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Revalorization of sunflower stalks as novel sources of cellulose nanofibrils and nanocrystals and their effect on wheat gluten bionanocomposite properties

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ABSTRACT

Novel gluten based bionanocomposites reinforced with cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC) extracted from sunflower stalks by respectively a steam explosion treatment and a hydrolysis procedure, were prepared by casting/evaporation. The extracted cellulose nanomaterials, both CNC and CNF, were embedded in gluten matrix and their effect was investigated. Morphological investigations highlighted that gluten based bionanocomposites showed a homogenous morphology, the absence of visible cellulose nanoreinforcements, and the presence of holes for Gluten_CNF nanocomposites. Gluten_CNF showed a reduction of water vapour permeability coefficients but the values are higher respect to gluten reinforced with CNC. This behaviour could be related to the ability of CNC to increase the tortuous path of gas molecules. Moreover, the results from thermal, mechanical and barrier properties confirmed the strong interactions obtained between CNC and gluten matrix during the process.

The study suggested the possibility to re-valorise agricultural wastes with potential applications as reinforcement in polymer matrix bionanocomposites.

1. Introduction

The development and use of green resources represent new objectives for reducing gas emissions and consequent pollution while, in this context, lignocellulosic materials represent renewable resources for production of fuel ethanol from sugars. Among lignocellulosic materials, the use of agricultural residues is of particular interest because it has also the benefit of disposal of problematic solid wastes which usually do not have any economic alternative.

Sunflowers have been considered as one of the major sustainable lignocellulosic materials used not only to extract oils but also for production of biofuels as an alternative to fossil fuels (Berglund, 2007; Vaithanomsat, Chuichulcherm, & Apiwatanapiwat, 2009). Sunflowers are renewable and are cultivated in large quantities (about 30–35 million metric tonnes) around the world; while sunflower seeds represent the fourth source of oil in the world, heads, stalks and leaves remain unutilized after harvesting (Ruiz, Cara, Manzanares, Ballesteros, & Castro, 2008). These residues are not eco-friendly because after harvesting they are typically burnt under not well-controlled conditions, causing a negative environmental impact. Every year, the volume of sunflower residues produced in the world represents a huge environmental impact with 3-7 t of dry matter/ha (Díaz, Cara, Ruiz, Pérez-Bonilla, & Castro, 2011; Vaithanomsat et al., 2009). For these reasons, the attention of the scientific community is now oriented to the revalorization of wastes after sunflower harvesting. Currently the most common use of residual stalks is for bioethanol production (Jung, Yu, Eom, & Hong, 2013). However, sunflower residues could be used also as precursors for the extraction of cellulose based materials. Cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) constitute the two main families of nanosized cellulose. The former is extracted from fibres after a complete dissolution of the non-crystalline fractions, while the latter results from the application of high shearing forces of disintegration leading to a high degree of fibrillation, which yields highly interconnected fibrils. Some different methods are known for the extraction of nanosized cellulosic materials, such as chemical, enzymatic, mechanical treatments, etc. Among the dif-

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ferent existing pre-treatment methods, steam explosion is one of the most commonly used for fractionation of biomass components. In steam explosion pre-treatment, biomass is exposed to pressurized steam followed by rapid reduction in pressure. The treatment results in substantial breakdown of the lignocellulosic structure, hydrolysis of the hemicellulosic fraction, depolymerization of the lignin components and defibrillation. Compared with alternative pre-treatment methods, the advantages of steam explosion include a significantly lower environmental impact, lower capital investment and less hazardous process chemicals (Chaker, Alila, Mutjé, Vilar, & Boufi, 2013).

Wheat gluten (WG) protein is an attractive material as agropolymer because of its high availability and it can be easily processed into films (Domenek, Feuilloley, Gratraud, Morel, & Guilbert, 2004; Mojumdar, Moresoli, Simon, & Legge, 2011). Besides the rapid biodegradability of wheat gluten films, such materials exhibit effective barrier properties against lipids and gases, such as oxygen, carbon dioxide and aroma compounds (Rafieian, Shahedi, Keramat, & Simonsen, 2014a). However, the poor mechanical properties and strong water absorption in humid environment of this material tremendously limit the applications in some industrial sectors as packaging. Solving these problems is a key research issue. Some actions have been taken to toughen the polymer matrix through using nanoparticles, for instance montmorillonite (Tunc et al., 2007) and cellulose nanofibrils (Rafieian et al., 2014a; Rafieian, Shahedi, Keramat & Simonsen, 2014b), which are simple and represent an effective way to make a high-performance protein polymer composite.

In the present research, we report the use of sunflower stalk wastes as precursors for the extraction of both cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC) to be used as reinforcement phases in wheat gluten natural matrix. The effectiveness of an optimized alkaline pre-treatment followed by an acid hydrolysis was compared with a steam explosion assisted treatment that led the extraction of cellulose nanocrystals and cellulose nanofibrils, respectively. Then, gluten based bionanocomposites, reinforced with CNC or CNF, were produced by solvent casting in water. Finally, the dispersion of CNF or CNC in wheat gluten matrix, the mechanical response and the thermal and barrier properties of WG nanocomposites reinforced with cellulosic materials were deeply investigated.

2. Experimental

2.1. Materials

Sunflower stalks were collected in Umbria, Italy. The chemical composition of sunflower stalks, expressed in% with respect to dry weight of matter, has been analysed by many authors (quite wide range of identified values to the variability of growing and harvesting conditions): glucose 27.0–36.3%, xylose 16.7–22.4%, α-cellulose 40.3–45.7%; holocellulose 54.0–71.85%; lignin 19.5–28.1%, ethanol/benzene extractives 5.8–16.7%, ash 7.8–10.7% (Akpinar, Levent, Sabanci, Uysal, & Sapci, 2011; Khristova, Bentcheva, & Karar, 1998; Kopania, Wietecha, & Chiechanska, 2010; Ruiz et al., 2013; Ruiz et al., 2008). Glycerol, used as plasticizer, was purchased from Panreac Química (Castellar del Vallés, Barcelona, Spain). Wheat gluten (WG protein content; >80%, moisture content: 5.5–8.0%) and all chemical reagents were supplied by Sigma–Aldrich (Sigma–Aldrich Chemie GmbH, Steinheim, Germany).

2.2. Cellulose nanocrystal extraction

Sunflower stalks were chemically pre-treated before the cellulose nanocrystal (CNC) extraction. Before the chemical pre-treatment, the stalks were washed several times with water and the internal white pith was manually removed. The external fibrous structure was then treated with 5% wt/v NaOH solution at room temperature (RT) for 72 h (liquid/fibre ratio 30:1) and successively with 5% wt/v NaOH solution at 98 °C for 2 h (liquid/fibre ratio 10:1). The fibrous structure was also treated with 5% wt/v of sodium chlorite (bleaching fibre/liquid ratio 1:50), boiled for 2 h at pH = 4. A treatment with sodium bisulphate solution at 5% wt/v was then carried out (30 min at RT) and finally a 17.5% wt/v NaOH solution was applied (20 min at RT) (see Fig. 1, Panel A).

Cellulose nanocrystal water suspensions were prepared from pre-treated fibres by sulphuric acid hydrolysis (Fortunati, Puglia, Monti et al., 2013; Luzi et al., 2014). The hydrolysis was carried out with 64% wt/wt sulphuric acid at 45 °C for 30 min. After the hydrolysis, a centrifugation (4400 rpm 20 min) and a dialysis procedure (around 5–7 days) were applied in order to remove the excess of acid while a mixed bed ion exchange resin (Dowex Marathon MR-3 hydrogen and hydroxide form) was added to the cellulose suspension for 48 h and then removed by filtration in order to adjust the negative charges induced by the hydrolysis. The resultant cellulose nanocrystal aqueous suspension was ultrasonicated by means of a tip sonicator (Vibracell, 750) for 5 min (Fig. 1, Panel B). The final CNC water suspension was approximately 0.5% wt/wt and the final yield after the hydrolysis was calculated as% of initial weight of the used pre-treated sunflower fibres.

2.3. Cellulose nanofibril extraction

The extraction procedure of cellulose nanofibrils (CNF) was done by a steam explosion treatment that involved (1) alkali treatment with steam explosion; (2) bleaching and (3) mild acid hydrolysis coupled with steam explosion (Fig. 1, Panel C). Initially the sunflower stalks were cut into small pieces with grinder. A laboratory autoclave, model no: KAUC-A1 which can work with 137 Pa was used for steam explosion treatment. 100 g of ground piece of stalks were treated with 5% wt NaOH solution and kept in an autoclave with the pressure of 137 Pa with the temperature of 180 °C in an autoclave for 1.5. After that, a bleaching of the resultant alkali treated stalk sample was done by treating with 5% wt sodium hypochlorite solution for 1.5. Bleaching was repeated six times until the residue become white in colour. After bleaching, the fibres were thoroughly washed, dried and subjected to mild acid hydrolysis using 5% oxalic acid under a pressure of 137 Pa in an autoclave for 20 min. The pressure was released immediately and the process was repeated six times. The fibres were taken out, washed and dispersed in water and homogenized under continuous stirring for 6 h and the resultant suspension became cellulose nanofiber aqueous suspension. The final product was washed with deionised water by successive centrifugations until neutralization.

2.4. Characterization of CNC and CNF

2.4.1. CNC characterization

The microstructure of CNC was investigated by field emission scanning electron microscopy (FESEM, Supra 25-Zeiss) after gold sputtering, while the shear-induced birefringence of 0.6% wt CNC solution was analysed in a dark box. For comparison, the microstructure of the cross section and the surface of pristine sunflower stalks and the surface of chemically pre-treated fibres were also investigated by FESEM. The images of the pristine and pre-treated fibres were analysed with the NIS-Elements BR (Nikon) software in order to determine the fibre average diameters.

Fourier infrared (FT-IR) spectra of pristine, chemically pre-treated fibres, and CNC were recorded using a Jasco FT-IR 615 spectrometer in transmission mode, while thermogravimetric