



Wheat starch carbamate: Production, molecular characterization, and film forming properties



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ABSTRACT

Wheat starch carbamates of different degrees of substitution were produced in laboratory experiments and for the first time their film forming performance were investigated. The carbamation reaction between urea and starch was investigated using a factorial design. Long reaction time, 2 h, and high urea content, 10 and 25%, resulted in a high degree of substitution, 0.07 and 0.15, respectively. These starch carbamates were assumed to be cross-linked and showed best film forming properties resulting in continuous and firm films. Furthermore, a high degree of carbamate substitution favored a decrease in glass transition temperature (T_g) in cast films. The addition of acid as a catalyst for carbamation of starch produced inconsistent results and mainly lead to degradation of starch molecules that caused brittle films. FTIR and ^{13}C NMR analyses confirmed the covalent bonding between urea and starch in starch carbamates. In a final step, production of starch carbamates was successfully scaled up. A potential industrial use of these starches is as oxygen barrier in multilayer food packaging.

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1. Introduction

Starch carbamates are produced by reaction of starch with urea above the melting point of urea (133 °C) through thermal decomposition of urea. This reaction has been studied in depth (Abd El-Thalouth, El-Kashouti, & Hebeish, 1981; Hebeish, Refai, Ragheb, & Abd-El-Thalouth, 1991; Khalil, Farag, Aly, & Hebeish, 2002; Khalil, Farag, Mostafa, & Hebeish, 1994) and the mechanism is proposed to be (Fig. 1):

Starch and cellulose carbamates are used in the textile and paper industries to improve surface properties, e.g., as flame retardants (Passauer, Fischer, Bender, Tech, & Wagenführ, 2013), reinforcing filler instead of carbon black in rubber compounds (Li & Cho, 2013), and as flocculants to remove heavy metals from wastewater (Khalil & Aly, 2001). Preliminary studies in our laboratory have shown that solution-cast films of starch carbamates have promising film forming and oxygen barrier properties. Furthermore, urea has been found to be a valuable plasticizer in biobased materials (Ma and Yu, 2004; Pushpadass et al., 2008). In theory, urea can also act as

an internal plasticizer when bound to starch as a carbamate ester. The introduced carbamate group can form hydrogen bonds with neighboring starch chains in a processed starch carbamate-based material, replacing the strong interaction between the hydroxyl groups of the starch molecules. Wang, Chen & Zu (2014) showed that urea addition lower than 10% resulted in an antiplasticization effect on starch films whereas 10–30% were sufficient to plasticize starch films. Furthermore, it has been shown that cross-linking of starch in the presence of urea occurred (Khalil et al., 1994; Khalil et al., 2002). Since cross-linking of starch is a well known technique to improve film formation and barrier properties, the starch modification with urea was expected to improve functional properties of starch carbamate films.

Considering that urea is generally recognized as safe (GRAS) by the U.S. Food and Drug Administration (FDA), we believe that combining starch and urea to produce starch carbamates might have potential applications in the food packaging industry. Also, urea plastified starch films have been used as fertilizer for improving plant growth (Rychter et al., 2016).

To the best of our knowledge, there are no previous studies on the film forming ability and film properties of starch carbamates. We produced wheat starch carbamates with different degrees of substitution (DS) by varying three process conditions

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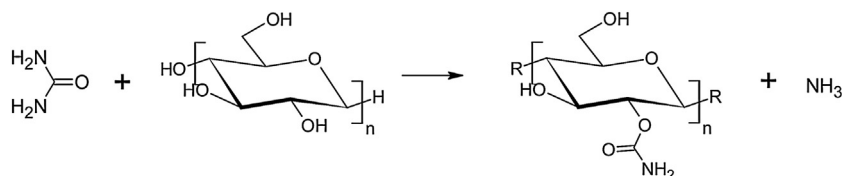


Fig. 1. Carbamation formation by starch and urea.

Table 1

Sample abbreviation, production parameters for wheat starch carbamates and color space values L^* , a^* , and b^* .

Sample	Urea [%] ^a	H ₂ SO ₄ [mmol] ^b	Time [h]	L*	a*	b*
1	10	0	0.5	92.3	−0.2	2.8
2	25	0	0.5	92.0	−0.1	3.1
3	10	2	0.5	88.4	1.1	9.7
4	25	2	0.5	90.9	0.0	5.0
5	10	4	0.5	57.6	5.2	16.5
6	25	4	0.5	89.7	0.3	8.2
7	10	0	2	91.7	−0.3	4.5
8	25	0	2	91.2	−0.2	5.5
9	10	2	2	84.5	2.5	17.2
10	25	2	2	84.4	2.0	16.1
11	10	4	2	54.5	7.3	20.1
12	25	4	2	78.6	3.8	20.6
13	25	4	4	74.2	5.3	23.4

^a % of amount of starch [g].

^b in EtOH.

(urea concentration, catalyst concentration, and heating time), and investigated the effect of DS on film forming ability, molecular structure, microstructure, and thermal properties.

2. Materials and methods

2.1. Materials

Wheat starch was kindly supplied by Lantmännen Reppe AB (Växjö, Sweden) and had an amylose content of 26% determined using size-exclusion chromatography as described below. All reagents (urea, sulfuric acid, phenol, sodium hydroxide, potassium bromide) and solvents (ethanol, DMSO-*d*6) used were of analytical grade and purchased from Merck (Darmstadt, Germany).

2.2. Methods

2.2.1. Preparation of starch carbamates

2.2.1.1. Small-scale preparation of starch carbamates. Wheat starch carbamates were produced according to Khalil et al. (2002). In principle, urea (10 and 25%, calculated on amount of starch) and H₂SO₄ (0, 2, or 4 mmol) were dissolved in 3 mL ethanol, added to 10 g starch, and blended using a mortar. The mix was transferred into a Petri dish, covered with a lid, and heated at 150 °C in an oven under normal pressure for either 30 min or 2 h, and after let cool down to room temperature. The parameters chosen were based on a 2 × 3 × 2 design with 12 samples, plus one extra sample with 25% urea, 4 mmol H₂SO₄, and heated at 150 °C for 4 h. All samples were produced in duplicate.

2.2.1.2. Upscaling of starch carbamate production. The carbamation process was scaled up to produce around 2 kg starch carbamates using five selected test points (samples 6–10, Table 2). The sample mixtures were then spread thinly on baking sheets and heated to 150 °C for 30 min or 2 h, respectively, in an oven at normal pressure. The thickness of the starch-urea mixture was slightly greater than for the small-scale samples described above.

2.2.2. Optical properties of starch carbamates

Color of the starch carbamates was measured using a Minolta chromameter (CR-310). Reflectance and color values were expressed as L^* (whiteness/darkness), a^* (redness/greenness), and b^* (yellowness/blueness).

2.2.3. Light microscopy for characterization of starch granule shape and size

Images of the unwashed starch granules were taken using a light microscope (Nikon Eclipse Ni-U microscope, Tokyo, Japan) equipped with a Nikon DS-Fi2-U3 Camera (Nikon Corporation, Japan). Crystallinity of starch granules was detected using polarized light.

2.2.4. Washing of starch carbamates to remove unreacted urea

Starch carbamates were washed in water:ethanol (30:70, v/v) to remove non-reacted urea. For this, 20 mL water:ethanol were added to 3 g sample and the mixture was stirred overnight. The starch slurry was then centrifuged at 1000g for 10 min and the supernatant discarded. This washing step was repeated several times until no urea was detectable in the EtOH extract. The starch carbamates were subsequently washed with 95% EtOH in water, filtered through a 45 μm filter, and dried in an oven at 35 °C for 48 h.

2.2.5. Water solubility of starch carbamates

Solubility of starch carbamates was measured according to Khalil et al. (2002) with minor modifications. In brief, 100 mg starch were suspended in 5 mL water and gently stirred for 2 h at 50 °C, allowed to cool to room temperature, and centrifuged at 2000g for 10 min. An aliquot of 25 μL of the supernatant was diluted to 5 mL and starch content was determined using the phenol-sulfuric method by reading absorbance at 485 nm (DuBois, Gilles, Hamilton, Rebers, & Smith, 1956). The starch content was calculated using glucose concentration measured colorimetrically.

2.2.6. Molecular characterization by size-exclusion chromatography on CL-2B

Size distribution of starches was measured using size-exclusion chromatography on a Sepharose CL-2B column, as described elsewhere (Menzel et al., 2013).

2.2.7. Nitrogen content of starch carbamates

The amount of nitrogen in the washed and dried starch carbamates was determined by the Kjeldahl method using a 2020 Digestor and 2400 Kjeltac Analyzer Unit (FOSS Analytical A/S Hilleröd, Denmark) (Nordic Committee on Food Analysis, 1976).

2.2.8. FTIR analysis

Fourier transform infrared (FTIR) spectra were obtained for solid samples on a Perkin Elmer Spectrum 100 FTIR system in a scanning range of 400–4000 cm^{−1} for four scans at a spectral resolution of 4 cm^{−1}. A portion of the sample was ground together with KBr and pressed into tablets. The average of four spectra was used to increase the signal to noise ratio.

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