Carbohydrate Polymers 82 (2010) 1010–1013

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Short communication

Influence of surface esterification with alkenyl succinic anhydrides on mechanical properties of corn starch films

Lili Ren[a], Man Jiang[b], Jin Tong[a], Xia Bai[a], Xiaogang Dong[a], Jiang Zhou[a,*]

[a] Key Laboratory of Bionic Engineering (Ministry of Education), College of Biological and Agricultural Engineering, Jilin University, 5988 Renmin Street, Changchun 130022, China
[b] College of Chemistry, Jilin University, 5988 Renmin Street, Changchun 130022, China

ARTICLE INFO

Article history:
Received 26 March 2010
Received in revised form 20 May 2010
Accepted 20 May 2010
Available online 27 May 2010

Keywords:
Starch film
Surface modification
Esterification
Alkenyl succinic anhydrides
Mechanical properties

ABSTRACT

The influence of surface esterification modification, by using dodecenyl succinic anhydride (DDSA) and octenyl succinic anhydride (OSA), on mechanical properties of corn starch films was investigated. The results showed that the surface modifications significantly increased tensile strength and Young's modulus of starch films; the modification decreased elongation at break of starch films at 75% RH but enhanced it at 95% RH. The effects of NaOH aqueous solution treating time on mechanical properties of starch films were more notable at 75% RH than at 95% RH. The films modified with DDSA were more strong and rigid, while the films modified with OSA were more flexible and ductile.

1. Introduction

There has been a growing interest in development of thermoplastic starch (TPS) because of its biodegradability, availability from renewable resources and low cost (Gandini, 2008; Liu, Xie, Yu, Chen, & Li, 2009). The hydrophilic nature of TPS leads to its moisture content changing with ambient humidity, which results in its mechanical properties sensitive to humidity. This disadvantage renders TPS unsuitable for many high humidity applications.

Surface modification of TPS products is an effective and promising approach that can lower humidity sensitivity without affecting TPS bulk composition. The superficial hydroxyl groups of TPS products can be substituted by hydrophobic groups or react with cross-linking agents to form starch molecule networks, so that surfaces of TPS products become less sensitive to moisture, moreover, the hydrophobic surface layer formed by surface modification could prevent or delay moisture exchange between environment and TPS products. (Yu & Liu, 2002; Bengtsson, Koch, & Gatenholm, 2003; Carvalho, Curvelo, & Gandini, 2005; Zhou, Zhang, Ma, & Tong, 2008; Zhou, Ma, Zhang, & Tong, 2009a).

Author's previous works showed that surface esterification modification of corn starch films significantly decreased surface hydrophilic character and moisture absorption of the films especially at higher relative humidity (Zhou, Ren, Tong, Xie, & Liu, 2009b; Zhou, Ren, Tong, & Ma, 2009c). Since mechanical properties are important criterion for many practical applications of TPS, it is necessary to investigate the influence of surface esterification modifications on mechanical properties of TPS. This article presented the research results.

2. Experimental

2.1. Materials

The corn starch was supplied by Changchun Jincheng Corn Development Co. Ltd. (Changchun, China). The DDSA (90% purity) and OSA (2-octen-1-ylsuccinic anhydride, 97% mixture of cis and trans) were purchased from Sigma–Aldrich (St. Louis, USA). Glycerol, sodium hydroxide and ethanol were from Beijing Beihua Fine Chemicals Co. Ltd. (Beijing, China). All these chemicals were used as received.

2.2. Film preparation and surface modification

TPS films with thickness about 0.18 mm were fabricated by solution casting method (Zhou et al., 2009b). The weight ratio of glycerol to starch in the films was fixed at 1:5. Specimens, 50 mm long dumbbell with 4 mm neck width, were cut from the fabricated films. The surface modifications were carried out according to the previous procedure (Zhou et al., 2009b,c). Briefly, specimens were soaked in NaOH aqueous solutions for a period of time, after

* Corresponding author. Tel.: +86 431 85095760x8409; fax: +86 431 85095760x8408.
E-mail address: jiang.zhou@jlu.edu.cn (J. Zhou).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.05.041

conditioned at 95% RH to moisture equilibrium, they were dipped in ethanol diluted alkenyl succinic anhydrides (ASAs). Afterwards, the specimens were placed in an oven at 35 °C for 6 h to finish esterification reaction.

2.3. Mechanical properties

Tensile tests were carried out by using an universal testing machine (Model QJ 210, Shanghai, Qingji, China) at a crosshead speed of 5 mm/min. A load cell of 100 N was used. At least five specimens were measured for each experimental condition and the average values were taken.

3. Result and discussion

Author's previous work showed the surface esterification modifications, by either soaking starch films in 0.7% NaOH aqueous solution for 60 s and dipping in DDSA diluted five times by ethanol (v/v) (Zhou et al., 2009b) or soaking the films in 1.0% NaOH aqueous solution for 10 s and dipping in OSA diluted three times by ethanol (v/v) (Zhou et al., 2009c) and then heating at 35 °C for 6 h, significantly reduced the equilibrium moisture content (EMC) of the starch films at high relative humidity. Table 1 presented the mechanical properties of these modified films. It can be seen that the surface esterification modifications considerably increased the tensile strength and Young's modulus of the films. At 75%RH, the DDSA treatment gave much higher tensile strength and Young's modulus than OSA treatment, but at 95% RH there was not marked difference for both treatments. Compared to the control one, the elongation at break of the modified films decreased at 75% RH, but increased at 95% RH. Since EMC of the modified films were very close, the effect of moisture content on mechanical properties could be ignored, the difference in mechanical properties of the modified films should mainly result from that the thickness and mechanical properties of the surface esterification layer are different. The results in Table 1 indicated that the starch film modified by using DDSA was more strong and stiff, while the film modified by using OSA was more flexible and ductile.

The mechanical properties of the modified starch films are related to the surface esterification extent which should include two parameters, the thickness of surface esterification layer and the degree of substitution (DS) of hydroxyl groups in the surface layer. However, it is difficult to quantitatively characterize the surface esterification extent of the starch films (Zhou et al., 2009b). For the modification in this study, the films were soaked in alkaline aqueous solution to activate the hydroxyl groups of starch for nucleophilic attack of the anhydride moieties and keep the reaction toward the esterification instead of hydrolysis. Under the conditions of fixing the concentration of alkaline aqueous solution, the dilution of DDSA or OSA by ethanol and reaction temperature and time, the soaking time in alkaline aqueous solution will determine diffusion depth of the alkali which eventually determines thickness of the surface esterification layer. Thus, it is deserved to examine the effect of soaking time in alkaline aqueous solution on mechanical properties of the films.

Figs. 1 and 2 showed effect of alkaline aqueous solution treating time on mechanical properties of the films modified by soaking in 1.0% NaOH aqueous solution, dipping in DDSA diluted five times by ethanol (v/v) and heating at 35 °C for 6 h. At 75% RH, tensile strength and Young's modulus increased but elongation at break decreased with increasing of NaOH aqueous solution treating time. The tensile strength and Young's modulus of the modified film with 90 s soaking increased 2.44 and 8.37 times of control one respectively, but the elongation at break reduced by 81%. While at 95% RH, elongation at break increased with increasing of soaking time, and reached

Table 1
Mechanical properties of control starch film and the surface esterification modified films at higher relative humidity.

Relative	Tensile strength (MPa)			Young's modulus (MPa)			Elongation at break (%)		
Humidity	Control	DDSA treated	OSA treated	Control	DDSA treated	OSA treated	Control	DDSA treated	OSA treated
75%	2.70 ± 0.24	9.70 ± 1.11	5.36 ± 0.55	34.98 ± 8.97	152.77 ± 18.28	70.88 ± 4.92	71.08 ± 2.66	22.97 ± 3.00	54.45 ± 3.61
95%	1.77 ± 0.20	2.49 ± 0.15	2.23 ± 0.14	7.56 ± 0.32	9.25 ± 0.38	11.51 ± 0.19	30.07 ± 3.13	55.03 ± 2.93	50.05 ± 0.75

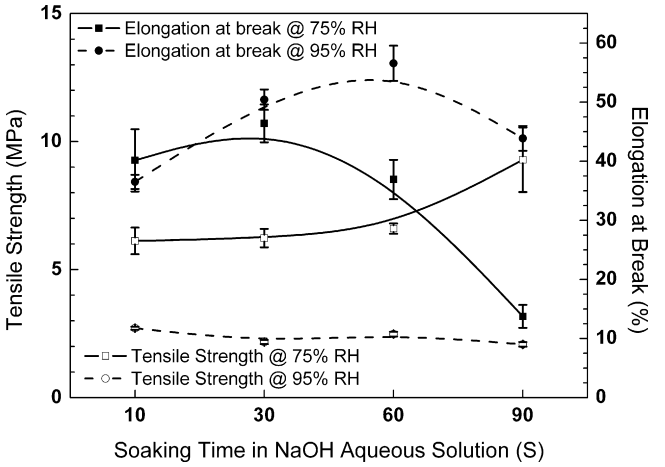

Fig. 1. Tensile strength (open symbol) and elongation at break (solid symbol) of the starch films soaked in 1.0% NaOH aqueous solution for different times (95% RH conditioned, 1/5 (v/v) DDSA/ethanol, 35 °C for 6 h).

a maximum (1.88 times of control one) at 60 s treatment, then declined at 90 s treatment. The influences of NaOH aqueous solution treating time on tensile strength and Young's modulus were not marked at 95% RH, these two parameters were only 1.18 and 1.26 times, respectively, of the control one after 60 s treatments.

Figs. 3 and 4 showed effect of alkaline aqueous solution treating time on mechanical properties of the starch films modified by soaking in 1.0% NaOH aqueous solution, dipping in OSA diluted three times by ethanol (v/v) and heating at 35 °C for 6 h. Comparing with the modified films using DDSA, an obvious difference was that the elongation at break increased continuously with increasing of soaking time; another difference was that, at 75% RH, both tensile strength and Young's modulus decreased with increasing of the soaking time. Similar to DDSA treatment, the effect of soaking time was not considerable at 95% RH for OSA treatment.

All the above results suggested that the starch films modified by using DDSA were more strong and rigid, while the films modified with OSA were more flexible and ductile. One reason probably is that using OSA could give rise to a higher DS in the surface layer because decrease of the alkenyl group chain length in ASAs can enhance diffusivity and mobility of the anhydride which increases probability of reactive moieties combining. A higher DS in the surface layer means that the number of available hydroxyl groups to form hydrogen bonding has been reduced, this could weaken interaction of the starch molecules and increase their mobility which

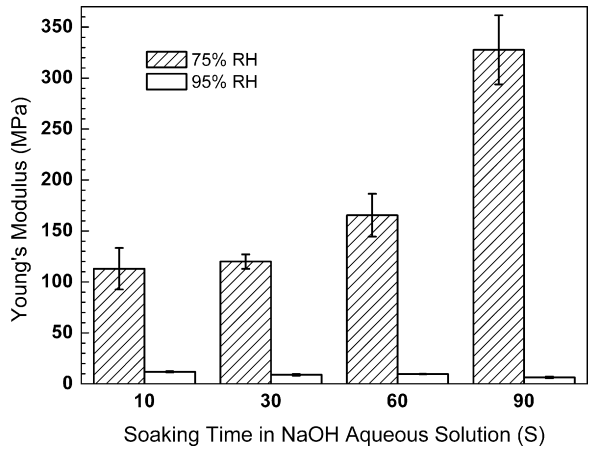

Fig. 2. Young's modulus of the starch films soaked in 1.0% NaOH aqueous solution for different times (95% RH conditioned, 1/5 (v/v) DDSA/ethanol, 35 °C for 6 h).

Table 2
Mechanical properties of the starch films modified with a mixture of DDSA/OSA.

	Tensile strength (MPa)		Young's modulus (MPa)		Elongation at break (%)	
	30 s	60 s	30 s	60 s	30 s	60 s
75% RH	6.94 ± 0.69	3.28 ± 0.24	166.43 ± 11.31	42.52 ± 6.03	40.06 ± 7.22	61.95 ± 8.53
95% RH	2.43 ± 0.26	2.39 ± 0.22	10.80 ± 0.50	12.92 ± 0.89	53.31 ± 1.37	60.73 ± 3.07

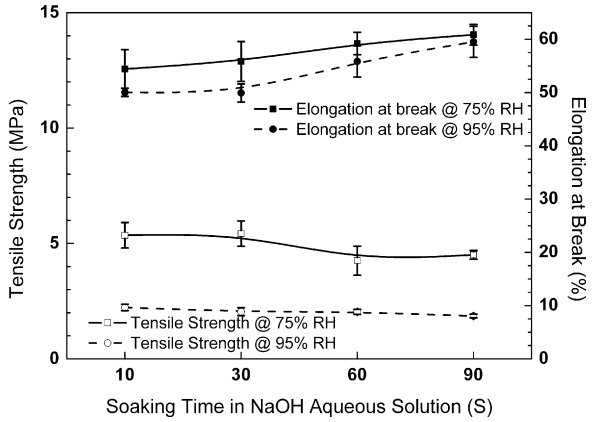

Fig. 3. Tensile strength (open symbol) and elongation at break (solid symbol) of the starch films soaked in 1.0% NaOH aqueous solution for different times (95% RH conditioned, 1/3 (v/v) OSA/ethanol, 35 °C for 6 h).

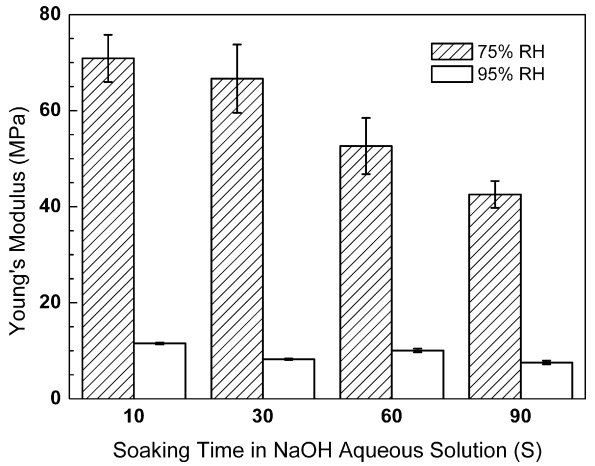

Fig. 4. Young's modulus of the starch films soaked in 1.0% NaOH aqueous solution for different times (95% RH conditioned, 1/3 (v/v) OSA/ethanol, 35 °C for 6 h).

will impact mechanical properties of the surface layer and in turn the mechanical properties of the starch films.

It is interesting to investigate how a modification using mixture of DDSA/OSA influences mechanical properties of starch films. A preliminary trial was carried out by soaking starch films in 1.0% NaOH aqueous solution for 30 s and 60 s, conditioned at 95% RH, dipping in a mixture of DDSA/OSA (1:1 in volume) diluted four times by ethanol (v/v) and heating at 35 °C for 6 h. Table 2 gave the mechanical properties of those starch films modified by using the mixture of DDSA/OSA. Comparing with using DDSA or OSA alone, using the mixture of DDSA/OSA gave rise to higher values of tensile strength and Young's modulus and lower value of elongation at break when the soaking time was 30 s, this modification seems DDSA dominant as the properties were closer to that of the DDSA modified one. However, the mechanical properties of the modified films with 60 s soaking time were closer to that of the OSA modified one, which suggested that the modification may be OSA dominant.

4. Conclusion

The surface modification through esterification by using DDSA, OSA or a mixture of DDSA/OSA can significantly increase the strength, stiffness and toughness of starch films at higher relative humidity (95% RH); but at 75% RH, only strength and Yong's modulus can be enhanced. The effects of NaOH aqueous solution treating time on mechanical properties of starch films were more notable at 75% RH than at 95% RH. The films modified with DDSA were stronger and more rigid than OSA modified one, while the films modified with OSA were more flexible and ductile than DDSA modified one.

Acknowledgement

The authors are grateful to the National Natural Science Foundation of China (no. 50673037) for financial support.

References

Bengtsson, M., Koch, K., & Gatenholm, P. (2003). Surface octanoylation of high-amylose potato starch films. *Carbohydrate Polymers*, *54*, 1–11.
Carvalho, A. J. F., Curvelo, A. A. S., & Gandini, A. (2005). Surface chemical modification of thermoplastic starch: reactions with isocyanates, epoxy functions and stearoyl chloride. *Industrial Crops and Products*, *21*, 331–336.
Gandini, A. (2008). Polymers from renewable resources: A challenge for the future of macromolecular materials. *Macromolecules*, *41*, 9491–9504.
Liu, H., Xie, F., Yu, L., Chen, L., & Li, L. (2009). Thermal processing of starch-based polymers. *Progress in Polymer Science*, *34*, 1348–1368.
Yu, J. G., & Liu, Z. H. (2002). Properties of the surface hydrophobicated thermoplastic starch. *China Plastics (Chinese)*, *16*, 35–38.
Zhou, J., Zhang, J., Ma, Y., & Tong, J. (2008). Surface photo-crosslinking of corn starch sheets. *Carbohydrate Polymers*, *74*, 405–410.
Zhou, J., Ma, Y., Zhang, J., & Tong, J. (2009). Influence of surface photocrosslinking on properties of thermoplastic starch sheets. *Journal of Applied Polymer Science*, *112*, 99–106.
Zhou, J., Ren, L., Tong, J., Xie, L., & Liu, Z. (2009). Surface esterification of corn starch films: Reaction with dodecenyl succinic anhydride. *Carbohydrate Polymers*, *78*, 888–893.
Zhou, J., Ren, L., Tong, J., & Ma, Y. (2009). Effect of surface esterification with octenyl succinic anhydride on hydrophilicity of corn starch films. *Journal of Applied Polymer Science*, *114*, 940–947.