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Mechanically improved polyvinyl alcohol-composite films using modified cellulose nanowhiskers as nano-reinforcement

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ABSTRACT

Cellulose nanowhiskers (CWs) extracted from cotton fibers were successfully modified with distinct anhydrides structures and used as additives in poly(vinyl alcohol) (PVA) nanocomposite films. The surface modification of CWs was performed with maleic, succinic, acetic or phthalic anhydride to compare the interaction and action the carboxylic groups into PVA films and how these groups influence in mechanical properties of the nanocomposites. CWs presented a high degree of crystallinity and good dispersion in water, with average length at the nanoscale. The addition of specific amounts (3, 6 and 9 wt.%) of modified-CWs increased up to 4.4 times the storage modulus (PVA88-CWSA 9 wt.%), as observed from dynamic mechanical analysis (DMA), compared to the bare PVA films. A significant increase in mechanical properties such as tensile strength, elastic modulus, and elongation at break showed a close relationship to the amount and chemical surface characteristics of CWs added, suggesting that these modified-CWs could be explored as reinforcement additives in PVA films.

1. Introduction

The use of cellulose nanowhiskers (CWs) in nanocomposites is a promising research field related to the development of mechanically responsive materials. In addition to the low cost of the raw material, the use of cellulose particles as a reinforcement phase in nanocomposites include advantages such as low density, low abrasiveness, and energy consumption during processing, biodegradability, and a reactive surface that can be chemically modified by specific groups. However, the high hygroscopic characteristic of unmodified CWs can result in poor adhesion to non-polar polymeric matrices. Depending on the polymer matrix used, the presence/addition of pure CWs can present some disadvantages, such as high water/moisture adsorption and poor adhesion to non-polar polymer matrix caused by the polar differences/interactions of the CWs. Hence, chemical modification of CWs bearing specific groups has been employed to tune phase to additive interaction/adhesion. (Abraham et al., 2016; Arjmandi, Hassan, Haafiz, & Zakaria, 2017; Fragal et al., 2017; Paralikar, Simonsen, & Lombardi, 2008; Wang, Shankar, & Rhim, 2017).

Cellulose is the most abundant biopolymer, so a special attention has been paid to its physicochemical properties, associating them to the development/obtainment/production of higher value-added polymer-based materials from sustainable and renewable resources (de Melo, da Silva Filho, Santana, & Airoldi, 2009; Dufresne, 2017; Follain, Marais, Montanari, & Vignon, 2010; Kim & Kuga, 2001; Klemm, Heublein, Fink, & Bohn, 2005). The repeating unit of cellulose (known as cellobiose) is composed of two glucose molecules linked by β-1,4-glycosidic bonds. The presence of six HO-groups in such structure permits intra and intermolecular hydrogen bond interactions, resulting in a strong tendency for cellulose to form crystals completely insoluble in water and most organic solvents (George & Sabapathi, 2015; Klemm et al., 2005; Silva, Haraguchi, Muniz, & Rubira, 2009). However, it is possible to prepare aqueous suspensions of these crystalline forms of cellulose (cellulose whiskers) through acid hydrolysis. Because permeability is higher in the amorphous phase, the kinetics of such hydrolysis is faster there than in the crystalline region, so one can—under controlled conditions—destructs amorphous regions around and among cellulose microfibrils while crystalline segments remain intact (Fragal et al., 2016; Silva et al., 2009). In this sense, the hydrolysis using hydrochloric acid can provide CWs with a minimum surface charge that allows for the chemical grafting maintaining its initial morphology and the mechanical properties.

Cellulose chemical modification using cyclic anhydrides such as succinic, maleic or phthalic anhydride provides ester-based surfaces bearing carboxylic groups that can be additionally reacted (Klemm et al., 2011; Liu et al., 2007). Some applications for the modified

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cellulose include the preparation of chelating materials for the adsorption of heavy metals and cations from aqueous solution (Gurgel & Gil, 2009; Malik, Jain, & Yadav, 2016), the preparation of adsorbent materials for the removal of dyes present in water (Fan, Liu, & Liu, 2010), and the fabrication of capacitive humidity sensors (Ducéré, Bernès, & Lacabanne, 2005). Moreover, due to its excellent biocompatibility, CWs have been studied for applications in drug delivery systems (de Oliveira Barud et al., 2016; Jackson et al., 2011), packaging and barrier films (Siró & Plackett, 2010), filtration membranes (Cao, Wang, Ding, Yu, & Sun, 2013; Ma, Burger, Hsiao, & Chu, 2011), medical implants (de Oliveira Barud et al., 2016; Dugan, Collins, Gough, & Eichhorn, 2013), and especially as reinforcement for polymer matrices (Arjmandi et al., 2017; Cho & Park, 2011; Iyer & Torkelson, 2015; Wang, Wang, & Shao, 2014). Also, tensile strength and Young's modulus of CWs are comparable to other engineered materials such as glass fibers, carbon fiber and Kevlar 49® (Wang, Sain, & Oksman, 2007; Wang & Chen, 2014), being promising options to increase mechanical properties of composites. For instance, the addition of CWs (0–15 wt.%) to a PVA (88–98% of hydrolyzed groups) polymer matrix produced via electrospinning increased up to 3 times the storage modulus of the final material (Peresin, Habibi, Zoppe, Pawlak, & Rojas, 2010). Likewise, other studies showed an increase in elasticity modulus of PVA nanocomposites containing progressive amounts of CWs (1, 3, 5 or 7 wt.%) incorporated in the bulk matrix (Cho & Park, 2011).

Among different techniques explored to prepare nanocomposites the solvent evaporation by casting has been the most used procedure to incorporate aqueous suspensions containing cellulose whiskers into the organic polymeric matrix (Habibi, Lucia, & Rojas, 2010). In this sense, in order to obtain polymer/nanowhiskers nanocomposites with better mechanical properties, one has to consider the dispersion process of the cellulose nanowhiskers into the polymer matrix as a crucial step (Habibi et al., 2010; Iyer, Flores, & Torkelson, 2015; Iyer, Schueneman, & Torkelson, 2015; Iyer & Torkelson, 2015).

Poly(vinyl alcohol) (PVA) is a water-soluble hydrophilic polymer with excellent film-forming property (Chiellini, Cinelli, Imam, & Mao, 2001; Pingan, Mengjun, Yanyan, & Ling, 2017), and due to its excellent chemical resistance, physical properties, and biodegradability, it has been used in a large number of industrial applications (Dai, Ou, Liu, & Huang, 2017; Tao & Shivkumar, 2007). Besides, PVA uses in biomaterials have attracted considerable attention due to its biocompatibility and biodegradability. The broad biomedical and pharmaceutical applications are due to non-toxicity, non-carcinogenic, bioadhesive and hemocompatible, and ease of processing properties (Tao & Shivkumar, 2007). In fact, a review paper reported by Villanova et al. (Villanova, Oréfice, & Cunha, 2010) featured PVA-based materials comprising hydrogels, contact lenses, dialysis membranes, membranes for the replacement of wounded tissues, artificial components of the organism and controlled release of drugs.

In this study, cellulose-rich cotton fibers were used to obtain CWs through acid hydrolysis. Chemical surface modification of the resulting CWs was performed using distinct anhydrides in order to investigate their influence on the crystalline structure and thermal stability. PVA nanocomposite films containing modified-CWs (3–9 wt.%) were prepared by casting. The influence of the hydrolysis degree of PVA (polymer matrix), and the amount of CWs (pure and modified) added, on the mechanical properties of the final material were especially evaluated through tensile strength (kPa), elastic modulus (kPa) and elongation at break (%) measurements.

2. Materials and methods

2.1. Materials

Cellulose-rich cotton fibers were purchased from Cocamar (Agroindustrial Cooperativa of Maringá, Brazil). Acetic anhydride, succinic anhydride, glycerol (99%), and poly(vinyl alcohol) containing 88% and 98% of hydrolyzed groups (M_w 13,000–23,000 g/mol), were purchased from Sigma-Aldrich (USA). Hydrochloric acid (HCl) was acquired from F. Maia (Cotia, Brazil), maleic anhydride, phthalic anhydride, sodium hydroxide from Vetec (Brazil), and N,N-dimethylacetamide (DMAC) from Nuclear (Brazil). All the reactants and solvents were used as received without further purification.

2.2. Cellulose nanowhiskers selective extraction

Cellulose-rich cotton fibers (2 g) was immersed in a NaOH solution (2% w/v) and kept under magnetic stirring for 1 h. This mixture was poured into a glass vial containing distilled water (excess) and kept at 80 °C under magnetic stirring (for 1 h) until the material has a neutral pH. The resulting cotton fibers were dried in a circulating air oven at room temperature to constant weight.

To obtain the cellulose nanowhiskers (CWs), 1 g of "cleaned" cotton fibers were hydrolyzed using concentrated HCl (20 mL, 37%) at 45 °C for 1 h, under magnetic stirring. The resulting suspension was centrifuged (10.000 rpm) for 5 min and washed several times with distilled water in order to remove the excess of acid (final pH ~6–7). Then, the final material was frozen and lyophilized.

2.3. CWs surface modification with maleic or succinic anhydride

8 g of maleic anhydride (MA) was added to a one-neck round flask (50 mL) and kept at 120 °C until complete melting. 1 g of the as-prepared CWs was added and the medium was allowed to react for 24 h under magnetic stirring. Then, 20 mL of dimethylacetamide (DMA) was added to the mixture and stirred for 20 min so the unreacted anhydride dissolves and can be removed from the reaction medium. It was filtered, washed with distilled water and dried at 110 °C for 24 h. A similar procedure was used to obtain modified-CWs with succinic anhydride, with the melting temperature for succinic anhydride being adjusted to 130 °C. The modified-CWs were named as CWMA and CWSA, respectively.

2.4. CWs surface modification with acetic anhydride

A mixture consisting of acetic anhydride (AA) (10 mL) and CWs (1 g) was added to a one-neck round flask (50 mL) and kept under magnetic stirring at 110 °C for 24 h. The medium was filtered, washed with distilled water and dried at 110 °C for 24 h. The modified-CWs was named as CWAA.

2.5. CWs surface modification with phthalic anhydride

The present procedure was adapted from item 2.3. Here, a mixture consisting of 9 g of melted phthalic anhydride (PA, 131 °C), 8 mL of DMA and 0.8 g of CWs was added to a one-neck round flask (50 mL) and kept at 135 °C under magnetic stirring for 20 h. Then, extra 20 mL of DMA was added to the mixture and stirred for 20 min so the unreacted anhydride dissolves and can be removed from the reaction medium. It was filtered, washed with distilled water and dried at 110 °C for 24 h. The modified-CWs was named as CWPA. For the route of synthesis of modified-CWs with all different anhydrides, see Supporting Information (Fig. S1).

2.6. PVA/CWs nanocomposite films

Nanocomposite films were prepared by initially mixing 100 mL of a PVA solution (60 g/L) (88 or 98% of hydrolyzed groups) and 8 wt.% of glycerol as plasticizer. Then, this mixture was stirred for 10 min and distinct amounts of as-prepared CWs (3, 6 or 9 wt.%) were added with the medium being kept under magnetic stirring for additional 15 min. This suspension was sonicated for 2 min and transferred to a glass mold (15 × 24 cm), and kept at 35 °C for 24 h so the nanocomposite films