



Synthesis of alkylated potato starch derivatives and their potential in the aqueous solubilization of benzo[a]pyrene

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ABSTRACT

For the development of renewable bioproducts able to solubilize organic persistent pollutant such as benzo[a]pyrene (BaP), modified potato starch was synthesized by alkylation. The addition of alkyl chains was performed with three different alkylation agents: epoxyalkane, alkenyl succinic anhydride and 1,4-butane sultone. Twelve alkylated starches were obtained with different molar substitutions (MS) and various alkyl chain lengths (to three carbons up to sixteen). The chemical structural characteristics were investigated by methods of ¹H NMR and FTIR. In comparison with the native starch, the ether modified starches showed in general an enhancement of their aqueous solubility whereas the ester modified starches stimulated the BaP aqueous solubilization. Indeed, the compounds P6 and P12, which increased 40-fold the BaP aqueous concentration, present high surfactant properties.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are very toxic chemical compounds in the environment which were identified as carcinogenic and mutagenic compounds (White, 1986). PAHs, especially high molecular weight ones such as benzo[a]pyrene (BaP), tend to persist in the environment because of their low water solubility and their tendency to be absorbed onto soil organic matter (Cerniglia, 1992; Wilson & Jones, 1993). Among the processes available for soil rehabilitation, the surfactant-enhanced remediation has been suggested as a promising remediation technology (Mulligan, Yong, & Gibbs, 2001; Zhu & Zhang, 2010). Desorption enhancement of hydrophobic organics from soil by surfactants is the key principle of the surfactant washing process. A surfactant containing both hydrophobic and hydrophilic portions can effectively enhance the aqueous solubility of hydrophobic organics by partitioning them into the hydrophobic core. Such surfactants could be used in pre-treatment washing of soil contaminated with PAHs in order to transfer them into the aqueous solution (Mulligan et al., 2001). This is a prerequisite to stimulate the first steps of PAHs oxidation (Flotron, Delteil, Padellec, & Camel, 2005) which is one of the most limiting factors for PAHs degradation by chemical

or/and biological processes (Rafin, Veignie, Fayeulle, & Surpateanu, 2009; Rosu, Veignie, Surpateanu, Brabie, Miron, & Rafin, 2011).

For this purpose, polysaccharides in particular modified biopolymers derived from chitin and starch could be used (Crini, 2005; Dias, Hussain, Marcos, & Roque, 2011; Zhu & Zhang, 2010). These polysaccharides which are abundant, renewable and biodegradable resources, have been more and more investigated as potential adsorbents materials for removing pollutants from contaminated water (Crini, 2005; Kim & Lim, 1999). Nevertheless, the weak aqueous solubility of starch is also known to be a major constraint that seriously limits the development of starch-based materials. For non-food uses, starch is generally modified in order to obtain products with properties suitable for various and searched applications (Wesslén & Wesslén, 2002).

The aims of the present work were to synthesize potato starch derivatives either by esterification or by etherification in order to fulfill two main objectives: firstly to increase the aqueous solubility of modified starch and secondly to allow BaP solubilization permitting therefore its retention in polysaccharide-based materials.

2. Materials and methods

2.1. Chemicals

The materials used were as follows: benzo[a]pyrene (BaP) at 96% HPLC purity was purchased from Fluka (St. Quentin Fallaviers,

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France); propylene oxide (C3) at 99% purity; 1,4-butane sultone (C4) at 99% purity; 1,2-epoxyhexane (C6) at 97% purity, 1,2-epoxydecane (C10) at 96% purity, 1,2-epoxyhexadecane (C16) at 96% purity and sodium hydroxide (NaOH) micropearls for analysis were provided by Acros Organics (Noisy-Le-Grand, France); 2-octen-1-ylsuccinic anhydride (C12) at 97% purity and 2-dodecen-1-ylsuccinic anhydride (C16) at 95% purity were purchased from Sigma Aldrich (Steinheim, Germany). Dimethyl sulphoxide (DMSO) at 99.5% purity and potato starch (**P0**) were provided by Panreac Quimica SA (Barcelona, Espana). Methanol (MeOH), dichloromethane (DCM), pyridine and other chemicals, except when specified otherwise, were obtained in the highest purity available from Fisher Scientific (Illkirch, France). Deionized water was used throughout this work.

2.2. Synthesis of monoalkylated starch derivatives

2.2.1. Synthesis with epoxyalkane

The reaction was carried out in a round-bottomed flask in continued high agitation at 21 °C. The dried potato starch (**P0**) was dissolved in DMSO at concentration of 1 g to 10 ml (Kavitha & BeMiller, 1998; Rosu et al., 2011). After starch solubilization (at 21 °C for 48 h), the 1,2-epoxyalkane was added at molar ratios of epoxyalkane to the alcohol function present in the starch anhydroglucose unit (OH-AGU) of 3–1.0. The reaction mixture was vigorously stirred at 21 °C for 6 h. Finally, the reaction was catalyzed by NaOH addition (in a concentration of 10% based on starch). On completion of reaction, the modified starch was neutralized with hydrochloric acid and, after solvent evaporation, dialyzed during 4 days using a cellulose membrane (Medicell International, MWCO of 12–14,000 Da) and lyophilized. Three products were obtained following this procedure: hydroxypropylated starch (**P1**) alkylated with propylene oxide, epoxyhexanylated starch (**P3**) obtained with 1,2-epoxyhexane, epoxydecanylated starch (**P4**) prepared with 1,2-epoxydecane.

2.2.2. Synthesis with 1,4-butane sultone

The reaction was carried out in a round-bottomed flask in continued high agitation at 50 °C. After starch (**P0**) solubilization (at 50 °C for 48 h) in DMSO at concentration of 1 g to 10 ml, 4.6 mol of 1,4-butane sultone were added for each mole of OH-AGU. The reaction mixture was vigorously stirred at 50 °C for 14 h. The reaction was catalyzed by NaOH addition (in a concentration of 90% based on starch). On completion of the reaction, the final procedure was followed as described previously. One product was obtained: sulfobutylated starch (**P2**).

2.2.3. Synthesis with alkenylsuccinic anhydride

After starch (**P0**) solubilization (at 21 °C for 48 h) in DMSO at concentration of 2 g to 40 ml, 0.03 mol of alkenyl succinic anhydride solubilized in 3.4 ml pyridine were added at molar ratios of alkenyl succinic anhydride to the OH-AGU of 1–10. The reaction was carried under nitrogen atmosphere for 24 h. On completion of the reaction, the final procedure was followed as described previously. Two products were obtained: octenyl succinic anhydride starch (**P5**) and dodecenyl succinic anhydride starch (**P6**).

2.3. Synthesis of bialkylated starch derivatives

The same procedure was followed for the synthesis of bialkylated starch derivatives, using hydroxypropylated starch (**P1**) previously obtained as stock product. Six products were obtained: hydroxypropyl-epoxyhexanylated starch (**P7**), hydroxypropyl-sulfobutylated starch (**P8**), hydroxypropyl-epoxydecanylated starch (**P9**), hydroxypropyl-epoxyhexadecanylated starch (**P10**), hydroxypropyl octenyl succinic anhydride starch (**P11**) and

Table 1
Characteristics of alkylated potato starches.

Code	Alkyl chain length	Chemical link	MS	Aqueous solubility (g/L)
Monoalkylated starch				
P0	–	–	–	0.35
P1	C3	Ether	1.70	14.41
P2	C4	Ether	1.00	20.63
P3	C6	Ether	0.06	15.64
P4	C10	Ether	0.03	3.98
P5	C12	Ester	0.32	2.79
P6	C16	Ester	0.63	0.82
Bialkylated starch				
P7	C3 + C6	Ether	0.04	16.72
P8	C3 + C4	Ether	2.80	18.63
P9	C3 + C10	Ether	0.01	15.64
P10	C3 + C16	Ether	0.02	2.68
P11	C3 + C12	Ester	1.63	4.41
P12	C3 + C16	Ester	2.38	2.26

hydroxypropyl dodecenyl succinic anhydride starch (**P12**). All the products synthesized are presented in Table 1 and Fig. 1.

2.4. Structural characteristics of starch

2.4.1. Infrared spectroscopy

The Fourier Transform Infrared (FTIR) spectroscopy analyses were done using a FTIR Bruker Tensor 27 apparatus. For all the products synthesized, FTIR spectra were recorded with a resolution of 4 cm⁻¹, with a total of 8 scans, over a region of 400–4000 cm⁻¹.

2.4.2. ¹H NMR spectroscopy

NMR spectra were measured with a 250 MHz Spectrospin NMR spectrometer (Bruker, France). Spectra were recorded either in deuterated water (D₂O) or in deuterated DMSO (DMSO-d₆), with the following spectra acquisition parameters: ambient temperature, relaxation delay 1 s, pulse angle 30 °C, acquisition time 6 s and with a total of 50 scans.

2.4.3. Determination of the aqueous solubility

In order to assess the aqueous solubility, a saturated solution of each modified starch (**P1–P12**) was done in deionized water at ambient temperature (21–22 °C). After 24 released hours, 10 mL of the solubilized starch were lyophilized and weighed. The same procedure was performed with native starch (**P0**) as control. The solubility was evaluated in three replicates for native and each modified starch and the solubility mean was expressed in Table 1.

2.4.4. Calculation of the molar substitution

MS represents the average number of substituents per mole of OH-AGU. The MS of each hydroxypropylated starch was determined from NMR spectra according to the method of De Graaf, Lammers, Janssen, and Beenackers (1995). The MS of other alkylated starches was calculated from the integral of the peak corresponding to CH₂ protons in the alkyl residues and the integral of the peak corresponding to the single proton in anomeric equatorial position of anhydroglucose unit (Bien, Wiege, & Warwel, 2001). The MS of each modified starch was expressed in Table 1.

2.5. BaP solubilization in the presence of modified starch

BaP was initially dissolved in DCM (40 mg/L), then deposited into a hemolysis tube by the addition of 375 μL of BaP solution and allowing DCM solvent to evaporate. 3 mL of water (as reference) or tested potato starch (native or modified one) was added into the hemolysis tube. All concentrations of carbohydrate polymers were tested at 5 mM equivalent AGU of starch. The tubes

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