Carbohydrate Polymers 143 (2016) 179–187

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Microfibrillated cellulose and borax as mechanical, O_2-barrier, and surface-modulating agents of pullulan biocomposite coatings on BOPP

Carlo A. Cozzolino[a], Gaetano Campanella[a], Hasan Türe[b], Richard T. Olsson[c], Stefano Farris[a,*]

[a] DeFENS, Department of Food, Environmental and Nutritional Sciences—Packaging Division, University of Milan, Milan, Italy
[b] Fatsa Faculty of Marine Science, Department of Marine Science and Technology Engineering, Ordu University, Ordu, Turkey
[c] Department of Fibre and Polymer Technology, School of Chemical Science and Engineering, KTH Royal Institute of Technology, Stockholm, Sweden

ARTICLE INFO

Article history:
Received 18 October 2015
Received in revised form 18 January 2016
Accepted 30 January 2016
Available online 2 February 2016

Keywords:
Contact angle
Food packaging
Composite coatings
Oxygen permeability

Chemical compounds studied in this article:
Pullulan (PubChem CID: 92024139)
Borax (PubChem CID: 10219853)

ABSTRACT

Multifunctional composite coatings on bi-oriented polypropylene (BOPP) films were obtained using borax and microfibrillated cellulose (MFC) added to the main pullulan coating polymer. Spectroscopy analyses suggested that a first type of interaction occurred via hydrogen bonding between the C_6—OH group of pullulan and the hydroxyl groups of boric acid, while monodiol and didiol complexation represented a second mechanism. The deposition of the coatings yielded an increase in the elastic modulus of the entire plastic substrate (from ~2 GPa of the neat BOPP to ~3.1 GPa of the P/B+/MFC-coated BOPP). The addition of MFC yielded a decrease of both static and kinetic coefficients of friction of approximately 22% and 25%, respectively, as compared to the neat BOPP. All composite coatings dramatically increased the oxygen barrier performance of BOPP, especially under dry conditions. The deposition of the high hydrophilic coatings allowed to obtain highly wettable surfaces (water contact angle of ~18°).

1. Introduction

The use of biopolymers represents one of the most promising strategies toward an optimized use of conventional nonbiodegradable petroleum-based plastic packaging materials due to both lower environmental impact and improved technical performance (Barlow & Morgan, 2013; Rhim, Park, & Ha, 2013). Especially within the food packaging sector, the deposition of high performance biopolymer coatings on plastic films has been proposed as a possible first step toward the environmental and functional goals (Farris, Introzzi, & Piergiovanni, 2009). According to the "packaging optimization" principle, the use of high-performance thin layers would allow down-gauging current packaging structures, e.g., laminates and/or co-extruded materials, without impairing (and, in fact, improving) the overall performance of the substrate beneath, at reasonable cost (Farris, Uysal Unalan, Introzzi, Fuentes-Alventosa, & Cozzolino, 2014).

Pullulan (Fig. 1a) has attracted much attention over recent years as potential food packaging material due to its peculiar characteristics. This non-ionic exopolysaccharide is obtained from the fermentation medium of the black yeast *Aureobasidium pullulans* (originally called *Pullularia pullulans*) under limiting conditions (e.g., nitrogen), with media composition and culture conditions highly affecting the final yield. Dry pullulan is white, nontoxic, tasteless, odorless and biodegradable, with high film forming abilities (Trovatti et al., 2012; Yuen, 1974). The α-(1 → 6) linkage between maltotriose residues contributes to the structural flexibility and high solubility of pullulan (Leathers, 2003), whereas the presence of hydroxyl groups on the molecular skeleton is responsible for the extensive inter-molecular hydrogen bonding and super-hydrophilicity, which have been profitably exploited to develop an oxygen barrier and anti-fog coatings, respectively (Farris et al., 2012; Introzzi et al., 2012a).

Another important feature of pullulan is its high transparency in the form of a thin layer, which is a sought-after property for all those applications envisaging adequate display (e.g., food packaging, optical devices, and monitors) (Introzzi et al., 2012a). Like most biopolymers, pullulan suffers some drawbacks,

* Corresponding author.
E-mail address: stefano.farris@unimi.it (S. Farris).

http://dx.doi.org/10.1016/j.carbpol.2016.01.068
0144-8617/

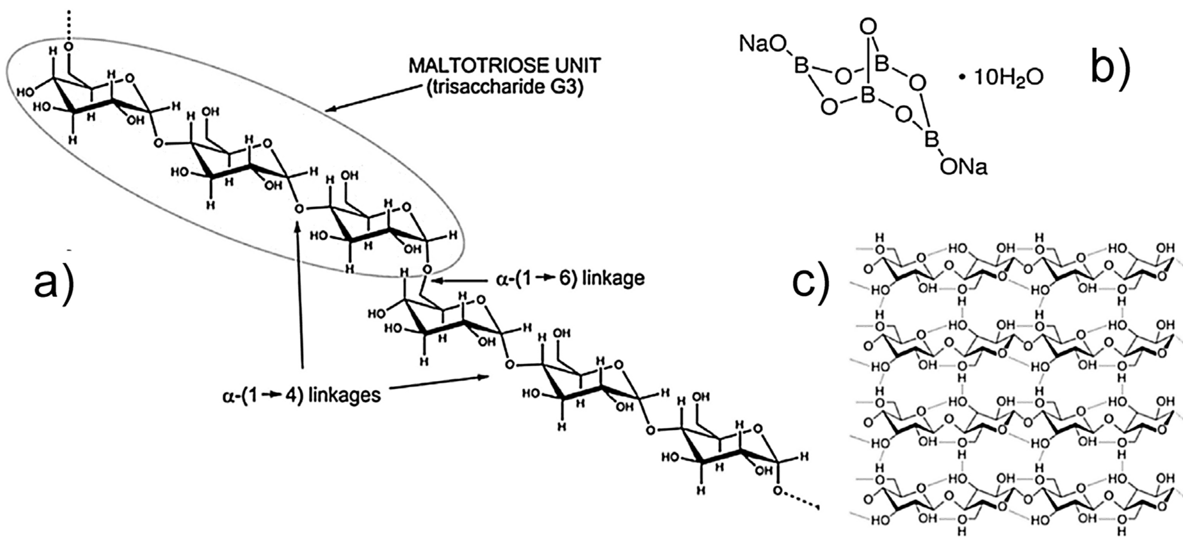

Fig. 1. (a) Pullulan molecule as a sequence of repeating units of maltotriose (adapted from Farris et al., 2014a,b); (b) sodium tetraborate decahydrate; (c) structure of cellulose (four molecular chains to form a strand) with intra- and inter-molecular hydrogen bonds (dashed lines) in evidence.

such as the sensitivity to moisture that dramatically affects its performance. Blending pullulan with other (bio)polymers has been shown as a valid strategy to control moisture sensitivity (Kristo & Biliaderis, 2007; Wu, Zhong, Li, Shoemaker, & Xia, 2013; Xiao, Lim, & Tong, 2012). More recently, pullulan has been used in combination with natural montmorillonite (Na^+-MMT) (Introzzi et al., 2012b) and graphene (Unalan et al., 2015) to produce bionanocomposite materials with enhanced properties even at high relative humidity values intended for food packaging applications.

Borax (Fig. 1b) is a salt of boric acid also known as sodium borate, sodium tetraborate, or disodium tetraborate. This water-soluble white powder is listed among the substances that can be used to produce plastic materials intended to come into contact with food (Annex I, Table 1, identification number 584 of EU Reg. 10/2011), with a specific migration limit of 6 mg kg^{-1} expressed as boron (Annex I, Table 2, group restriction number 16 of EU Reg. 10/2011). Recently the use of borax has been questioned due to its potential adverse effects on human health (genotoxicity). In 2013, the EFSA Panel on Food Additives and Nutrient Sources added to Food (ANS) provided a scientific opinion re-evaluating the safety of borax and boric acid as food additives (E 285 and E284, respectively) in the EU. Exposure estimates to boron from its use as food additive at the highest 95th percentile for consumers only, for children, adolescents, adults and the elderly would be 0.56, 0.37, 0.13 and 0.15 mg kg^{-1} bw/day, respectively. The Panel concluded that it is unlikely that a regular exceedance of the admitted daily intake (ADI) occurs (EFSA ANS, 2013). Borax finds a variety of applications as an additive of detergents and cosmetics, to make buffer solutions, as a fire retardant, and as a texturing agent and antimicrobial agent in the food industry (Yanjuan, Yanxiong, Wei, & Chunying, 2013). Borax dissociates completely into equal quantities of trigonal planar [boric acid, $B(OH_3)$] and tetrahedral [monoborate ions, $2B(OH)_4^-$] that interchange rapidly in water system according to (Han, Lei, & Wu, 2014):

$$Na_2B_4O_7 + 7H_2O = 2B(OH_3) + 2B(OH)_4^- \qquad \text{(reaction 1)}$$

The co-existence of both forms can be exploited profitably to generate water-based systems with enhanced hydrogen bonding (due to the hydroxyl groups) while preserving long-term stability (due to the hydroxide ions). Borax has desirable properties as a component of polymeric composites because polar —OH groups facilitate strong interactions and mechanical stability (Yunus Gumus, Unal, Erol, & Sari, 2011).

Cellulose (Fig. 1c) is a widely available, low cost, renewable, and biodegradable polymer. Its chemical structure and physical properties have been widely reported in the literature (Berglund, 2006; Cabiaca et al., 2011). Cellulose is mostly obtained from wood and cotton, although cellulose pulp can be also extracted from agricultural byproducts such as bagasse, stalks and crop straws and is also produced by many species of bacteria (e.g., *Gluconacetobacter* spp.) (Huang et al., 2014). Cellulose fibers can be disassembled into their structural nano-components (Chinga-Carrasco, Miettinen, Luengo Hendriks, Gamstedt, & Kataja, 2011)—cellulose nanoparticles (CNs), such as microfibrillated cellulose (MFC; or cellulose microfibrils, CMF); cellulose nanofibrils (CNF; or nanofibrillated cellulose, NFC); and cellulose nanocrystals (CNCs). CNC elements are much shorter than both MFC and CNF and does not have, therefore, the same ability as the MFC and CNF elements to form networks. Various definitions may be found in the literature, but in the proposal for the new TAPPI Standard, MFC have widths in the range of 10–100 nm, while CNF have widths of 5–30 nm (Wernersson Brodin, Gregersen, & Syverud, 2014). Cellulose derivatives are among the most employed natural fillers for the genaration of composite materials (Faruk, Bledzki, Fink, & Sain, 2012; Klemm et al., 2011). MFC, in particular, has successfully been used in the food packaging field to produce composite films and coatings to improve barrier properties—for example, against oxygen (Hult, Iotti, & Lenes, 2010; Minelli et al., 2010) and water vapor (Azeredo et al., 2009, 2010; Kaushik, Singh, & Verma, 2010)—mechanical properties (Cozzolino, Cerri, Brundu, & Farris, 2014; Hansen, Blomfeldt, Hedenqvist, & Plackett, 2012; Peng, Ren, Zhong, & Sun, 2011), thermal properties (Jonoobi, Harun, Mathew, & Oksman, 2010; Tingaut, Zimmermann, & Lopez-Suevos, 2009), and the antimicrobial attribute of the final package (Cozzolino et al., 2013; Lavoine, Tabary, Desloges, Martel, & Bras, 2014; Lavoine, Desloges, Sillard, & Bras, 2014; Lavoine, Desloges, & Bras, 2014; Lavoine, Desloges, Manship, & Bras, 2015; Saini, Belgacem, Mendes, Elegir, & Bras, 2015).

The objective of this study was to investigate the potential advantages eventually coming from the association of borax and MFC as fillers included in the main biopolymer matrix pullulan. In particular, the composite materials were developed in the form of thin coatings aiming to improve the oxygen and water barrier, mechanical, optical, and surface properties of a BOPP film, a commonly-used plastic for food packaging applications.