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Thermal properties and stability of cassava starch films cross-linked with tetraethylene glycol diacrylate

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Abstract

The thermal stability of starch cross-linked with tetraethylene glycol diacrylate was studied under nitrogen atmosphere by thermogravimetry (TG) and infrared spectroscopy (FTIR). The cross-linking reaction was confirmed by the increase in intensity of the absorption band at ca. 3330 cm^{-1} indicating the reinforcement of hydrogen bonds and the appearance of a new band at 1726 cm^{-1} associated with the carbonyl group of the cross-linking agent. After cross-linking the solubility of starch in water decreased to the range 9%–16%. The thermogravimetric curves of pure and cross-linked starches showed an initial stage of degradation (up to ca. 150 °C) associated with the loss of water. The main stage of degradation occurred in the range 250–400 °C corresponding to ca. 60%–70% mass loss. The activation energy (E) for the degradation process increased from 145 kJ mol^{-1} (pure starch) to 195 kJ mol^{-1} and 198 kJ mol^{-1} for starch treated for 60 min by UV (30 °C) and at 90 °C, suggesting high stability after cross-linking. A higher value (240 kJ mol^{-1}) was obtained for starch treated by UV for 120 min. The main volatile products determined by FTIR which correspond to hydrocarbons and carbonyl groups are apparently associated with the scission of weak bonds in the chain (probably branched groups) and the scission of stronger bonds (glycosidic linkages), respectively.

Keywords: Cassava starch; Thermal stability; Activation energy; Cross-linking effect

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1. Introduction

Starch is a renewable biopolymer of amylose (linear α-(1 → 4) linked D-glucopyranosyl residues) and amylopectin (composed of linear chains of (1 → 4)-α-D-glucose residues connected through (1 → 6)-α-linkages). Starch has gained considerable interest because it is inexpensive, available in large amounts from different sources and has provided a viable alternative to replace synthetic polymers, decreasing in consequence the environmental pollution [1–3]. Because starch itself is very brittle and has poor mechanical properties most of the applications have been associated with starch modifications including plasticisers, cross-linking agents and blending with other polymers [4–9]. Depending on the process, a higher temperature is needed affecting, in consequence, the thermal stability of the starch. Many polysaccharides have been analysed in terms of their thermal degradation, mainly considering the mechanism

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of chain breakdown, volatile products and activation energy. For example, cellulose and cellulose derivatives have been extensively studied in terms of the processes of degradation, reaction products of degradation and pyrolysis under different conditions [10–13]. Sodium hyaluronate, xanthan and methylcellulose were compared considering the kinetic (activation energy) and thermogravimetric parameters associated with the thermal degradation under nitrogen atmosphere [14]. The activation energy was also analysed for the process of thermal degradation of chitosan and a mercaptan derivative of chitosan under nitrogen and air atmospheres [15]. In general, depolymerisation processes (including thermal degradation) for polysaccharides are commonly described by equations which consider that the chain scission of the glycosidic linkage follows a pseudo first-order reaction [16,17]. However, the mechanism of thermal degradation of polysaccharides, such as starch, depends on the products of degradation, formation of radicals and temperature for the chain breakdown.

Considering that cassava starch is produced in large quantities and, in general, has been used as a raw material for different processes in food industries, in this study the thermal stability of starch films was evaluated before and after cross-linking with tetraethylene glycol diacrylate by two different methods: (i) UV irradiation at 30 °C and (ii) thermally at 90 °C. Kinetic and thermogravimetric parameters and volatile products for the thermal degradation of starch were analysed.

2. Experimental

2.1. Materials

The cassava starch (named Polisize55) was kindly donated by Poliamidos (Curitiba, Brazil) and was used as received. The percentage of amylose determined by titration was 16%. The molecular weight determined by light scattering was in the range 10^6 g mol^{-1}–10^8 g mol^{-1} depending on the solvent and temperature. Tetraethylene glycol diacrylate was purchased from Aldrich (St. Louis, USA) and was used without further purification.

2.2. Film preparation

Cassava starch films were prepared by casting from solutions in the concentration 1.5% (m/v) in distilled water. For both cross-linking methods the tetraethylene glycol diacrylate was added in the proportion of 5% (m/v) to the starch solution. In the UV cross-linking, first the starch solution was heated to 75 °C–80 °C (gelatinization temperature) for 40 min under stirring, cooled to room temperature and the cross-linking agent was added. The samples were kept in the absence of light during the irradiation process ($\lambda = 230$ nm) which was carried out for periods of 30 min, 60 min and 120 min at 30 °C. For the thermal process (90 °C) starch and the cross-linking agent were mixed before the starch gelatinization. All the solutions after irradiation or heating (90 °C) were spread on Teflon plates for solvent evaporation (casting process) to obtain the films. The films were stored in a desiccator under vacuum until analysis.

2.3. Thermogravimetry

The thermogravimetric analysis was performed with a Shimadzu (TGA-50) instrument. The measurements were performed at heating rates of 10 °C min^{-1}, 20 °C min^{-1} and 40 °C min^{-1} under nitrogen (50 cm^3 min^{-1}). The thermogravimetric data were analysed by the Ozawa's method [18] and the activation energy (E) was determined from the slope of the plot of $\log \beta$ (heating rate) versus $1/T$ as defined by the Arrhenius equation [19].

2.4. Infrared spectroscopy

The FTIR spectra of pure and cross-linked starch samples (films) were obtained in KBr support with a 16 PC Perkin Elmer instrument with a resolution of 4 cm^{-1}, in the range 4000 cm^{-1}–400 cm^{-1}. For the analysis of gas products, samples of ca. 150 mg were submitted to degradation in a tubular oven connected to the infrared equipment. The samples were heated under nitrogen (50 cm^3 min^{-1}) at a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Cross-linked starch characterization

Fig. 1 shows the FTIR spectra of starch before and after thermal cross-linking considering two wave number regions: (I) 4000 cm^{-1}–2400 cm^{-1} and (II) 2000 cm^{-1}–400 cm^{-1}. In region I, spectrum A (dotted line) shows a broad band at 3600 cm^{-1}–3000 cm^{-1}, in which the main absorption band (3530 cm^{-1}) is related to free hydroxyl groups of pure starch. The shoulder at ca. 3300 cm^{-1}–3200 cm^{-1} indicates the presence of intramolecular hydrogen bonding for this system. The absorption band at ca. 2930 cm^{-1} refers to the C–H stretching present in the starch. In the spectra related to cross-linked starch (B–D) a shift of the main absorption band to ca. 3330 cm^{-1} is observed indicating the reinforcement of hydrogen bonds with covalent bonds (ether linkages). In the region 2000 cm^{-1}–400 cm^{-1}, the main absorption bands related to non-cross-linked