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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).

The RI and UV profiles were reproducible for same sample injected several times and different solutions of same compositions (irradiated and unirradiated) analyzed on different days.

2.7. NMR analysis

^{1}H NMR analysis of the maltodextrin samples (40 mg in 0.5 mL of DMSO-d6) was carried out on a 250 MHz Bruker spectrometer. Two solutions were prepared for each formulation irradiated at a given dose and two spectra were recorded at the aforementioned conditions for each of the two solutions. The calculation of the integrals of the ethylene and methylene protons of the CA in the blend was carried out to calculate its fractional conversion after irradiation (average value based on 5 integration measurements).

2.8. Gas chromatography analysis

CA in the unirradiated blends was extracted with MeOH and quantified by gas chromatography. The formulations prepared for this study were of the composition maltodextrin:(glycerol + water):CA = 70:50:5.6 where CA was 0.1 equiv. for 1 mol of AGU. The glycerol content was varied in such a manner that the total solvent of the formulation was always 50 parts by weight for 70 parts by weight of maltodextrin. The formulations were prepared in duplicates and each formulation weighed 4.5 g having maltodextrin around 2.5 g with 0.2 g of CA weighed to an accuracy of 0.001 g. After addition of glycerol and water, the formulations were mixed manually to obtain a paste showing no macro-phase separation and left to stand at room temperature for 2 days covered by a parafilm. The formulations were then transferred to flasks containing around 300 mL of MeOH mechanically shaken for 8 h. All flasks were kept on the same stirrer and thus received the same amount of agitation. The solutions were then filtered over a Whatman 42 paper to remove the undissolved maltodextrin. The filtrates were collected into titration flasks and diluted exactly to 500 mL with MeOH. These solutions were filtered over a 0.20 μm PTFE syringe filter and injected into the GC system (Agilent 7890A) equipped with a capillary column (DB-624 of length 30 m, diameter 0.32 mm and film thickness 1.8 μm) and flame ionization detector (FID). The injector temperature was maintained at 250 °C (boiling point of CA 233–235 °C) and 10 μL of the solution was injected by an auto-sampler of which 1 μL was loaded on to the column for analysis (split 1:10). The oven was kept at 100 °C initial temperature and given a ramp of 10 °C/min up to 250 °C. The flow rate of nitrogen gas was kept at 1 mL/min and the detector was maintained at 250 °C. A calibration curve was prepared of CA of concentrations varying between 1 and 5000 ppm having a regression correlation coefficient $R = 0.9975$.

3. Results and discussion

The present investigation addresses the complex reactions taking place in polysaccharide blends irradiated in the form of paste-like mixtures including maltodextrin as the major component. The relative importance of chromophore formation, chain scission and cross-linking is influenced by the nature and amount of fluids (water, glycerol, CA) and are assessed as a function of the radiation dose. The limited content in fluid additives is known to induce favorable conditions for inter-chain coupling by free radical combination (Yoshii et al., 2003).

A first series of experiments was conducted with maltodextrin blends including varying amounts of water and glycerol in the absence of any aromatic additive (Section 3.1). The specific influence of glycerol on the protective effect of CA on maltodextrin degradation upon exposure to radiation is presented in Section 3.2. Section 3.3 examines the role of glycerol on the physico-chemical interactions of maltodextrin chains with CA in the unirradiated blends, with emphasis on the impact of this behavior onto the final trend on radiation induced gel formation.

3.1. Maltodextrin blends with varying glycerol and water content

The extent of radiation-induced degradation of maltodextrin (i.e. chain scission and chromophore formation) was studied for the aqueous blends containing varying water:glycerol (w/w) ratio keeping constant the total amount of fluid. These blends were studied for chromophore formation using the UV absorption spectroscopy and changes in molecular mass using the SEC analyses.

As discussed in Section 1, the formation of chromophores (aldehydes, ketones, carboxylic acid functionalities) on the polysaccharide chains is frequently reported on a qualitative basis (Bhat & Karim, 2009; Phillips, 1962). The formation of carbonyl unsaturations is confirmed by comparing the FTIR spectra (the blends before and after irradiation showing new bands of intensity increasing with the dose at about 1735 cm^{-1}, corresponding C=O valence vibrations) (Braşoveanu, Nemţanu, & Duţa, 2013; Kizil, Irudayaraj, & Seetharaman, 2002; Sokhey & Hanna, 1993). We have assessed in a quantitative manner the gradual generation of chromophores by UV–vis spectroscopy of blends dissolved in DMSO/water mixture (20:80, v/v). The unirradiated maltodextrin used in our study only showed a slight absorbance between the regions 260 and 270 nm. The average molar absorptivity of irradiated maltodextrin was compared with the absorbance of unirradiated maltodextrin to quantify the formation of chromophore groups by the increase of average molar absorptivities at 270 and 282 nm (ε_{app}) with respect to the initial number of AGU in the solution.

The corresponding values are gathered in Table 1. These data show that the increase in absorbance depends on the amount of water and glycerol. Irradiation at 400 kGy of maltodextrin in powder form (moisture content 5–6% as measured by Karl–Fischer method) results in almost 17 times more absorption than that observed for the unirradiated maltodextrin. In the presence of increasing amounts of water, the enhancement in UV absorbance takes place to a lesser extent (6 and 5 times for 30 and 53 parts of water for 70 parts by weight of maltodextrin, respectively). Thus, water inhibits or at least limits the formation of chromophores on the maltodextrin chains, though the additional amount of reactive species formed by water radiolysis could have induced more degradation on the polysaccharide chains.

The presence of glycerol in a blend of initial composition maltodextrin:water = 70:53 parts by weight was found to further decrease the radiation-induced chromophore formation. For the blends maltodextrin:glycerol:water = 70:7:46 parts by weight the ε_{app} value at 270 nm is 12.1 ± 0.5 L/mol cm. This value is reduced to 9.2 ± 0.5 L/mol cm for the blend maltodextrin:glycerol:water = 70:30:23 parts by weight. Maltodextrin irradiated in the presence of glycerol but no added water (maltodextrin:glycerol = 70:53 parts by weight) gave ε_{app} value at 270 nm only two times higher than that calculated for the unirradiated maltodextrin. Glycerol obviously provides better protection than water with respect to the radiation-induced chromophore formation onto the maltodextrin chains. The quenching by glycerol of the primary free radicals generated by radiolysis is likely at the origin of the reduced damages caused to the maltodextrin.

The SEC analyses of blends without any CA were primarily performed using refractive index detection (RID) well-suited for the detection of carbohydrates. The RID traces of unreacted and irradiated blends were examined with the assumption that maltodextrin is the only component contributing to the refractive index of the blend. The contribution of aromatic chromophores possibly attached on polysaccharide chains, when CA is present in the blend, was negligible. Having shown that the irradiation was leading to

Table 1
Apparent average molar absorptivity per AGU of the irradiated maltodextrin in blends not containing CA (spectra recorded for solutions prepared in DMSO:water = 20:80 (v/v) and analyzed against water as a reference solvent).

Maltodextrin (parts by wt)	Glycerol (parts by wt)	Water (parts by wt)	Dose (kGy)	ε_{app} (L/mol cm)[a]	
				270 nm	282 nm
70	0	0	Unirradiated	3.2 ± 0.5	2.6 ± 0.5
70	23	30	Unirradiated	2.2 ± 0.5	1.8 ± 0.5
70	53	0	Unirradiated	2.3 ± 0.5	1.9 ± 0.5
70	0	0	400	52.5 ± 0.5	38.2 ± 0.5
70	0	30	400	19.2 ± 0.5	16.0 ± 0.5
70	0	53	400	14.8 ± 0.5	10.9 ± 0.5
70	7	46	400	12.1 ± 0.5	9.1 ± 0.5
70	23	30	400	10.1 ± 0.5	8.2 ± 0.5
70	30	23	400	9.2 ± 0.5	6.9 ± 0.5
70	53	0	400	5.8 ± 0.5	4.1 ± 0.5

[a] Apparent (average) molar absorptivity in DMSO/water solution (20:80, v/v) of AGU chromophores in unirradiated and irradiated maltodextrin blends.

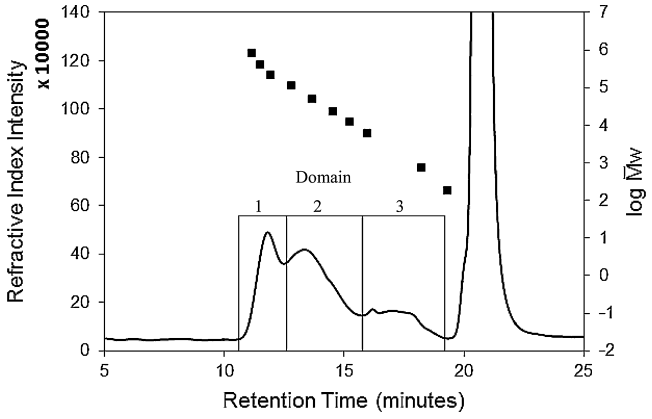

Fig. 1. RI trace of unirradiated maltodextrin showing the three domains defined by the retention times (R_t). Domain 1 is the high MW fraction (R_t range 10.2–12.5 min), Domain 2 is the medium MW fraction (R_t range 12.5–15.6 min), and Domain 3 is the low MW fraction (R_t range 15.6–19.2 min) of the maltodextrin used in this study.

changes in the UV spectra of the maltodextrin blends, UV detection at 282 nm was also used for comparison with the RID traces.

For the purpose of quantitative comparison of the effects of radiation treatment, the RID trace of unirradiated maltodextrin (Fig. 1) was split into three sub-domains. The integrated areas were defined by fixed retention times representing the high molecular mass fraction (domain 1), medium molecular mass fraction (domain 2), and low molecular mass fraction (domain 3) of the maltodextrin. The range of retention times (R_t) used for the calculation of peak areas in all the blends was set to 10.2–12.5 min for domain 1, 12.5–15.6 min for domain 2, and 15.6–19.2 min for domain 3.

Though not of quantitative significance for the comparison of absolute molecular weights in the present analysis, it is worth to indicate the weight average molecular mass (M_w) for each domain as calculated from pullulan standard calibration: 788,000–112,000 Da for domain 1, 112,000–6000 Da for domain 2, and 6000–180 for domain 3. For each blend (unirradiated and irradiated), the area fraction of each domain was calculated within well-defined retention times and plotted against the applied radiation dose. The evolution of area fractions of the different domains for increasing radiation dose indicates the extent of radiation-induced chain scission. The peak area fractions of maltodextrin irradiated in powder form and in presence of solvent (water and glycerol) are shown in Fig. 2.

Maltodextrin irradiated in the form of powder with no added solvent shows a greater loss in domain 1 than that irradiated in the presence of water and glycerol. The loss in domain 1 observed for the water-only blend is however much lower than that observed for blends containing glycerol. This indicates that though radiation-induced chain scission in the maltodextrin is reduced to a certain extent by the presence of a protic solvent, water is a more effective solvent than glycerol in providing protection against radiation-induced chain scission of maltodextrin, that competes with cross-linking. The observed behavior can be interpreted, at least in part, by the increase of mobility provided by solvation and plasticization, that enhances for both additives, the probability of inter-chain coupling by free radical combination (Yoshii et al., 2003). The stronger interaction of glycerol with the anhydroglucose units of maltodextrin can nevertheless induce the formation of a molecular shield reducing the occurrence of close contacts between two macroradicals. However, the chemical influence of glycerol through quenching reactions, particularly toward OH• radicals, must also be taken into consideration.

Both UV–vis spectroscopy and SEC analyses indicate that the presence of an aqueous medium (water and glycerol) provides a certain degree of protection against radiation-induced chain scission and formation of chromophore groups on the maltodextrin chains. However, among the two solvents (water and glycerol), radiation protection with regard to chain scission is relatively better with water, but radiation protection with regard to chromophore formation is relatively better by glycerol. While the protection against chromophore formation by glycerol can be reasoned to arise from its OH• scavenging property, it cannot explain why the presence of glycerol results in higher chain scission and greater loss in high molecular mass fraction of the maltodextrin. The lesser extent of chain scission in presence of water, however, can be explained by the increased chain mobility of maltodextrin in aqueous medium. This would result in higher efficiency for the radicals on adjacent chains to yield cross-linking. Now, considering that glycerol can interact with the polysaccharide chains through H-bonding between hydroxyl groups, the maltodextrin chains may have reduced accessibility in presence of glycerol and hence no tendency toward cross-linking. It is also likely that glycerol acts as a physical barrier between adjacent chains and hence prevents the radicals formed on maltodextrin chains from cross-linking by recombination.

3.2. Radiation processing of maltodextrin blends containing CA and varying glycerol and water content

The reactivity under radiation of the blends containing cinnamyl alcohol was conducted on samples with a CA content equal to 0.2 equiv. for 1 mol of AGU, so that no macro-phase separation of the additive can take place in the processing conditions. Upon EB irradiation, contrarily to blends irradiated containing no CA, the presence of the aromatic additive induced the formation of a macrogel. CA seems to act as a cross-linker involving the ethylenic and the benzyl alcohol functionalities. This behavior confirms our previous study

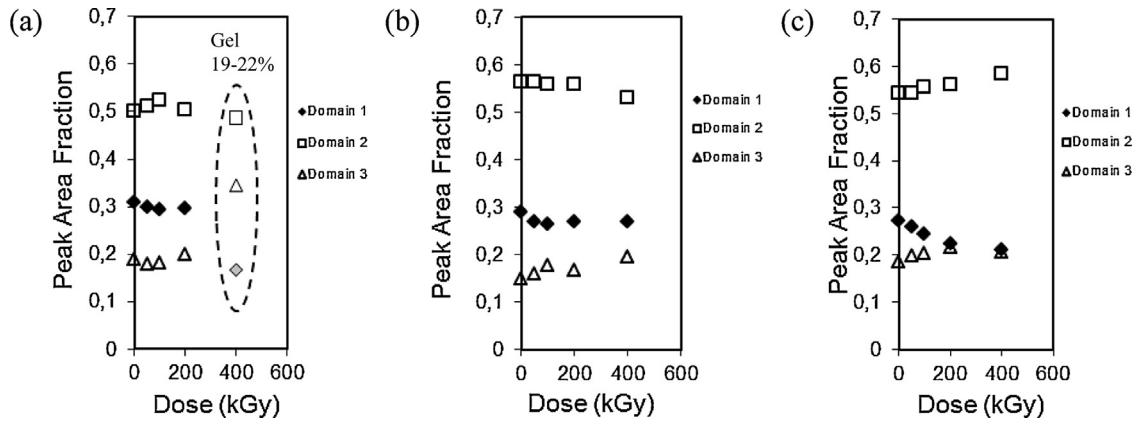

Fig. 2. Evolution of the peak area fractions of domain 1 (high MW), domain 2 (medium MW), and domain 3 (small MW) as a function of irradiation dose for the maltodextrin blends: (a) maltodextrin in its native powder form without any added solvent; (b) maltodextrin:glycerol:water = 70:53:0 (in wt-parts); (c) maltodextrin:glycerol:water = 70:0:53 (in wt-parts).

Table 2
Weight fraction (%, w/w) of gel in the formulation (corrected for the actual maltodextrin in the blend) for various blend compositions and applied EB radiation dose.

Blend number	Blend composition (in wt-parts)				Gel content (wt%)	
	Maltodextrin	Glycerol	Water	CA	200 kGy	400 kGy
1	70	0	30	0	0	0
2	70	0	30	11.6[a]	6–8	16–19
3	70	0	53	11.6[a]	<1	19–22
4	70	7	46	11.6[a]	0	2–5
5	70	10	42	11.6[a]	0	0
6	70	23	30	11.6[a]	0	0
7	70	53	0	11.6[a]	0	0

[a] Corresponds to 0.2 equiv. of CA for 1 mol of AGU.

with evidence of maltotriose–CA adducts supported by MALDI-TOF MS analysis (Lepifre, Froment, et al., 2004). The gel content based on the anhydrous maltodextrin content in the initial formulations is listed in Table 2.

Obviously, radiation-induced gelation is correlated with the amount of CA in the blend. The concentration dependence is currently being studied in terms of radiochemical yields of scission and cross-linking of another polysaccharide, namely pullulan. This investigation will be the subject of a forthcoming article. However, at constant CA content in the blend, the gel fraction depends on the water:glycerol content in the blend and the radiation dose. In absence of any glycerol (Table 2, entries 2 and 3), the influence of dilution by increased water content apparently delayed the formation of macrogel but allowed for the formation of large gel fraction at 400 kGy. This can be expected from simple considerations of the probability of inter-chain interactions in dilute systems. The presence of glycerol in the formulations, on the other hand, was found to impede gel formation (Table 2, entries 4–7 compared to 3). The gel fraction isolated in the case of water-based formulations (maltodextrin:water:CA = 70:53:11.6, w/w/w) at 400 kGy accounted for almost 19–22% of the total maltodextrin weight in the formulation. In contrast, the addition of slight amount of glycerol (maltodextrin:glycerol:water:CA = 70:7:46:11.6, w/w/w/w) led to a significant decrease in gel fraction to 5–6% of initial maltodextrin weight in the formulation. Further increase in the amount of glycerol in the formulation completely impeded gelation. The absence of gel in presence of glycerol, however, suggests higher efficiency of chain scission and/or reduced inter-chain coupling in the corresponding blends.

The occurrence of grafting and its efficiency as a function of varying water and glycerol content in the blend were studied by SEC and NMR analyses. This methodology was used previously for studying the influence of glycerol over the three MW fractions in the maltodextrin in the presence of radioprotection by the aromatic additive (Khandal et al., 2012, 2013). As observed for the blends exempt from CA, the blends containing the aromatic additive also showed the evolution of the 3 maltodextrin fractions of large, medium, and small MW to depend greatly on the presence of glycerol. As reported previously for blends containing no glycerol, the grafting of CA results not only in limited of degradation of the maltodextrin (area fraction of domain 1 almost unchanged) but also induces an increase in molecular mass at 200 kGy with an extension of the corresponding SEC trace toward low retention times to be discussed in the next section. In presence of glycerol, the radiation protection afforded by CA is reduced as a slight decrease in the domain 1 fraction is observed for increasing glycerol content (Fig. 3).

Thus, the presence of glycerol leads to a decrease of the high MW fraction (domain 1) of maltodextrin together with the absence of any shift of the SEC trace toward higher molecular mass. Glycerol obviously impedes radiation-induced gelation despite the presence of CA.

In order to ascertain the formation of cinnamyl grafts despite the radiation-induced chromophore formation on maltodextrin chains, chromatograms recorded with the UV detection at 282 nm were compared to those of samples irradiated without CA.

A qualitative comparison was done and the profiles of the CA containing blends had a more than 2 times greater absorbance than those not containing it. This observation therefore supports the presence of aromatic grafts on the chains. Another interesting observation was made by comparing the RI profiles with the UV profiles of the CA containing formulations. Fig. 4(a) and (b) shows the RI and UV profiles of the water-based blend and Fig. 5(a) and (b) shows the RI and UV profiles of the glycerol-based blend containing CA. From Fig. 4(a) and (b) the greater absorbance of domain

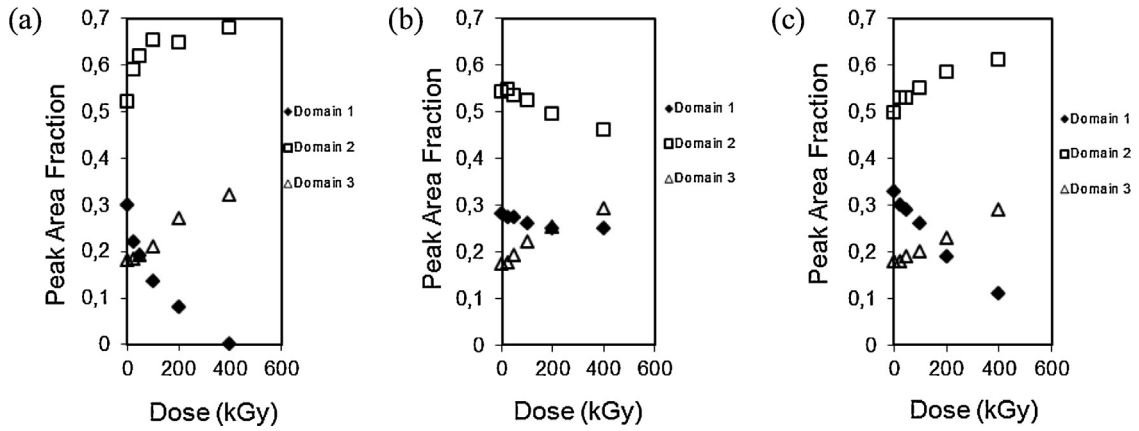

Fig. 3. Evolution of the peak area fractions of domain 1 (high MW), domain 2 (medium MW), and domain 3 (small MW) as a function of irradiation dose for the maltodextrin blends: (a) maltodextrin:glycerol:water:CA = 70:0:53:11.6 (in wt-parts); (b) maltodextrin:glycerol:water:CA = 70:23:30:11.6 (in wt-parts); (c) maltodextrin:glycerol:water:CA = 70:53:0:11.6 (in wt-parts).

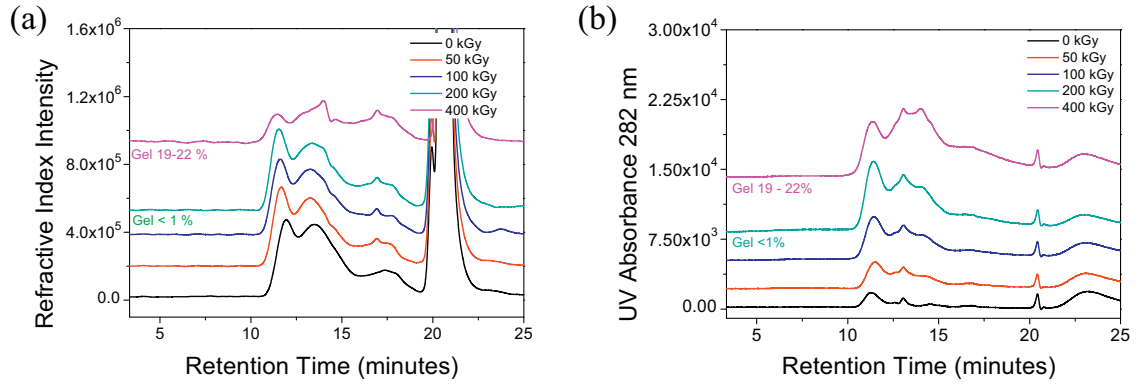

Fig. 4. SEC chromatograms for the blend of composition maltodextrin:glycerol:water:CA = 70:0:53:11.6 (parts by wt), irradiated at different doses: (a) RI traces; (b) UV traces at 282 nm.

1 (compared to domain 2 and 3) in the UV profile than seen in its corresponding RI profile indicates a grafting preference of CA for the high MW fraction of maltodextrin in the water-based blend. This behavior is absent for blends containing glycerol. The difference in the grafting preference is more apparent from the profiles of blends irradiated at 200 kGy. Thus, it can be deduced from UV profiles that CA grafting does take place in presence of glycerol but the preference for the high MW fraction is lost. This suggests that the close proximity between CA and large MW maltodextrin chains is favored by presence of water and somehow impeded by presence of glycerol.

Additional information was obtained from the quantitative analysis of ^{1}H NMR spectra recorded from the different blends. The number of the aromatic protons was assumed to remain unchanged after irradiation and was used for calculating the relative change in the integral values of the ethylene (at 6.5 ppm and 4.8 ppm) and methylene protons (at 4.1 ppm) with respect to the five aromatic protons of CA (multiplet at 7.3 ppm), considered unaffected by the reaction.

The results gathered in Table 3 show that increasing the dose enhances the amount of reacted CA for all the blends. The blend maltodextrin:water:CA of composition 70:53:11.6

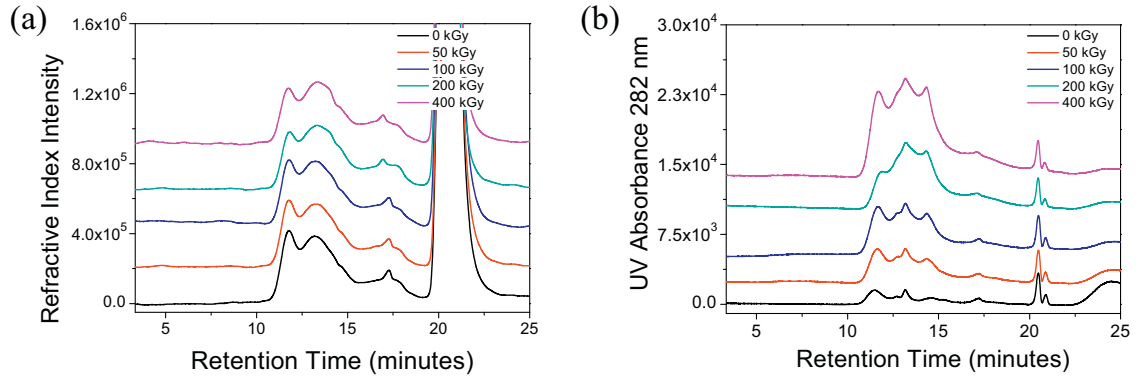

Fig. 5. SEC chromatograms for the blend of composition maltodextrin:glycerol:water:CA = 70:53:0:11.6 (parts by wt), irradiated at different doses: (a) RI traces; (b) UV traces at 282 nm.

Table 3
Fractional conversion of ethylene and methylene protons of CA in the maltodextrin blends irradiated at different doses as calculated from the quantitative ^{1}H NMR spectra.

Maltodextrin (parts by wt)	Glycerol (parts by wt)	Water (parts by wt)	Radiation dose (kGy)				
			0	50	100	200	400
Conversion of ethylenic protons of CA							
70	0	53	0	15 ± 1%	24 ± 1%	32 ± 3%	45 ± 3%
70	7	46	0	12 ± 1%	29 ± 1%	26 ± 2%	41 ± 3%
70	23	30	0	11 ± 1%	19 ± 1%	26 ± 2%	38 ± 2%
70	53	0	0	14 ± 1%	21 ± 1%	26 ± 2%	35 ± 2%
Conversion of methylene protons of CA							
70	0	53	0	7 ± 1%	12 ± 1%	24 ± 3%	32 ± 3%
70	7	46	0	12 ± 1%	29 ± 1%	26 ± 2%	41 ± 3%
70	23	30	0	8 ± 1%	11 ± 1%	23 ± 2%	26 ± 2%
70	53	0	0	5 ± 1%	1 ± 1%	15 ± 2%	19 ± 2%

(w/w/w) irradiated at 400 kGy has the highest conversion of ethylene proton at 45 ± 3% and CH_2 (methylene) protons at 32 ± 3%. The presence of glycerol in small amounts (maltodextrin:glycerol:water:CA = 70:7:46:11.6 parts by weight) does not affect CA conversion. For the glycerol-based blend (maltodextrin:glycerol:CA = 70:53:11.6 parts by weight) at 400 kGy the conversion of ethylenic proton was calculated to be at 35 ± 3% and for CH_2 (methylene) protons at 19 ± 2%. It can be concluded that the presence of glycerol does affect the percent conversion of both the methylene and the ethylene protons of CA but only to a small extent. The blends containing iPr-OH and t-BuOH in place of glycerol (maltodextrin:iPr-OH or t-BuOH:water:CA = 70:23:30:11.6 parts by wt) were also studied and showed formation of gel accounting for about 14–16% of the initial maltodextrin weight. Therefore, the small decrease in grafting reactivity of CA in presence of glycerol cannot explain the absence of macrogel and/or the loss in loss in large MW fraction of maltodextrin.

We have taken into consideration the likely interactions of glycerol with the $OH^{\bullet}$ radicals produced by water radiolysis that can in turn affect to some extent the nature and the number of free radical reactions at the origin of the damages caused to polysaccharide chains. The values for CA conversion measured by NMR establish that the aromatic additives are significantly affected by the radiation treatment, even in the presence of glycerol. This conclusion tends to indicate that the presence of glycerol affects the global behavior of the irradiated blends by a physico-chemical effect rather than by some influence on the reactivity of the aromatic additive. The possible role of glycerol on the affinity of CA for the maltodextrin was therefore considered more precisely.

3.3. Influence of glycerol on maltodextrin–CA complexes

The linear chains of amylose and related polysaccharides are known to adopt a helix conformation in aqueous medium where the interior of the helix has a comparatively hydrophobic character while the exterior has a hydrophilic character due to the orientation of the hydroxyl groups (Jouquand, Ducruet, & Bail, 2006; Putseys et al., 2010). The hydrophobic cavity of the helix is capable of complexing with suitable sized hydrophobic molecules, such as flavor or aroma compounds (Buleon, Colonna, Planchot, & Ball, 1998; Gessler et al., 1999). The size of the inclusion complex depends on the cross-section of the guest molecule. Molecules with small cross sections such as butanol or fatty acids form complexes involving 6 glucose units per pitch, whereas larger cross section molecules such as 1-naphthol induce the formation of a larger cavity with up to 8 glucose residues per pitch (Jane, 2009, chap. 6). Maltodextrin chains can also be assumed to undergo such interactions with the aromatic additives in the aqueous based blends because the linear α-poly(anhydroglucose) chains are sufficiently long to take up helix conformation and CA closely resembles the aroma compounds

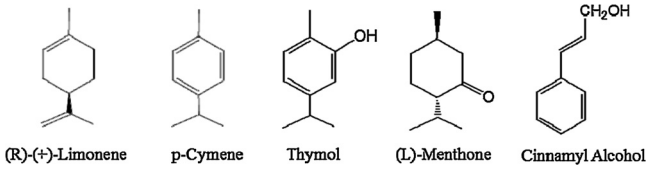

Fig. 6. Chemical structure of various flavors known to form inclusion complexes with amylose and related polysaccharides and of CA.

previously published and known to participate in inclusion complex formation with starch (see Fig. 6).

The concentration of non-polar compound available for complexation in the aqueous phase is an important criterion as reported by Thompson and co-workers through their work on starch complexation with flavor compounds (R)-(+)-limonene, p-cymene, thymol, and (L)-menthone (Tapanapunnitikul, Chaiseri, Peterson, & Thompson, 2008). The compounds with greater hydrophobicity readily form inclusion complex. Their low water solubility also affects the quantity of available ligand in the aqueous solution to participate in the complex formation (Fig. 6). The other interesting feature of their study revealed that complexation of starch with the added non-polar flavor compound was always possible in spite of the presence of starch–lipid complexes in the native starch.

Therefore, it can be reasonably assumed that while the amorphous regions of starch (flexible linear chain fragments) are responsible for the helix conformation and inclusion complexes with aromatic compounds, they are also the regions preferred by glycerol for physically binding at the hydroxyl sites. Chanzy reported that glycerol presence reduces the ability of starch to take up the helix conformation but does not completely prevent the formation of the helices. Glycerol was reported to occupy the exterior space between the different helices and its presence inside the helix was neither established nor ruled out by the authors (Hulleman, Helbert, & Chanzy, 1996). Hence, the interactions between glycerol and maltodextrin can be assumed to compete with the maltodextrin–CA inclusion complexes that are very likely to be formed in the aqueous blends. For studying the extent of maltodextrin–CA physico-chemical interactions in the presence of glycerol, the free or unbound CA in the unirradiated maltodextrin–CA blends containing varying amounts of glycerol in the aqueous solvent was quantified by using GC after extensive extraction.

Formulations containing 0.1 equiv. of CA for 1 mol of AGU with varying amounts of glycerol (keeping the total solvent amount same in all blends) were prepared. These unirradiated formulations were left to stand 2 days to allow enough time for the formation of inclusion complexes between maltodextrin and CA (this time also corresponds to the time between blend preparation and irradiation for the irradiated blends discussed above). The unbound or unsequestered CA in these unirradiated blends was then extracted

in a large volume of MeOH and quantitatively analyzed using gas chromatography (GC) with the help of a CA calibration curve.

The plot of Fig. 7 shows the influence of the presence of glycerol on the fractional amount of CA recovered from the maltodextrin blends. When the aqueous medium of the formulation does not contain glycerol, the extracted CA was only 49% of the actual amount present in the blend. As the glycerol content in the solvent was increased, the amount of extracted CA was also found to increase dramatically, with 92% of the added CA extracted with glycerol as the only solvent.

This clearly demonstrates the existence of a strong physical interaction between maltodextrin and CA in the absence of glycerol, likely under the form of an inclusion complex involving the helices of linear segments of maltodextrin. The presence of glycerol is seen to impede or destabilize these maltodextrin–CA interactions resulting in more unbound CA in the blend. It is very likely that the binding of glycerol to the maltodextrin chains by H-bonding either affects the flexibility of the polysaccharide chains thereby preventing them from taking up the helix conformation or results in glycerol molecules acting as a physical shield preventing the maltodextrin chains from inter-chain interactions or both. These interactions can explain why the presence of glycerol leads to loss in domain 1 and absence of macrogel formation despite the

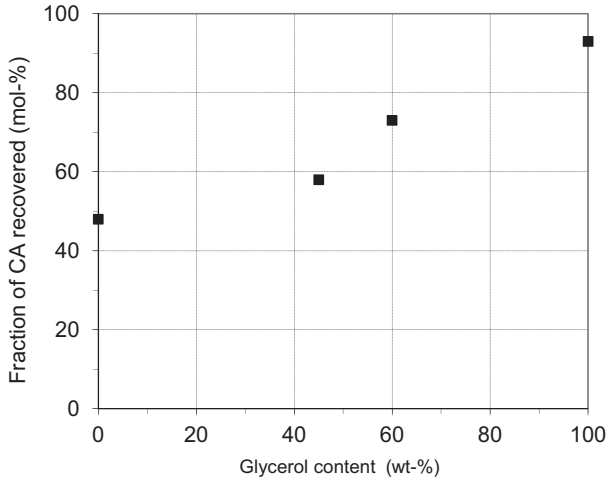

Fig. 7. Recovered mole fraction of CA quantified by GC as a function of the glycerol content in the unirradiated blends (total water and glycerol content was constant in all the blends).

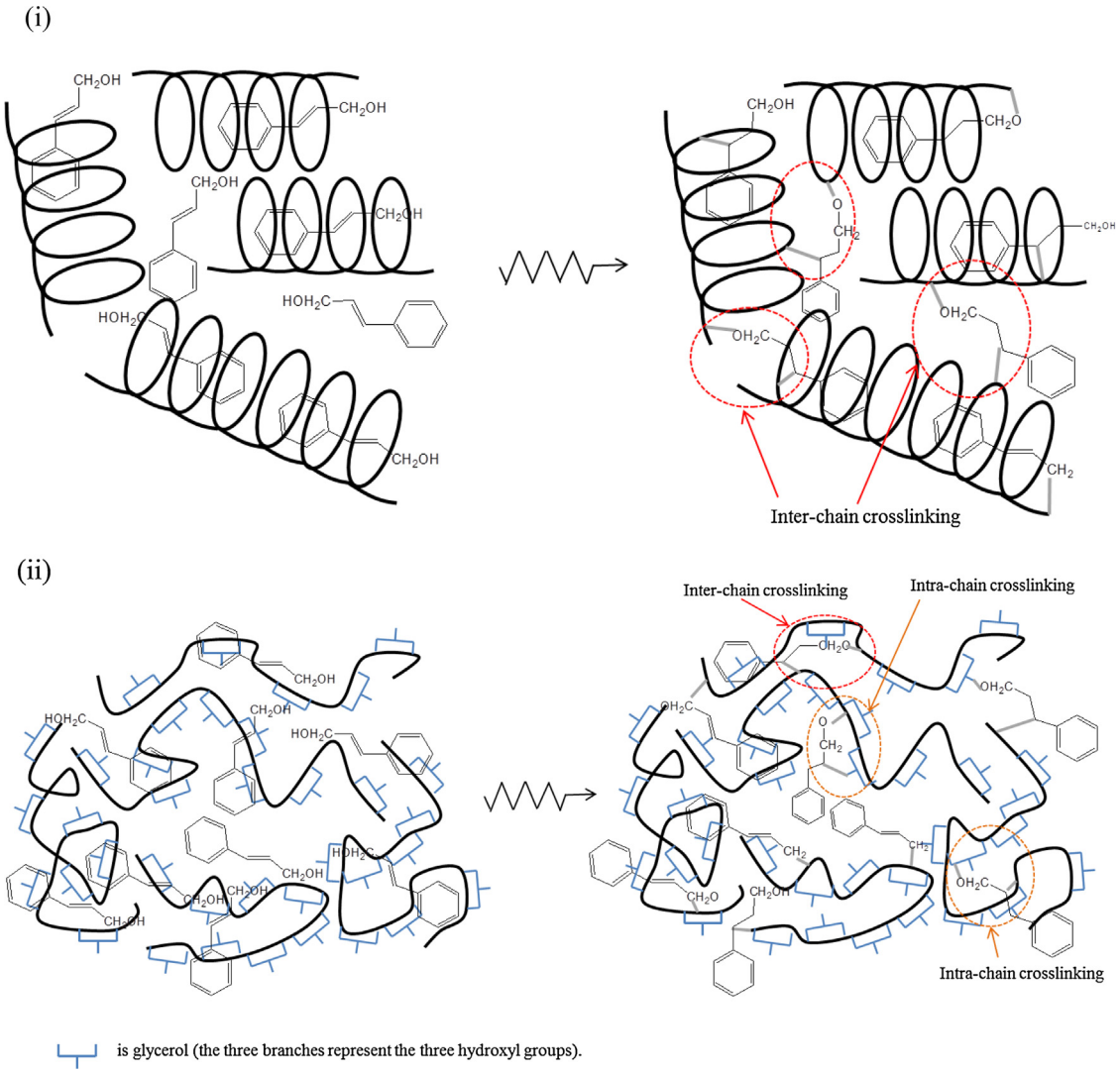

Fig. 8. Schematic representation of the possible conformations of maltodextrin chains and their interaction with CA in the aqueous blends (i) without glycerol and (ii) in the presence of glycerol, explaining the inter-chain or intra-chain cross-linking tendencies upon irradiation.

irradiated blends containing CA. The reduced proximity or affinity of maltodextrin and CA along with the reduced tendency for inter-chain cross-linking would collectively result in relative dominance of scission phenomenon and absence of macro-gel even when grafting is not significantly affected.

The changes of conformation shown in Fig. 8 illustrate our interpretation of the role of glycerol on the interactions between maltodextrin and CA and their result influences the cross-linking phenomenon between the chains involving CA moieties. In the absence of glycerol the maltodextrin–CA inclusion complexes take place due to the helix conformation, inter-chain cross-linking is more likely. In presence of glycerol the maltodextrin chains have random coil conformation with little or no formation of inclusion complex with CA, intra-chain coupling competes with intermolecular cross-linking.

Though not drawn in Fig. 8, the helix conformation in presence of glycerol may be reduced but cannot be completely ruled out. The structures of the CA grafts in the figure are in accordance with the MALDI-TOF study on irradiated maltotriose–CA blends published previously by our group (Lepifre, Froment, et al., 2004).

We are currently investigating the precise nature of these interactions. Maltodextrins, as the one selected for this study, are convenient model compounds given their good solubility in water and structural similarity to starch, however, they do not present all the structural regularities required for a straightforward and unambiguous characterization of supramolecular complexes between polyglucoside and CA. Amylose is considered as a better model in this respect.

4. Conclusion

This paper has discussed in some detail the influence of glycerol on the radiation-induced modification of polysaccharides with respect to its propensity to react with $OH^{\bullet}$ radicals and to its capacity for H-bonding. While glycerol protects maltodextrin chains from radiation-induced chromophore formation by degradation, the shielding effect resulting from its H-bonding ability with anhydroglucose units limits inter-chain coupling, resulting in an overall process dominated by maltodextrin chain scission. The presence of CA can provide radiation protection to the maltodextrin chains, but the degree of protection against chain scission depends on glycerol content. In the presence of the latter, the radiation-induced grafting does not seem significantly affected, but the formation of covalent bridges between maltodextrin chains is critically reduced or precluded. Thus, by varying the amount of water:glycerol content, one can orient the properties of the final blend after irradiation. Work is being pursued on the quantitative determination of radiochemical yields of scission and cross-linking for pullulan irradiated in presence of CA and of glycerol, in order to further quantify the competing phenomena described here.

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