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Electron beam irradiation of maltodextrin and cinnamyl alcohol mixtures: Influence of glycerol on cross-linking

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ABSTRACT

The influence of glycerol on the electron beam-induced changes in maltodextrins–cinnamyl alcohol (CA) blends is examined with respect to its influence on the degree of chain scission, grafting, and cross-linking. The study is relevant to radiation-induced polysaccharide modification, specifically in the perspective of using blended starch as a thermoplastic material, where glycerol is commonly used as a plasticizer. In the absence of CA, glycerol protects maltodextrin from chromophore formation onto the main chain, but also induces more chain scission. The presence of CA provides efficient radiation-protection against scission. Glycerol is shown to affect the interaction between maltodextrin and CA, most likely in the form of an inclusion complex when glycerol is absent. The global behavior under radiation is therefore governed by the physical interactions between the blend constituents rather than on the role of glycerol role as a plasticizer, or as an OH• radical scavenger.

1. Introduction

Starch is an economically advantageous renewable resource with large potential to substitute the current oil-based plastics. It can be converted to a thermoplastic material by applying high temperature and shearing on a mixture of dry starch and a suitable plasticizer such as water, polyols, amides and acid salts (Halley & Avérous, 2014).

However, thermoplastic starch faces serious limitations because of its water sensitivity and its tendency toward retrogradation (Shogren, Swanson, & Thompson, 1992). Radiation grafting of synthetic additives onto starch has been proposed for improving the physical and mechanical properties of the blended materials (Kollengode, Bhatnagar, & Hanna, 1996; Olivier, Cazaux, & Coqueret, 2000; Olivier, Cazaux, Gors, & Coqueret, 2001; Sagar, Villar, Thomas, Armstrong, & Merrill, 1996a, 1996b). More recently, we have reported on the possibility of using ionizing radiation on starch in the presence of lignin, a hydrophobic biopolymer, as a means for improving the surface water resistance of the starch blends along with the enhanced physical stability arising from radiation-induced covalent linkages between starch and lignin (Lepifre, Baumberger, et al., 2004; Lepifre, Froment, et al., 2004). The study of blends of model compounds for starch and lignin, namely starch-derived maltodextrin and aromatic additives such as lignin-like monomers, gave insight on how the mechanical properties of thermoplastic starch can be adjusted in the presence of aromatic additives upon irradiation (Khandal et al., 2012; Khandal, Mikus, Dole, & Coqueret, 2013). However, the role and the influence of glycerol, the plasticizer commonly used for processing starch, over the relative importance of chain scission, grafting, and cross-linking in the presence of additives such as CA was still unclear. We initially assumed that glycerol could influence radiation-induced modification of maltodextrin in two ways: (i) by modifying the inter-chain interactions between polysaccharide chains through dilution and plasticization and/or (ii) by affecting the radiation sensitivity of thermoplastic starch as a result of its scavenging properties for the oxidative species generated by radiolysis.

The first effects expected from the presence of glycerol are associated to the solvation of the polysaccharide that modifies its sorption properties as well as its plasticization (Kruiskamp, Smits, van Soest, Feil, & Vliegenthart, 2001; Lourdin, Coignard, Bizot, & Colonna, 1997; Smits, Kruiskamp, van Soest, & Vliegenthart, 2003; Van der Burgt, Van der Woude, & Janssen, 1996; Zullo, & Iannace, 2009). Godbillot, Dole, Rogé, and Mathlouthi (2006) proposed various stoichiometric interactions to starch via H-bonding by varying amounts of water and glycerol. According to this model, when the number of starch binding sites and plasticizer content is quite similar, then both glycerol and water compete for the hydroxyl groups

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on starch and water can progressively replace glycerol for these sites. We can conclude that glycerol, present in sufficient amount, is capable of shielding starch chains from their neighbors, limiting the efficiency of intermolecular reaction between polysaccharide chains. In our radiation-induced experiments, this phenomenon would affect the cross-linking of two adjacent radicals formed on the maltodextrin polymer chains.

The formation of the radicals on hydrated starch and related polysaccharides subjected to high-energy radiation results from the direct effects of ionization, and for aqueous polysaccharides, by H-abstraction reactions effected primarily by the radical species generated from water (Tyler, Munno, & Cadman, 1968). The more reactive species are $OH^{\bullet}$ and $H^{\bullet}$, whereas hydrated electrons are essentially non-reactive toward glucans (Al-Assaf, Phillips, Williams, & du Plessis, 2007; Von Sonntag, Bothe, Ulanski, & Adhikary, 1999). Since the radiochemical yield of radical $OH^{\bullet}$ formation is higher than that of radical $H^{\bullet}$ and hydrated electrons (e^{-}_{aq}) (Spinks & Woods, 1976) and the reactivity of $OH^{\bullet}$ is almost two orders of magnitude higher than that of $H^{\bullet}$ (Sharpatyi, 1982; Von Sonntag & Schuchmann, 2001, chap. 6), the main radical species responsible for modification of starch blends subjected to EB radiation is the $OH^{\bullet}$. In general, the reaction of free radicals on starch results in chain scission and/or formation of new chromophores (COOH, CHO, etc.), the mechanisms of which are well discussed in the literature (Korotchenko & Sharpatyi, 2004; Sharpatyi, 2003, 2006). Inter-chain cross-linking by coupling between free radical sites generated on the polysaccharide chains competes with the degradation processes (chain scission and chromophore formation). The relative importance of cross-linking is strongly dependent on polymer concentration and on chain mobility in the solution or blend (Phillips, 1962).

The presence of additives that can interact with the $OH^{\bullet}$ radicals is expected to compete with the polysaccharide chains and hence, to reduce the degree of chain scission and chromophore formation. Particularly, isopropanol (iPr-OH), glycerol and t-butanol (t-BuOH) are known to exert a protective effect by quenching $OH^{\bullet}$ radicals, forming carbon-centered free radicals of lower reactivity toward polysaccharides (Eiben, & Fessenden, 1971). The corresponding rate constants have been determined with values as high as 1.9×10^9, 1.0×10^9 and 0.6×10^9 L/mol s respectively, for the 3 mentioned alcohols (Baugh et al., 1982; Gao, Yuan, Ding, & Liu, 1998; Zhang, Yu, Ge, & Zhu, 2005).

Hydro-alcoholic blends of maltodextrin and CA are, therefore, complex mixtures not just because of their chemically different natures but also because of the way they can physically interact with each other. The aim of this study is to understand how these interactions influence the radiation-induced modification of the polysaccharide with respect to chain scission, chromophore formation, grafting of CA, and cross-linking between the chains. Various analytical methods including size exclusion chromatography (SEC), UV spectroscopy, ^{1}H NMR, as well as gel fraction measurements were carried out for comparing the influence of blend composition on the effects of radiation.

2. Experimental

2.1. Materials

Maltodextrin sample (Glucidex 2) was supplied by Roquette Freres, Lestrem, France in the form of an amorphous powder exhibiting a dextrose equivalent number DE = 2. Water was deionized using the Waters Milli-Q purification system. Reagent grade glycerol and cinnamyl alcohol (CA), both from Sigma–Aldrich, were used as received.

2.2. Preparation of the formulations

The maltodextrin (Glucidex 2) was mixed with glycerol and water to form thick pastes with maltodextrin:glycerol:water weight ratios at 70:0:53, 70:26:26, 70:53:0, and 70:0:30 resulting in homogeneous thick non-flowing pastes. The parts by weight ratio for water and glycerol were calculated for the 70 parts of maltodextrin in the blend. The blends containing CA were also prepared with the amount of CA being 11.6 parts by weight for every 70 parts by weight of the maltodextrin powder, which corresponds to 0.2 equiv. of CA for 1 mol of anhydroglucose units (AGU) of the maltodextrin in the blend. Thus, the CA containing blends had composition maltodextrin:glycerol:water:CA of 70:0:53:11.6, 70:26:26:11.6, 70:53:0:11.6, and 70:0:30:11.6 in parts by weight ratio. The CA containing blends were also thick pastes with no macro-phase separation.

2.3. Irradiation of blends

The maltodextrin samples and blends were sealed in low density polyethylene (LDPE) bags removing any residual air from the bags before irradiation. The samples were processed with an industrial 10 MeV accelerator (CIRCE II, 20 kW), applying a unit dose of 50 kGy per pass.

2.4. Gel content analysis

Gel content determination was carried out by filtration after dispersing about 1 g of the precisely weighed samples in a controlled volume of water:DMSO (95:5, v/v). The sample dispersion was achieved at 60 °C for 1 h and followed by filtration on a Whatman 42 paper. The complete dissolution of the unirradiated sample would take place giving a clear solution without any filtration residue while the gel formed in the irradiated sample collected on the filter paper would be transferred back into the vial and treated with water:MeOH (80:20, v/v) for 30 min. The gel was again filtered and successive washings with increasing MeOH content in the water:MeOH solvent were given resulting in a dry gel. The gel was then filtered over a pre-weighed Whatman 42 paper placed over a crucible of porosity 3 and rinsed with MeOH. The gel was dried in the oven at 50 °C till constant weight.

2.5. UV–vis analysis

The apparent molar absorptivities (ε_{app}) of the AGU of maltodextrin in blends containing no CA were calculated using a Varian UV–vis spectrometer (Cary 50 Bio model). Solutions of known concentrations were prepared in DMSO:water (20:80, v/v) and analyzed against water as a reference solution in a 1 cm cuvette. The spectra were recorded between 600 and 200 nm and absorbance was considered only at wavelengths above 260 nm to avoid any interference from the presence of DMSO.

2.6. Size exclusion chromatography characterization

Size exclusion chromatography (SEC) analysis was performed with a Jasco HPLC system on two Polargel columns of type M and L (Varian – Agilent Technologies) using the mobile phase DMSO–water mixture (20:80 (v/v) with 0.02% NaN_3) at 1 mL/min maintained by pulse pump (Jasco PU-1580). Double detection was achieved with a UV absorbance detector (Jasco UV-1575) and a refractive index detector (Precision Instruments IOTA 2) in series. The sample solutions were prepared by dissolving 80 mg of formulation in 4 mL of the mobile phase and were filtered over a 0.45 μm PTFE filter. Injections of 50 μL volume were carried out using an autosampler (Jasco AS-350).