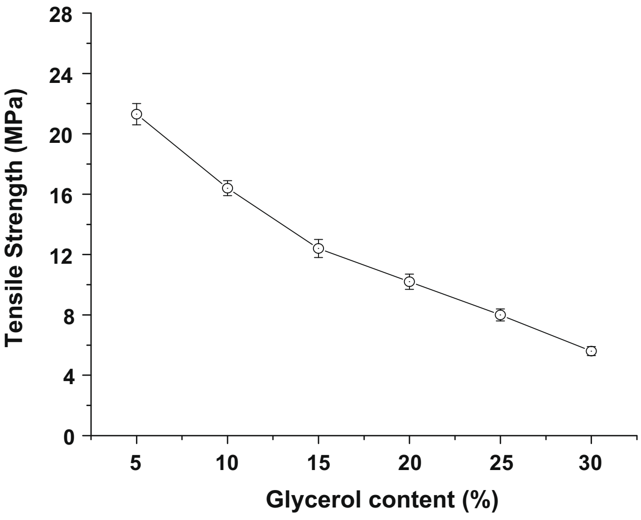

Fig. 2. Effect of glycerol on the tensile strength of TPOS38.5.

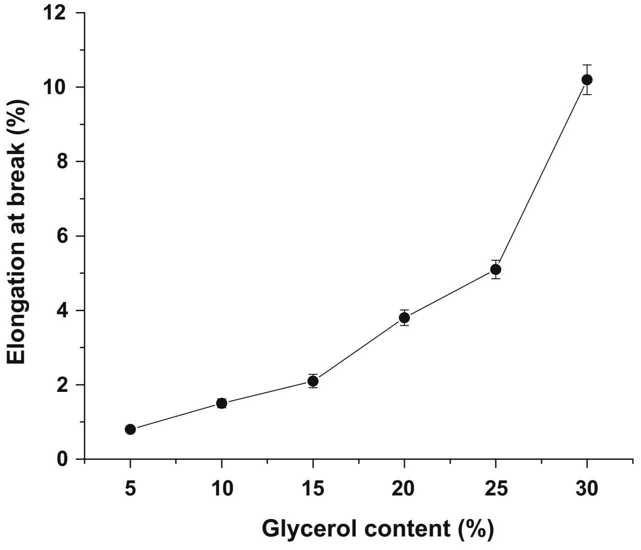

Fig. 3. Effect of glycerol on the elongation at break of TPOS38.5.

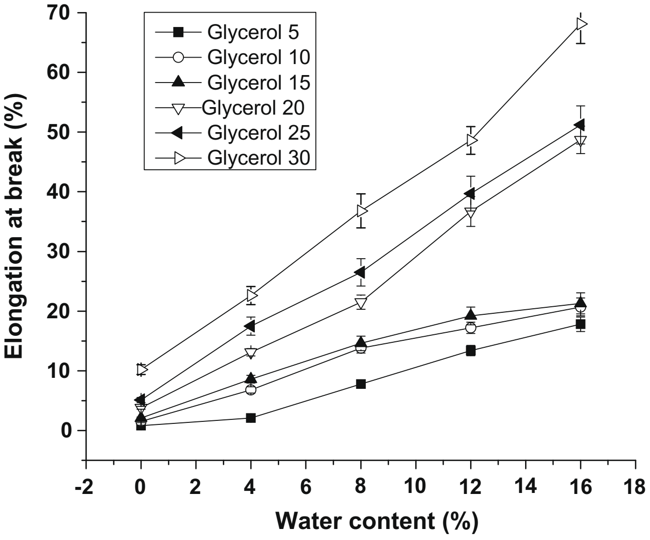

Fig. 5. Effect of water on the elongation at break of TPOS38.5.

content of glycerol increased from 5% to 30%. When the glycerol content was lower than 20%, the plasticizer scarcely affected the elongation at break. When the glycerol content ranged from 20% to 30%, the elongation at break of TPOS 38.5 increased from 4.1% to 10.2%. The results prove that glycerol had significantly effect on the tensile strength and the elongation at break of TPOS38.5 when its content was higher than 20%. As the glycerol content was higher than 25%, TPOS38.5 showed definite flexible properties.

3.4.2. Effect of water content on the mechanical properties of TPOS38.5

Compared with thermoplastic starch, TPOS38.5 could be prepared at 120 °C by thermal processing with water and glycerol as plasticizers. The effect of the water content on the mechanical properties of TPOS38.5 was shown in Figs. 4 and 5. Water significantly affected the mechanical properties of TPOS38.5. When water content ranged from 0% to 16%, the tensile strength of TPOS38.5 decreased, while the elongation at break increased gradually. It was found that the effect of water content on the mechanical properties of TPOS38.5 depended on the glycerol content. With the glycerol content of less than 15%, TPOS 38.5 still had accredited mechanical properties even if the water content was as high as 16%. At the same time, the elongation at break increased. When TPOS38.5 had a higher content of glycerol, the mechanical properties of TPOS38.5 were affected obviously by water content. The tensile strengths of TPOS 38.5 with glycerol contents of 20%, 25% and 30% decreased to 3.1 MPa, 2.1 MPa and 1.1 MPa, respectively, as the water content increased from 0% to 16%. The elongation at break of TPOS 38.5 showed an obvious increase, and the values were 48.7%, 51.2% and 68.1%, respectively.

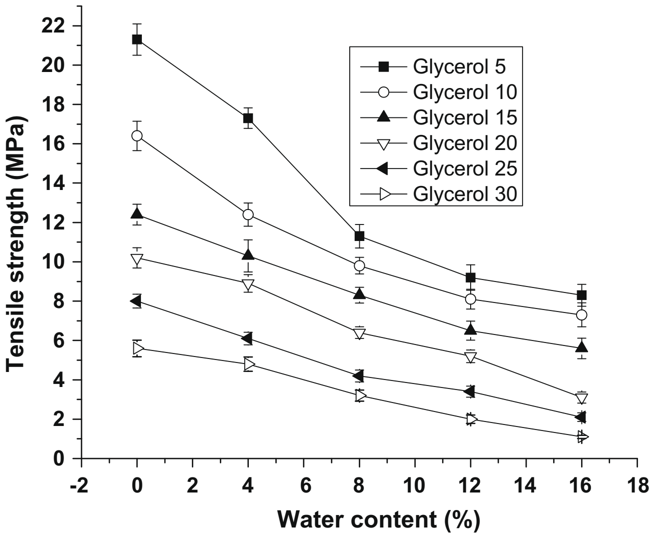

Fig. 4. Effect of water on the tensile strength of TPOS38.5.

The intramolecular and intermolecular hydrogen bonds have significant effect on the mechanical properties of TPOS, and the glycerol and water could destroy the intramolecular hydrogen bonds. As a result, the tensile strength of TPOS38.5 decreased with the increase of plasticizer content. The results indicated that the effect of the water on the mechanical properties of TPOS38.5 was more significant than that of glycerol. The reason might be that water is easier to diffuse into the molecular chains of TPOS and exhibit better plasticization than glycerol. Fortunately, TPOS38.5 with 5 wt% glycerol had better mechanical properties and less dependence on the water content.

3.4.3. Effect of glycerol content on moisture absorption of TPOS38.5

Both starch and glycerol easily absorbed moisture in the environment, leading to the sharp decrease of mechanical properties of thermoplastic starch. Moisture absorption of TPOS was discussed in Section 3.2. In this section, the moisture absorption of TPOS38.5 with different glycerol contents was studied. The results were shown in Fig. 6. The moisture absorption significantly increased from 13.2% to 35.6% as the glycerol content of TPOS38.5 increased from 5% to 30%. It was obvious that moisture absorption of TPOS38.5 with glycerol 5% was lowest in all the samples. To achieve reliable mechanical properties and lower moisture absorption of TPOS, the glycerol content should be as low as possible.

The above results showed that TPOS38.5 with 5% glycerol would maintain accredited mechanical properties, even in the environment of 100% relative humidity, and its maximal moisture absorption was only 13.2%, while its tensile strength could be higher than 10.0 MPa.

4. Conclusion

TPOS with original carbonyl contents of 17.6%, 38.5%, 49.3% and 55.4% were prepared by adding 15 wt% glycerol as plasticizer. The

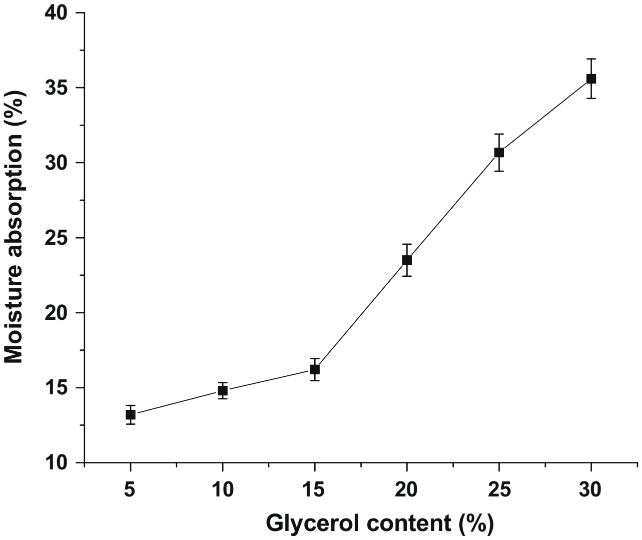

Fig. 6. Effect of glycerol content on the moisture absorption of TPOS38.5.

DSC results indicated that T_g of TPOS was influenced greatly by the carbonyl content. The moisture absorption and mechanical properties of TPOS were also affected by the carbonyl content. TPOS with higher ketone or aldehyde groups would show better water resistance and mechanical properties. For all the samples, TPOS38.5 with 5% glycerol would maintain good mechanical properties, and its highest moisture absorption was only 13.2%, while its tensile strength could be higher than 10.0 MPa. All the results demonstrated that the novel TPOS presented good properties and would have potential applications as environmental materials.

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References

Biswas, A., Shogren, R. L., Selling, G., Salch, J., Willett, J. L., & Buchanan, C. M. (2008). Rapid and environmentally friendly preparation of starch esters. *Carbohydrate Polymers, 74*, 137.

Bodil, W. K., & Bengt, W. (2002). Synthesis of amphiphilic amylose and starch derivatives. *Carbohydrate Polymers, 47*, 303.

Chang, L. J. (2000). Reactive blending of biodegradable polymers, PLA and starch. *Journal of Polymers and the Environment, 8*, 33.

Forssell, P., Hamunen, A., Autio, K., Suortti, P., & Poutanen, K. (1995). Hypochlorite oxidation of barley and potato starch. *Starch/Stärke, 47*, 371.

Hank, D. B., Ewan, S., Marianne, G., Roper, John A., & Robert, G. G. (2007). Starch–graft – (synthetic copolymer) latexes initiated with Ce4+ and stabilized by amylopectin. *Journal of Polymer Science, Part A: Polymer Chemistry, 45*, 4185.

Kanth, S. V., Madhan, B., Rao, J. R., Nair, B. U., Sadulla, S., & Ramasami, T. (2006). Studies on the stabilization of collagen using dialdehyde starch. Part I. Effect of autoclaving on dialdehyde starch. *Journal of the American Leather Chemists Association, 101*, 444.

Kapusnia, J. K., & Siemion, P. (2006). Thermal reactions of starch with long-chain unsaturated fatty acids. Part 2. Linoleic acid. *Journal of Food Engineering, 78*, 323.

Kuakpetoon, D. S., & Wang, Y. J. (2001). Characterization of different starches oxidized by hypochlorite. *Starch/Stärke, 53*, 211.

Kuakpetoon, D. S., & Wang, Y. J. (2008). Locations of hypochlorite oxidation in corn starches varying in amylose content. *Carbohydrate Research, 343*, 90.

Kweon, D. K., Choi, J. K., Kim, E. K., & Lim, S. T. (2001). Adsorption of divalent metal ions by succinylated and oxidized corn starches. *Carbohydrate Polymers, 46*, 171.

Liu, H. S., Yu, L., Dean, K., Simon, G., Petinakis, E., & Chen, L. (2009). Starch gelatinization under pressure studied by high pressure DSC. C.. *Carbohydrate Polymers, 75*, 395.

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

Maliger, R. B., McGlashan, S. A., Halley, P. J., & Matthew, L. G. (2006). Compatibilization of starch–polyester blends using reactive extrusion. *Polymer Engineering and Science, 46*, 248.

Marsman, J. H., Pieters, R. T., Janssen, L. P. M. B., & Beenackers, A. A. C. M. (1990). Determination of degree of substitution of extruded benzylated starch by H-NMR and UV spectrometry. *Starch/Stärke, 42*, 192.

Müller, C. M. O., Yamashita, F., & Laurindo, J. B. (2008). Evaluation of the effects of glycerol and sorbitol concentration and water activity on the water barrier properties of cassava starch films through a solubility approach. *Carbohydrate Polymers, 72*, 82–87.

Para, A. (2004). Complexation of metal ions with dioxime of dialdehyde starch. *Carbohydrate Polymers, 57*, 277.

Para, A., & Karolczyk-Kostuch, S. (2002). Metal complexes of starch dialdehyde dithiosemicarbazone. *Carbohydrate Polymers, 50*, 151.

Shi, R., Zhang, Z. Z., Liu, Q. Y., Han, Y. M., Zhang, L. Q., Chen, D. F., et al. (2007). Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending. *Carbohydrate Polymers, 69*, 748–755.

Singh, J., Singh, N., & Saxena, S. K. (2002). Effect of fatty acids on the rheological properties of corn and potato starch. *Journal of Food Engineering, 52*, 9.

Tang, R. P., Du, Y. M., & Fan, L. H. (2003). Dialdehyde starch-crosslinked chitosan films and their antimicrobial effects. *Journal of Polymer Science Part B: Polymer Physics, 41*, 993.

Wang, X. L., Zhang, S. D., Zhang, Y. R., & Wang, Y. Z. (2007). Method for manufacturing oxidized starch with high carbonyl content. CN200710050652.6.

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.

Wang, Y., & Wang, L. (2003). Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite. *Carbohydrate Polymers, 52*, 207.

Wang, N., Yu, J. G., & Ma, X. F. (2007). Preparation and characterization of thermoplastic starch/PLA blends by one-step reactive extrusion. *Polymer International, 56*, 1440.

Wing, R. E., & Willett, J. L. (1997). Water soluble oxidized starches by peroxide reactive extrusion. *Industrial Crops and Products, 7*, 45.

Yang, J. H., Yu, J. G., & Ma, X. F. (2006). Study on the properties of ethylenebisformamide and sorbitol plasticized corn starch (ESPTPS). *Carbohydrate Polymers, 66*, 110–116.

Zhang, S. D., Zhang, Y. R., Zhu, J., Wang, X. L., Yang, K. K., & Wang, Y. Z. (2007). Modified corn starches with improved comprehensive properties for preparing thermoplastics. *Starch/Stärke, 59*, 598.