



Water proof and strength retention properties of thermoplastic starch based biocomposites modified with glutaraldehyde



Jen-taut Yeh^{a,b,c,*}, Yuan-jing Hou^a, Li Cheng^a, Ya-Zhou Wang^a,
Liang Yang^a, Chuen-kai Wang^c

^a Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Ministry of Education, Key Laboratory for the Green Preparation and Application of Functional Materials, Faculty of Materials Science and Engineering, Hubei University, Wuhan, China

^b Department of Materials Engineering, Kun Shan University, Tainan, Taiwan

^c Graduate School of Material Science and Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

ARTICLE INFO

Article history:

Received 31 December 2014

Received in revised form 13 March 2015

Accepted 15 March 2015

Available online 30 March 2015

Keywords:

Water proof

Strength retention

Thermoplastic starch

ABSTRACT

Water proof and strength retention properties of thermoplastic starch (TPS) resins were successfully improved by reacting glutaraldehyde (GA) with starch molecules during their gelatinization processes. Tensile strength (σ_f) values of initial and aged TPS₁₀₀BC_{0.02}GA_x and (TPS₁₀₀BC_{0.02}GA_x)₇₅PLA₂₅ specimens improved significantly to a maximal value as GA contents approached an optimal value, while their moisture content and elongation at break values reduced to a minimal value, respectively, as GA contents approached the optimal value. The σ_f retention values of (TPS₁₀₀BC_{0.02}GA_{0.5})₇₅PLA₂₅ specimen aged for 56 days are more than 50 times higher than those of corresponding aged TPS and TPS₁₀₀BC_{0.02} specimens, respectively. New melting endotherms and diffraction peaks of V_H-type starch crystals were found on DSC thermograms and WAXD patterns of aged TPS or TPS₁₀₀BC_{0.02} specimens, respectively, while negligible retrogradation effect was found for most aged TPS₁₀₀BC_{0.02}GA_x and/or (TPS₁₀₀BC_{0.02}GA_x)₇₅PLA₂₅ specimens.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Thermoplastic starches (TPS) are generally prepared by the application of heat, pressure, mechanical work or by addition of plasticizers such as, glycerine, polyols or water (Biliaderis, Lazaridou, & Arvanitoyannis, 1999; Lourdin, Bizot, & Colonna, 1996; Lourdin, Coignard, Bizot, & Colonna, 1997) in native starches. Thermoplastic starch processing typically involves an irreversible order–disorder transition termed gelatinization. Starch gelatinization is the disruption of molecular organization within the starch granules and this process is affected by starch–water interactions. TPS products already have applications in the plastic market to take the place of nondegradable petrochemical based products (Bastioli, 1998; Biliaderis et al., 1999; Tatarka & Cunningham, 1998; Willett & Shogren, 2002). However, the resistance of TPS to shock or moisture is still relatively poor in

comparison with many other commodity resins (Halley, 2005). There has been an increasing research interest in thermoplastic starch reinforced with various available lignocellulosic fibers in order to improve their mechanical properties as well as to obtain the characteristic needed for actual application (Kurosuni, Sasaki, Yamashita, & Nakamura, 2009). Most recently, bacterial cellulose (BC) nanofibers were reported as an efficient reinforcing additive for preparing polymeric nanocomposites (Khaled, Richard, & Joel, 2007; Yeh et al., 2014; Yu, Wang, & Ma, 2005).

The hydrophilic nature of starch causes rapid rise in moisture contents of TPS resins and hence, leads to significant reduction of their mechanical properties if the TPS resins were not modified during their preparation processes (Cova, Sandoval, Balsamo, & Müller, 2010; Zhou, Ren, Tong, Xie, & Liu, 2009). There are mainly three types of crystallinity in starch as observed in their X-ray diffraction patterns (Halley, 2005; Van Soest & Vliegenthart, 1997). “A” and “B” types of crystallinity are mainly present in cereal (e.g. maize, wheat and rice) and tuber (e.g. potato and sago) starches, respectively, while “C” type crystallinity is the intermediate between A and B type crystallinity, normally found in bean and other root starches (Van Soest & Vliegenthart, 1997). In contrast, amylose “V_H”, “V_A” or “E_H” types of crystallinity is processing-induced crystallinity, which is formed during thermomechanical processing (Choi, Kim,

* Corresponding author at: Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Ministry of Education, Key Laboratory for the Green Preparation and Application of Functional Materials, Faculty of Materials Science and Engineering, Hubei University, Wuhan, China. Tel.: +86 13545228955.

E-mail address: jyeh@mail.ntust.edu.tw (J.-t. Yeh).

& Shin, 1999; Huang, Yu, & Ma, 2005; Van Soest & Vliegenthart, 1997). However, aging of starch materials in the rubbery state occurs by retrogradation, where the starch molecules reorganize in more ordered structures, for example by forming simple juncture points and entanglements, helices and crystal structures (Kainuma, 1988; Van Soest, Hulleman, de Wit, & Vliegenthart, 1996a; Van Soest & Knooren, 1997). The rate of retrogradation and crystallization is dependent on the plasticizer content and related to the glass-transition temperature of the starch molecules. Higher amounts of plasticizer cause an increase in the mobility of the starch chains and a reduction in the glass-transition temperature. Yu and coauthors (Yu et al., 2005) reported that thermoplastic starch plasticized by glycerol (GTPS) stored at relative humidity (RH) 0 and 50% for 70 days showed V_A -type crystallinity, i.e. double-helix conformation, while GTPS stored at RH 100% for 70 days recrystallized and showed a B-type crystallinity, i.e. single-helix conformation (Van Soest, Hulleman, de Wit, & Vliegenthart, 1996b). By contrast, as evidenced by wide angle X-ray diffraction analyses, citric acid-modified GTPS (CATPS) effectively inhibited starch recrystallization (i.e. retrogradation) into V_A -type or B-type crystallinity (Yu et al., 2005), because strong hydrogen-bond interaction was found between citric acid and starch molecules during their modification processes. Huang et al. (2005) reported that most of the crystallization in GTPS was disrupted and only a little inconspicuous V_H style crystallization occurred, which was induced in the process of plasticizing starch. The aged GTPS showed a gradually enhanced diffraction peak originated from re-crystallization of V_H style crystals, when it was stored at RH=50% for 30, 60 and/or 90 days. As suggested by Van Soest and Knooren (1997), V_H type is a single helical structure “inclusion complex”, which is made up of amylose and glycerol. Besides, cocrystallization of amylopectin with amylose probably also occurs, which has been suggested for the retrogradation of starch in starch gels (Kainuma, 1988; Van Soest et al., 1996a). In fact, re-crystallization of starch molecules restrains starch from practical use, because the starch easily becomes too weak to use during long-term storing, and loses the value in use (Van Soest et al., 1996b).

Much effort has been made to improve the water proof properties of thermoplastic starches by substitution, esterification or acetylation of hydroxyl groups of starch molecules using organic acids or anhydrides (e.g. citric acid, succinic, maleic and phthalic anhydrides) (Cova et al., 2010; Van Soest et al., 1996b; Yu et al., 2005), inorganic esters (e.g. trisodium trimetaphosphate (TSTMP)), hydroxydiethers (e.g. epichlorohydrin) (Carvalho, Curvelo, & Gandini, 2005; Sagar & Merrill, 1995). Yu et al. (2005) showed that citric acid can form stable hydrogen-bond interactions with starch and improve water proof properties of glycerol-plasticized thermoplastic starch at high RH values, although the tensile stress of thermoplastic starch specimen reduces significantly after modification by citric acid. It was reported that hydrophobicity of TPS improved greatly when TPS was modified by prepolymers containing $-NCO$ groups (Van Soest et al., 1996b). Carvalho et al. (2005) used several reagents, i.e., phenyl isocyanate, a phenol blocked polyisocyanate, stearyl chloride and poly(styrene-co-glycidyl methacrylate) to react with the superficial hydroxyl groups of TPS films in the medium of methylene chloride or xylene, and found that all the treatments were effective in decreasing the hydrophilic character of the TPS surfaces.

In contrast, irradiation or chemical cross-linking technologies were also used for water proof improvement of thermoplastic starches (Jane, Lim, Paetau, Spence, & Wang, 1994; Sagar & Merrill, 1995; Zhou, Zhang, Ma, & Tong, 2008). Jane et al. (1994) reported that the tensile and water proof properties of starch compounds made from starch and zein mixtures were significantly improved by crosslinking the compounds using dialdehyde. The modified TPS resins with improved water proof properties are expected

to exhibit significantly improved strength retention properties during aging processes. However, none of the above investigations (Carvalho et al., 2005; Cova et al., 2010; Jane et al., 1994; Sagar & Merrill, 1995; Van Soest et al., 1996b; Yu et al., 2005; Zhou et al., 2008) has reported the resulted strength retention properties of modified TPS resins and/or the correlation with their improved water proof properties.

In this study, water proof and strength retention properties of BC reinforced TPS resins were successfully improved by reacting with glutaraldehyde (GA) in their gelatinization processes. After blending 25 wt% of poly (lactic acid) (PLA) with GA modified TPS resins, their processibility, water proof and strength retention properties were further improved. In order to understand these interesting water proof and strength retention properties found for GA and/or PLA modified TPS specimens, morphological, thermal and WAXD analyses of initial and aged GA and/or PLA modified TPS specimens were also performed in this investigation. Possible reasons accounting for the significantly improved water proof and strength retention properties of GA and/or PLA modified TPS specimens are proposed.

2. Materials and methods

2.1. Materials and sample preparation

Tapioca starch powders and poly(lactic acid) (PLA) 4032D resins used in this study were purchased from Eiambeng Tapioca Starch Industry Corporation, Samutprakarn, Thailand and Nature Works Company, Blair, Nebraska, USA, respectively. The water proof and strength retention properties of tapioca starches were improved using a 25 wt% glutaraldehyde (GA) solution, which was purchased from Sinopharm Chemical Reagent Corporation, Shanghai, China. Detailed experimental procedures used for preparation of bacterial cellulose (BC) nanofibers were described in our previous investigation (Yeh et al., 2014).

Thermoplastic starches (TPS) were prepared by mixing 50 g tapioca starch, 50 ml water and 20 g glycerol at 25 °C using a high speed mixer for 1 h. Prior to gelatinization, BC nanofibers at 0.02 part per hundred parts of TPS resin (PHR) and 25 wt% GA solutions at various contents (i.e. 0–4 PHR) were added and mixed with the basic media prepared above, in which the BC nanofibers and GA solution were used to improve the water proof and strength retention properties of TPS. The above prepared mixtures were gelatinized in 250 ml flask at 90 °C under stirring condition for 15 min, wherein the pH value of the gelatinized mixtures was adjusted to 4.0 by citric acid during all gelatinization processes. The TPS and modified TPS resins prepared above were dried in an air dry oven and then in a vacuum dry oven both at 80 °C for 24 h to have the water content under 1 wt%. Small amounts (i.e. 25 wt%) of PLA were melt-blended with the dried TPS resins in a Changzhou Suyuan SU-70ML internal mixer at 180 °C for 3.5 min to improve their processibility and strength retention properties. The injected specimens used for determination of moisture content, tensile and tensile retention properties of the above prepared resins were prepared in accordance with ASTM D638 type IV with a specimen thickness of 0.254 cm using a Wuhan Reiming SZ-05 mini-injection machine at 180 °C and then cooled in the mold at 80 °C for 30 s. Table 1 summarized the sample codes and compositions of TPS, $TPS_{100}BC_{0.02}$, $TPS_{100}BC_{0.02}GA_x$ and $(TPS_{100}BC_{0.02}GA_x)_{75}PLA_{25}$ specimens prepared in this study. After preparation, the samples were maintained or aged at 20 °C/50% RH for certain amounts of time.

2.2. Fourier transform infra-red spectroscopy

Fourier transform infrared (FT-IR) spectroscopic measurements of GA, $TPS_{100}BC_{0.02}$, $TPS_{100}BC_{0.02}GA_x$ and $(TPS_{100}BC_{0.02}GA_x)_{75}PLA_{25}$

Download English Version:

<https://daneshyari.com/en/article/7788411>

Download Persian Version:

<https://daneshyari.com/article/7788411>

[Daneshyari.com](https://daneshyari.com)