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Physical properties of starch nanocrystal-reinforced pullulan films

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Abstract

Nanocomposite materials were prepared using sorbitol-plasticized pullulan as the amorphous matrix and an aqueous suspension of starch nanocrystals (prepared by submitting native granules from waxy maize starch to acid hydrolysis at 35 °C) as the reinforcing phase. Wide-angle X-ray diffraction analysis showed an increase of the crystallinity of the composite biopolymer films with increasing of starch nanocrystal content. The water absorption isotherms and kinetics as well as the water barrier properties of nanocomposite films filled with 0–40% (w/w) starch nanocrystals (starch nanocrystals/pullulan + sorbitol) were investigated. The water uptake of pullulan–starch nanocomposites decreased with increasing filler content whereas water vapor permeability (measured at 25 °C and 53/100 relative humidity (RH) gradient) remained constant up to 20% (w/w) and, then decreased significantly with further addition of nanocrystals. The thermo-mechanical behaviour of nanocomposite films was also investigated by means of dynamic mechanical thermal analysis (DMTA) and large deformation mechanical tests (tensile mode). The glass transition temperature (T_g) shifted towards higher temperatures with increasing amount of nanocrystals, which can be attributed to a restriction of the mobility of pullulan chains due to the establishment of strong interactions not only between starch nanocrystals but also between the filler and the matrix. Moreover, the addition of nanocrystals caused strong enhancement of the Young modulus and the tensile strength, but led to a drastic decrease of the strain at break in samples conditioned at different environments (from 43% to 75% RH).

Keywords: Pullulan; Edible films; Tensile properties; Thermomechanical analysis; Nanocomposite; Starch crystalline particles; Water permeability; Plasticization

1. Introduction

Nanocomposites are a relatively new class of composites consisting of polymers filled with particles that have at least one dimension in the nanometer range. Because of their very high surface area to volume ratio, nanoparticle incorporation into polymer matrices leads to composites with unique outstanding properties in comparison to their conventional microcomposite counterparts (Smith, Bedrov, & Smith, 2003). The biocompatibility and biodegradability of synthetic materials used in nanocomposite preparation are more limited than those of natural polymers. In this context research has been focused on using natural nanofillers in various polymer matrices. The main advantages of such fillers are their renewable nature, availability, high specific strength, non-abrasive nature that allows easier processing even at high filling levels, biodegradability as well as the relatively reactive surface which can be modified accordingly (Anglès, Salvadó, & Dufresne, 1999; Azizi Samir, Alloin, & Dufresne, 2005). Thus, nanocomposites obtained by incorporation of cellulose, chitin or starch nanocrystals as nanofillers in both synthetic polymeric matrixes (Chazeau, Cavaillé, Canova, Dendievel, & Boutherin, 1999; Dufresne, Cavaillé, & Helbert, 1996; Dufresne & Cavaillé, 1998; Favier, Chanzy, & Cavaillé, 1995a) and biopolymers (Anglès & Dufresne, 2000; Dubief, Samain, & Dufresne, 1999; Dufresne, Kellerhals, & Witholt, 1999; Noshiki, Nishiyama, Wada, Kuga, & Magoshi, 2002) showed desirable improvement of different properties

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e.g., related with mechanical reinforcement and/or water resistance. The outstanding reinforcement reported in nanocomposites is mostly, defined by the nature of the polymer-particle interface (Dionne, Ozisik, & Picu, 2005; Smith et al., 2003; Zhu & Sternstein, 2003) and/or strength of filler–filler interactions leading in the establishment of a particle percolating network (Dubief et al., 1999; Dufresne & Cavaillé, 1998; Favier et al., 1995a; Morin & Dufresne, 2002).

By submitting native starch granules to an extended-time acid hydrolysis at temperatures below the gelatinization temperature, the amorphous regions are rapidly hydrolyzed allowing the separation of crystalline lamellae, which are more resistant to hydrolysis. This procedure is expected to give lamellar structures that would contain linear chains of DP (Degree of Polymerization) 15 and single-branched molecules of DP 25 as determined by molecular sieve chromatography (Robin, Mercier, Charbonnière, & Guilbot, 1974; Biliaderis, Grant, & Vose, 1981) and supported by TEM measurements (Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003). The starch crystalline particles show platelet morphology with a thickness of 6–8 nm. However, individual starch crystallites could hardly be obtained since the starch platelets flocculate and form aggregates (Putaux et al., 2003). Nevertheless, since at least one of the dimensions of aggregates is at the nanometer scale, the term 'nanoparticle' is applicable for starch crystalline particles derived by acid etching of granular starch (Angellier, Molina-Boisseau, Lebrun, & Dufresne, 2005b).

Pullulan is an extracellular microbial polysaccharide produced by the fungus-like yeast, *Aureobasidium pullulans* (Yuen, 1974). It is water-soluble and forms excellent, colourless, transparent and flexible films. The α $(1 \rightarrow 6)$ linkages that interconnect the repeated maltotriose units along the chain are responsible for the flexible conformation and the ensued amorphous character of this polysaccharide in the solid state (Gidley, Cooke, & Ward-Smith, 1993). Being amorphous, pullulan was considered as a suitable matrix to incorporate waxy maize starch nanocrystals (obtained by hydrolysis of native granules with hydrochloric acid) and to study the properties of the resulting nanocomposites as a function of filler content without the intervention of any inherent polymer crystallinity that would make the system more complex. Therefore, this work was focused on processing and characterization of pullulan–starch nanocrystal composites in terms of thermomechanical as well as water sensitivity and moisture barrier properties.

2. Materials and methods

2.1. Materials

Pullulan was a food grade preparation from Hayashibara Biochemical Laboratory, (Okayama, Japan). Inorganic salts (reagent grade) used for adjusting the relative humidity (RH) (saturated salt solutions) were from Merck KgaA (Darmstadt, Germany). Silica gel used as desiccant was purchased from Sigma–Aldrich GmbH (Germany). Waxy maize starch (WAXILUS 200) was kindly supplied by Roquette S.A. (Lestrem, France).

2.2. Preparation of the starch nanocrystals

Starch nanocrystals were prepared by acid hydrolysis of waxy maize starch according to Dufresne et al. (1996). Starch powder (50 g) was mixed with 1 L of 2.2 N HCl (820 mL of water and 180 mL of 36% HCl) and the suspension was stored at 35 °C for 30 days. The suspension was stirred daily to resuspend the starch granules. After the defined period of time the insoluble residues were recovered by multiple washings and repeated centrifugations until acid free using deionized water. An ultrasonic treatment was then employed to ensure better dispersion of nanocrystals in water. The dispersion was refrigerated until used after sodium azide addition to prevent microbial growth.

2.3. Film processing

A film-forming solution was prepared by mixing the appropriate amount of aqueous suspension of starch nanocrystals with aqueous solution of pullulan and addition of sorbitol as plasticizer. The content of starch nanocrystals ranged from 0% to 40% (w/w) (starch nanoparticles/(pullulan + sorbitol)), namely 0%, 3%, 6%, 10%, 15%, 20%, 30% and 40% (w/w), for all the performed tests except DMTA measurements. For DMTA analysis the concentration of filler was restricted to 15% (w/w), because the use of higher filler level to prepare such thick specimens (~1.5 mm) led to brittle materials that were difficult to handle. Sorbitol was used as plasticizer at a constant concentration of 30% (w/w) relative to the total mass of pullulan and sorbitol (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Anglès & Dufresne, 2001). The aqueous mixtures were degassed under vacuum to avoid the formation of air bubbles during water evaporation. Then, the preparations were cast in polystyrene plates and evaporated at 35 °C in an oven until the formation of films, which could be easily removed from the plate. Dry films of different thickness depending on the testing procedure, were thus obtained.

2.4. Film characterization

2.4.1. X-ray diffraction

The wide angle X-ray diffraction analysis was performed on unfilled sample, composite films (filled with 6%, 15% and 30%, w/w starch nanocrystals) and powders of native waxy maize starch granules and air-dried starch crystals, after exposure at 100% RH for ~2 h. The samples were attached to specifically made Plexiglas holders and examined with a Philips X-ray generator PW 1830 equipped with a graphite–crystal monochromator and a vertical goniometer PW 1820. The operating conditions for the refractometer were: copper *Ka* radiation, voltage 40 kV, amperage 30 mA, sampling interval time 0.4 s.