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Composite films prepared from agricultural by-products

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ABSTRACT

In our study we used holocelluloses from sugar beet and bagasse for film preparation. Films from sugar beet holocellulose have better mechanical properties than from bagasse holocellulose. By subsequent carboxymethylation of bagasse holocellulose, films with better properties were produced. Specimens prepared from combined sugar beet and bagasse carboxymethylated holocellulose had the best mechanical properties. The results could be explained by the ratios of cellulose, arabinan, polygalacturonan and xylan content in individual films, based on the elemental analysis data. The use of microwaves to prepare holocellulose film speed up the process, but negatively affected the mechanical properties. Lignin content of the sugar beet holocellulose and bagasse samples was low and did not affect the mechanical properties. Both types of agricultural by-products could be used for preparation of composite film with high strength and stiffness suitable for broad range of applications.

1. Introduction

Many authors consider sugar beet residue (SBR) and bagasse (B) are important agricultural byproducts that could be used for composite and film preparation, with possible applications in civil engineering, packaging, and the food industry (Ghaderi, Mousavi, Yousefi, & Labbafi, 2014; Dufresne, Cavailé, & Vignon, 1997; Heux et al., 1999; Agoda-Tandjawa, Durand, Gaillard, & Doublier, 2012). Also chitosan composite films were studied for film applications (Tripathi, Mehrotra & Dutta, 2009a; 2009b; Dutta, Tripathi, Mehrotra, & Dutta, 2009). Chitosan films are known for their antimicrobial and antifungal activity however, their weak mechanical properties, gas and water permeability limit its uses (van den Broek, Knoop, Kappen, & Boeriu, 2014; Elsabee & Abdou, 2013). For that reason composites with improved mechanical properties must be prepared. Also the combination of chitosan with synthetic polymers is not environmentally safe. It is known that cellulose-containing composites have better mechanical properties than chitosan composites (Khalil et al., 2016). Besides cellulose, non-cellulosic polysaccharides in SBR and B might also support composite formation (Šimkovic, 2012, 2013). The non-cellulosic polysaccharides of SBR mostly form a pectin/arabinogalactan network that is hard to characterize due to polysaccharide branching (Šimkovic et al., 2009; Šimkovic, Uhliariková, Yadav, & Mendichi, 2010). Attempts to combine sugar beet pulp with plastics like polylactic acid (PLA) seem to be economically non-optimal for making composites since the preparation of PLA requires energy to both transform starch to lactic acid and to polymerize it to PLA (Li et al., 2012). New methods are needed for preparation of composites solely from SBR and similar agricultural resources are of high interest without the use of synthetic polymers. Bagasse hemicelluloses are also intensively studied (Bian et al., 2012Bian, Peng, Peng, Xu, Sun, & Kennedy, 2012). They can be isolated from the source by the holocellulose method. This method is well established for delignification studies on wood (Tetard, Passian, Farahi, Davison, Jung, Ragauskas, Lereu, & Thundat, 2011) as well as for bagasse cellulose studies (Yue et al., 2015). Also lignin composites are studied (Doherty, Mousavioun, & Fellows, 2011). The use of chitosan and lignin for composite preparation methods could be useful also for other polysaccharide composites (Rai & Mehrotra, 2016).

In the present work we have used the holocellulose procedure and subsequent introduction of carboxymethyl-groups for film composite preparation from SBR and B. The goal was to learn about their properties with the help of mechanical testing, elemental analysis, SEC – MALS, TG/DTG/DTA and AFM techniques. Also microwave procedure was applied to improve the procedure for possible application in the packaging industry.

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2. Experimental

2.1. Materials and methods

2.1.1. Holocellulose preparation

SBR (*Beta vulgaris, L.*; 10 g of mealed powder; C, 39.98; H, 5.82; N, 1.28; 6.85% Klason lignin; 8.00% of proteins) from local sources was mixed with water (320 ml) in 1 l Erlenmeyer flask. After adding 1 ml of concentrated acetic acid and 3 g of $NaClO_2$ (recalculated on pure sodium chlorite from 80%; Sigma-Aldrich, 144155-100G) the mixture was tempered at 85 °C/500 RPM for seven hours. Subsequently the mixture was cooled and stirred at room temperature (RT) overnight and separated into soluble part and insoluble residue by centrifuge (10 000 RPM/30 min). The soluble part was dialyzed (12–14 kDa MWCO; SERVA 44126, 49 mm diameter), preconcentrated with a vacuum evaporator and poured on Petri dishes to dry at RT to constant weight (SBSH, 1.8816 g, 19%; C, 40.38; H, 5.54; N, 1.31; 8.19% of proteins; 0.1% Klason lignin). The insoluble residue was also poured on a Petri dish and dried (6.8256 g; 68%, SBH; C, 38.65; H, 5.42; N, 1.42; 8.88% of proteins; 0.5% Klason lignin). The experiment was repeated several times after which the samples were lyophilized and used for chemical modification or for film preparations by mixing one gram of material with 30 ml of water. After one hour of stirring at 1250 RPM/RT the suspension was poured onto plastic Petri dishes and dried to constant weight in a refrigerator at 5 °C. When the soluble part was not separated and the whole mixture was dialyzed according to an analogous treatment, SBH' was prepared (6.8521 g; C, 31.53; H, 4.76; 69%; N, 1.15; 7.19% of proteins; 0.6% of Klason lignin).

The microwave-assisted experiments on SBR were run on a CEM Discover® S-class instrument (Matthews, NC 28106-0200, USA) with a home-made glass adapter equipped with air cooler and glass rod. To ten grams of mealed sample 10 g of $NaClO_2$ was added and mixed with 101 ml water solution containing 1 ml of acetic acid. The mixture was treated at 50 W constant power, high stirring for one hour with occasional water (cca 30 ml) washing down of the foam and mechanical releasing of gases by glass rod. After the treatment the pH of the mixture was increased from 6.0 to 7.2, and the sample was dialyzed and lyophilized (6.5 g; C, 39.95; H, 5.64; N, 1.37; 8.6% protein; 3.1% lignin). Subsequently the sample was separated into a soluble part and insoluble residue on fritted glass (4–16 μm) and treated as above. SBH (C, 40.56; H, 5.61; N, 0.13; 0.8% protein; 0.7% lignin) represented 52% of the starting material and 41% of soluble holocellulose (C, 40.61; H, 5.83; N, 2.34; 14.6% protein; 0.1% of Klason lignin). When the components were not separated, then SBH'(C, 37.81; H, 5.36; N, 0.85; 5.3% protein; 0.4% lignin; 76% yield) was obtained.

Analogous holocellulose was also prepared from bagasse (*Saccharum officinarum*, L.; 5 g; C, 45.21; H, 6.05; 27.8% Klason lignin; Davies Hamakua Company, P.O.Box 250, Paaulino, Hawaii 96776, USA), but the treatment and addition of $CH_3COOH/NaClO_2$ was repeated five times. The resulting mixture was dialyzed and poured on Petri dish to form a film (0.4408; BH'; C, 38.78; H, 5.53) and part of it also separated to soluble part (0.6960 g; C, 40.06; H, 5.35) and insoluble residue (2.0548 g; 41%, BH; C, 39.86; H, 5.66; 1.10% Klason lignin) and poured on Petri dishes.

The optimal microwave treatment for bagasse was ten grams on ten grams of $NaClO_2$ at 40 W power/high magnetic stirring and 110 ml of water supply with additional 150 ml added during the run.

2.1.2. Carboxymethylation of holocellulose

SBH (2 g) was mixed with water (40 ml) containing NaOH (4 g) and subsequently 8 g of $ClCH_2COONa$ was added and reacted at 60 °C/500 RPM/24 h and dialzyed until the pH dropped to 6.75. Then the mixture was lyophilized or cast on plastic or glass Petri dishes and dried at RT to constant weight (2.1072 g, CMSBH'; C, 34.88; H, 4.92; 99% total yield). Alternatively when SBH (1.6 g) was mixed with water (32 ml) containing 3.2 g NaOH and subsequently 6.4 g of $ClCH_2COONa$ and carboxymethylated as above. After dialysis the soluble part was filtered off and both the soluble part (CMSBS; 1.1101 g; 69%) and insoluble residue (CMSBH; 0.7846 g, 49%; C, 35.06; H, 5.27) were cast separately onto Petri dishes for film preparation. Under alternative treatment when the soluble part was not filtered off CMSBH' (2.1075 g; C, 34.88; H, 4.92; 0.1% of Klason lignin) was prepared.

BH (2 g) was carboxymethylated using water (40 ml) containing NaOH (4 g) and subsequently 8 g of $ClCH_2COONa$ was added and reacted at 60 °C/500 RPM/24 h and dialyzed until the pH reached 5.54. Subsequently part of the sample was cast onto plastic (CMBH'; 0.8286 g; C, 36.10; H, 5.49; 0.1% of Klason lignin) or glass (1.855 g) Petri dishes to prepare composite films, while the rest of the sample was lyophilized (0.4162 g; C, 38.42; H, 5.42; 99% total yield). Alternatively, CMBH was prepared after dialysis when the suspension was separated on fritted glass and only the insoluble residue was cast on a Petri dish (0.6387 g, 64%; C, 37.84%; H, 5.79).

2.1.3. Extraction of holocellulose

SBH (5 g) was extracted with 10% KOH in 100 ml of water at RT/500 RPM/11 h, filtered through fritted glass (4–16 μm), preconcentrated with a vacuum evaporator and cast on Petri dish and treated as above (4.52 g of ESBH film; C, 33.89; H, 5.07). Analogously, by extraction of BH, the EBH specimen was also prepared (4.1927 g; C, 40.21; H, 6.02).

2.2. Analytical methods

All the analytical methods were described previously (Šimkovic, Tracz, Kelnar, Uhliariková, & Mendichi, 2014; Šimkovic, Kelnar, Uhliariková, Mendichi, Mandalika, & Elder, 2014). Mechanical testing was performed on cut dog-bone specimens (type B, ISO 527-2) with working part length of 10 mm. Tensile tests were carried out at 22 °C and 40% relative humidity (RH) using an Instron 5800 apparatus at a crosshead speed 1 mm/min. At least eight specimens were tested for each sample. The stress-at-break (σ_b), strain-at-break (ε_b) and Young's modulus (E) were evaluated. The film thickness was measured by the micrometer with 0.001 mm accuracy. AFM images were performed using a BioScope Catalyst (Bruker, Santa Barbara, USA) with the PeakForce quantitative nanomechanical mapping technique in air and evaluated by NanoScope Analysis 1.40 software (Bruker). The conditions/parameters for these images were: silicon nitrate cantilever tip curvature radius, R = 12 nm (Max), 2 nm (Nom); 0.3 sample Poisson's ratio; 15° tip front angle, 25° back angle and 17.5° side angle; 0.4 N/m nominal cantilever spring constant [0.2 N/m (Min.), 0.8 N/m (Max.)]; cantilever resonant frequency 70 kHz (Nom.) and 0.250401 Hz scan rate.

The lignin content of samples was determined by the modified Klason method (Bunzel, Schüßler, & Tchetseubu Saha, 2011). Briefly, to one gram of sample 15 ml of 72% sulfuric acid cooled to 5 °C was added and the mixture stirred at RT for two hours. Subsequently the mixture was diluted with 560 ml of water and refluxed for four hours at 121 °C and the insoluble part filtered on fritted glass (4–16 μm). The amount of collected sample on fritted glass was vacuum-dried in oven at 105 °C for two hour, cooled under vacuum to RT, balanced and determined as lignin content in% from the amount used for determination.

3. Results and discussion

3.1. Film preparations and mechanical properties

Mechanical properties of all prepared holocellulose-based films are summarized in Table 1. It is obvious that very strong (ten-