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Tailoring the properties of thermoplastic starch by blending with cinnamyl alcohol and radiation processing: An insight into the competitive grafting and scission reactions

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ABSTRACT

The present paper focuses on the effects of electron beam (EB) irradiation on thermoplastic materials based on destructured starch including glycerol and water as plasticizers to assess the potentiality of cinnamyl alcohol as reactive additive capable of counterbalancing the degradation of the polysaccharide by inducing interchain covalent linkages. The tensile properties at break of test specimens of controlled composition submitted to EB irradiation at doses ranging from 50 to 200 kGy revealed the presence of competitive chain scission and bridging in samples containing cinnamyl alcohol at a relative concentration of 2.5% with regard to dry starch. The occurrence of crosslinking under particular conditions was evidenced by gel fraction measurements. The treatment under radiation was also applied to model blends including maltodextrin as a model for starch and the other ingredients to gain an insight into the radiation induced mechanisms at the molecular level. The presence of cinnamyl alcohol is found to limit degradation. Size exclusion chromatography and gel fraction allowed to monitor the effects and confirmed unambiguously the attachment of UV-absorbing chromophores onto the maltodextrin main chain. The combination of the obtained results demonstrates the possibility of altering in a favorable way the tensile properties of plasticized starch by applying high energy radiation to properly formulated blends including aromatic compounds like cinnamyl alcohol.

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1. Introduction

Over the past decades, there has been a great interest in developing biodegradable materials for replacing conventional thermoplastics. Starch-based materials are particularly attractive because they can be produced from a cheap, biodegradable and annually available resources (Doane et al., 1992). For obtaining thermoplastic starch (TPS) materials, native granular starch is destructured at temperatures above 100 °C and plasticized with the aid of relatively low molecular weight additives with polar functions like water (Forssell et al., 1996; Kirby et al., 1993), glycerol (Van Soest and Knooren, 1997; Van der Burgt et al., 1996), sorbitol (Funke et al., 1998; Lourdin et al., 1997a,1997b) and urea (Willet et al., 1995; Shogren et al., 1992). The possibility of using fatty acids as plasticizers has been examined as well (Pushpadass et al., 2009).

A major problem with TPS is the physical instability of the bulk material, caused by its strong hydrophilicity, by the limited compatibility of the additives in the amorphous blends (Lu et al., 2009), as well as by the retrogradation of the starch component (Lourdin et al., 1997a,1997b; Röper and Koch, 1990; Poutanen and Forssell, 1990).

To overcome the water-sensitivity of starch, various methods based on chemical modification and blending have been proposed. Etherification or esterification of starch hydroxylic groups, as well as blending with synthetic polymers exhibiting a lower hydrophilicity than starch allowed improving the properties of the final TPS material. The combination of these two methods by grafting or graft polymerization on the starch backbone even offered additional advantages.

We have also reported (Ruckert et al., 1999; Olivier et al., 2000; Olivier et al., 2001; Lepifre et al., 2004a,2004b) on a novel approach to this problem, by treating with accelerated electrons the blends of native potato starch with various synthetic or natural additives in the presence of water and glycerol. The radiochemical grafting within bulk blends presents significant advantages over the chemical modification of starch in solution

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by avoiding the use of solvents and limiting the need of thermal activation. A generally recognized weakness of the radiation processing applied to polysaccharides is the degradation with a significant contribution of chain scission (Bhat and Karim, 2009; Kollengode et al., 1996; Tyler et al., 1968). For this reason, we are currently exploring the possibility to exploit the potential protective effects against the adverse consequence of irradiation of lignin and of lignin-like aromatic additives intimately mixed with deconstructed starch.

The present paper is focused on the effect of cinnamyl alcohol in TPS blends subjected to electron beam radiation. For gaining a better understanding of the complex phenomena underlying the evolution of macroscopic features of the materials, the effect of cinnamyl alcohol was assessed in model blends including maltodextrin, water and/or glycerol.

2. Experimental section

2.1. Materials

Wheat starch and the maltodextrin sample (Glucidex 2) were supplied by Roquette Freres, Lestrem, France. The maltodextrin is in the form of an amorphous powder exhibiting a dextrose equivalent number DE=2. Water was de-ionized using the Waters milli-Q purification system. Reagent grade glycerol and cinnamyl alcohol, both from Sigma-Aldrich, were used as additives in the blends.

2.2. Preparation of the formulations

A mixture of wheat starch and glycerol in 80:20 ratio by weight was extruded to obtain starch pellets. For every 100 g of these pre-extruded starch pellets, 2 g of cinnamyl alcohol was added to the mixture and processed in a single screw extruder (SCAMIA, France). The extrusion barrel was heated in three zones at temperatures 105, 110 and 110 °C and the die plate was heated to 115 °C. The mixing screw of diameter 2 cm with a length to diameter ratio of 11 was operated at 70 rpm to obtain the final formulation in the form of 30 mm-broad ribbons of thickness 1 mm. The ribbons were stored at 20 °C and at relative humidities (R.H.) of 11%, 33%, 50% and 75% before irradiation.

The blends of maltodextrin (Glucidex 2) with glycerol and water were prepared in the ratio of maltodextrin:glycerol:water=70:20:30 in parts by weight. Upon careful manual mixing at RT, the blend forms a thick and stable paste. The formulations containing cinnamyl alcohol were prepared in a similar manner with a ratio of maltodextrin:glycerol:water:cinnamyl alcohol=70:23:30:11.6 in parts by weight to obtain similarly a paste without any macro-phase separation. The amount of cinnamyl alcohol corresponded to 0.2 equivalent of cinnamyl alcohol for one mole of anhydroglucose units in Glucidex 2. The pasty blends were sealed in polyethylene packs one day before irradiation.

The electron beam accelerator used for irradiation was a 10 MeV Circe II industrial scale accelerator (Linac Technology, France) operated at IONISOS, Chaumesnil, France. The samples were irradiated at 50 kGy, 100 kGy, 200 kGy and 400 kGy by applying 50 kGy per pass. After irradiation, the samples were transferred to glass sealed vials in order to limit moisture evaporation.

2.3. Tensile test setup

The tensile strength experiments were conducted on ISO 527 1BA dumbbell specimens conditioned at R.H. 50% before irradiation and for a minimum of 2 weeks of sample conditioning once they had been irradiated. The tensile properties were determined with a TEST 108 2 kN instrument (GT-TEST) equipped with a load

cell of 500 N with a crosshead speed of 10 mm min⁻¹ under constant storage conditions (50% R.H.) and at 20 °C in an environmentally controlled instrument chamber. Six experiments were done for each sample.

2.4. Determination of gel fractions

The gel fraction was determined by calculating the insoluble part of the irradiated samples used for tensile strength measurements. The unirradiated TPS samples were found to be soluble in dimethylsulfoxide (DMSO). The gel content was consequently determined by immersing the samples in an excess of DMSO at 25 °C for 48 h. After filtration, the insoluble part was wiped and further washed, first by immersing in water and then in ethanol in order to remove the remaining DMSO. The insoluble part was then dried at 80 °C for 24 h and reconditioned at 50% R.H. before weighing so as to avoid uncontrolled moisture absorption that would affect the determined mass of gel. The gel fraction GF is given by Eq. (1), where m_c is a corrected weight (i.e. only starch weight content) because of simultaneous glycerol extraction during immersion in DMSO; m_c is then a calculated weight obtained with respect to the plasticizer amount introduced initially.

$$GF = 100 \frac{m_d}{m_c} \quad (1)$$

2.5. Chromatographic characterization

The size exclusion chromatographic (SEC) system used for this study was based on a DMSO and water mixture as mobile phase in the ratio of DMSO:water=20:80 v/v containing 0.02% NaN₃ as an anti-bacterial agent. This solvent mixture was found to be well suited for solubilizing both the maltodextrin and cinnamyl alcohol thereby allowing detection of the two components in a single injection. The sample solutions were prepared by weighing 80 mg of formulation and dissolving in 4 mL of the mobile phase. The solution was heated at 60 °C for 30 min to ensure good solubility of the formulation in the mobile phase. They were then filtered using 0.45 μm PTFE syringe filters. Separation was carried out on two Polargel columns M and L kept in series (obtained from Varian-Agilent Technologies) with a guard column (specific for Polargel, Varian-Agilent Technologies). The columns were connected to two detectors in series, a UV Absorbance detector set at 284 nm (Shimadzu SPD-6A) and refractive index detector (precision instruments IOTA 2). The data were recorded using a multimeter over time interval of one second with input of 1 V from refractive index detector and 10 mV from UV absorbance detector (Keithley 2000 multimeter). The flow rate was maintained at 1 mL/min using a pulse pump (Shimadzu LC 6 A) and the injector loop was of 50 μL obtained from Interchim.

The continuous monitoring of aromatic compounds in chromatography is generally done using the UV detector whereas the carbohydrate samples are monitored using refractive index detector. After thorough UV-visible analysis of the formulations with and without cinnamyl alcohol, 284 nm was found to have sufficient absorbance of cinnamyl alcohol with minimum interference from the carbonyl functional groups that can be formed during irradiation of maltodextrin and limited interference from the mobile phase.

3. Results and discussions

The primary objective of this exploratory work was to assess the possibility to balance the radiation-degradation of thermoplastic

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