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Thermoplastic starch modification during melt processing: Hydrolysis catalyzed by carboxylic acids

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Abstract

The melt processing of glycerol-plasticized starch in the presence of non-volatile carboxylic acids resulted in a progressive loss of its molar mass, because the residual moisture in the mixture induced an acid-catalyzed hydrolysis of the ether linkages in its polysaccharide chains. The study of this reaction provided a useful means of adjusting its course and thus of preparing starch materials with controlled properties.

Keywords: Thermoplastic starch; Biodegradable polymers; Melt processing

1. Introduction

The chemical modification of starch constitutes a very broad field covering numerous different reactions and products, particularly in the realm of food chemistry (Tomasik & Schilling, 2004, & Tomasik , Fiedorowicz, & Para, 2004). Most of these modifications are carried out in aqueous media in which starch readily swells. The study of thermoplastic starch (TPS) has received increasing attention in the last decade, because of the growing interest in materials from renewable resources, which are often biodegradable (Stepto, 2003). The processing of TPS always requires a plasticizer (mostly glycerol) and is frequently carried out in the presence of a second polymer (e.g. polyvinyl alcohol, ethylene-vinyl alcohol copolymers and natural rubber) in order to improve certain specific properties of the ensuing blends. The need of a more appropriate additive to modify the physical performance of TPS, led us to study the controlled degradation of starch as a means of preparing a fully compatible alternative. Several applications for TPS, such as injection molding and thermal forming require low viscosity of the melt in order to allow the complete mold filling. Applications such as TPS hot melts also require high tack which can be improved by decreasing the DP of starches. At the same time, these lower DP starches constitute interesting materials as such.

This study describes the use of ascorbic and citric acid as catalysts for the controlled hydrolytic cleavage of the starch macromolecules, carried out by melt processing in bulk in the presence of added glycerol and the equilibrium moisture content. Both acids had been employed previously to promote starch hydrolysis, but within an entirely different context, viz. food processing in the presence of a large proportion of water (Hirashima, Takahashi, & Nishinari, 2004; Sriburi, & Hill, 2000, & Sriburi, Hill, & Mitchell, 1999).

2. Experimental

2.1. Materials

The starch used in this investigation was a native commercial cornstarch (Amidex 3001®), kindly provided by Corn Products Brazil, containing 28% of amylose. Its average moisture content was 11 wt%. Reagent grade ascorbic acid, citric acid and twice-distilled glycerol were used as received.

2.2. Processing

Starch (with its equilibrium moisture), glycerol and the carboxylic acid were pre-mixed in polyethylene bags until a homogeneous system was obtained. These mixtures were processed in a Haake Rheomix 600 batch mixer equipped with roller rotors. Each starch/glycerol/acid mixture was loaded into the mixer chamber preheated at 160 °C. The rotors were

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operated at 50 rpm and the mixing time was varied from 6 to 15 min. Each sample was prepared in duplicate to validate the procedure and showed good reproducibility.

2.3. High-performance size exclusion chromatography (HPSEC)

These analyses were conducted at 35 °C with a high-performance liquid chromatograph equipped with a refractive index detector, as previously described (Carvalho, Zambon, Curvelo, & Gandini, 2003). The three linear columns used for SEC separation were Ultrahydrogel (7.8 mm i.d. × 300 mm length) and the eluent was a 0.1 M $NaNO_3$ solution adjusted at pH 11.5 with NaOH. The standards utilized were Pullulan (polymaltotriose) with molar masses of 180; 738; 5800; 12,200; 23,700; 48,000; 100,000; 212,000; 380,000 and 1,600,000, respectively. The starch samples were dissolved in a 1 M sodium hydroxide solution by stirring for 2 h, and the ensuing solutions filtered through a 1 μm glass fiber filter before injection.

2.4. Differential scanning calorimetry (DSC)

DSC analyses were run on a Shimadzu DSC 50 instrument, using a nitrogen flow rate of 30 mL/min and a heating rate of 10 °C/min from room temperature to 260 °C. The samples were cut in circular disks of the same inner diameter as the aluminum pans (6 mm diameterx1.5 mm thickness) and their mass varied between 42 and 47 mg.

2.5. X-ray diffraction

The conditioned samples were analyzed using a Rigaku X-ray diffractometer with nickel-filtered Cu K_α rays ($\lambda = 1.542$ Å). The rotating-anode generator was operated at 50 kV and 100 mA. The 2θ range went from 3 to 40°, scanned at 1.0 deg/min.

2.6. Water uptake

Circular samples (11 mm in diameter and 2.5 mm thick), previously dried overnight at 105 °C, were weighed and conditioned in hermetic containers kept at 25 ± 2 °C and 97% relative humidity (RH), using a saturated K_2SO_4 solution, as specified in ASTM E 104. The amount of water absorbed by the samples was determined by weighing them periodically until a constant value was attained. The water uptake (W) of the samples was calculated as follows

$$W(\%) = \frac{M_t - M_0}{M_0} 100 \qquad (1)$$

where M_t is the mass at time t and M_0 the dry mass before exposure to the moist air.

2.7. Acid titration

The amount of free carboxylic acid remaining in the processed samples was determined by stirring a weighed amount of each one of them (10 g) in distilled water (100 ml) for four hours and then titrating the ensuing suspension with 0.1 N NaOH. The reference for the calculations was the titration of the sample processed without any added acid. Given the specific pKa values of the two acids used, only one COOH group of ascorbic acid, but all three groups of citric acid were titrated.

3. Results and discussion

The compositions and the processing conditions of the thermoplastic starch mixtures prepared in this study are given in Table 1. The three relevant variables here were the carboxylic acid used, its content and the mixing time.

During processing, the melt viscosity decreased appreciably, as shown in Fig. 1, and the ensuing molten materials displayed an increased tack (adhesive character). The evolution of the torque as a function of the processing time and the composition (Fig. 1) clearly suggested that the molecular weight of the samples containing a carboxylic acid was reduced, whereas the blank sample was much less affected. The extent of this decrease depended on: (i) the amount of acid added, (ii) the acid used and (iii) the processing time. These observations indicated that the reaction responsible for the macromolecular fragmentation was not due to mechanical shearing, but, instead, to the specific action of the added carboxylic acid. All the processed materials were clear and colorless and showed no sign of degradation other than chain scission.

The rheological observations were confirmed by the HPSEC results, which are quantified in Table 2 and displayed in part in Figs. 2–4.

The reproducibility of the HPSEC analyses was consistently satisfactory, as shown in the typical example of sample 10 (Table 2). Fig. 2 (see also Table 2) clearly shows that the presence of a carboxylic acid induced a severe decrease in the starch molar mass, compared with the sample without added

Table 1
Composition of the TPS/acid mixtures and mixing times

Sample #	Carboxylic acid	Content of carboxylic acid (wt%)	Mixing time (min)
0	None	–	6
1	Ascorbic acid	0.5	6
2		1.0	6
3		1.0	9
4		1.0	12
5		1.0	15
6		1.5	6
7		2.0	6
8		3.0	6
9	Citric acid	1	6
10		2	6

All samples contained 30 wt% of glycerol relative to dry starch.

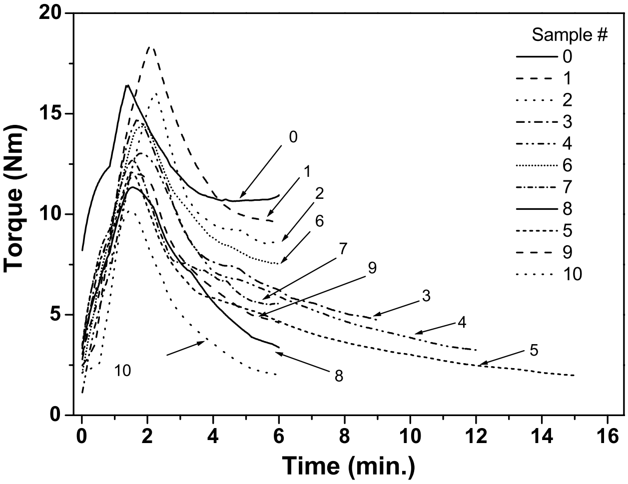

Fig. 1. Evolution of the torque as a function of the processing time for the samples in Table 1.

acid and that, moreover, citric acid (pKa1 = 3.14) was more efficient in this role than ascorbic acid (pKa1 = 4.10) under the same processing conditions, because of its greater strength. Fig. 3 (see also Table 2) shows that major chain scissions took place during the first nine minutes of processing in the presence of ascorbic acid, but that thereafter they became less pronounced. Finally, Fig. 4 (see also Table 2) shows that the higher the ascorbic acid concentration in the mixtures, the more severe was the molecular mass decrease for the same processing time.

In all these systems, the decrease in average chain length was accompanied by a narrowing of the molar mass distribution, indicated by the decrease in the M_w/M_n ratio, suggesting that the longer (or the more branched) starch macromolecules were more susceptible to scission.

The DSC thermograms of the processed materials gave similar melting features and did not show any trend in the melting temperature or in the heat of fusion with respect to the three variables studied. The average values for melting temperature, T_m and for melting enthalpy, ΔH_m were, respectively, 170 ± 12.6 °C and 120 ± 5.9 J/g. The scatter in the data arose mostly from the well-known difficulty in reproducing DSC with starch or TPS and not from substantial differences among samples.

The kinetics of moisture uptake were followed with each sample and displayed the same behavior, irrespective of the sample composition and processing time. The samples exposed to a 52% humidity atmosphere reached a constant mass within about 140 h and their mass gain was 11.5 ± 0.3%, whereas their exposure to a 97% humidity air required about 100 h for equilibration and gave a mass gain of 63 ± 3%. Clearly, neither the molar mass decrease, nor the presence of the acid affected the moisture affinity of these materials, which was exclusively determined by their constant starch/glycerol composition. A change in the water absorption characteristics will probably be affected only for a very drastic reduction in molar mass.

The X-ray diffraction spectra of all the processed samples displayed remarkably similar features typical from glycerol-plasticized TPS. These results confirmed the DSC evidence suggesting that the nature and extent of the starch crystalline microphases in these materials had not been affected by the addition of the carboxylic acid or the processing time, within

Table 2
HPSEC-based molar masses of samples in Table 1

Sample #	Molar mass (g/mol)		M_w/M_n
	$10^5\ M_n$	$10^6\ M_w$	
0	1.41	1.64	11.6
1	1.29	1.30	10.0
2	1.22	1.24	10.1
5	0.87	0.773	8.9
6	0.76	0.677	8.9
7	0.56	0.377	6.7
3	0.54	0.370	6.8
4	0.53	0.341	6.4
8	0.46	0.248	5.4
9	0.41	0.190	4.7
10	0.25	0.079	3.1
10	0.25	0.078	3.1

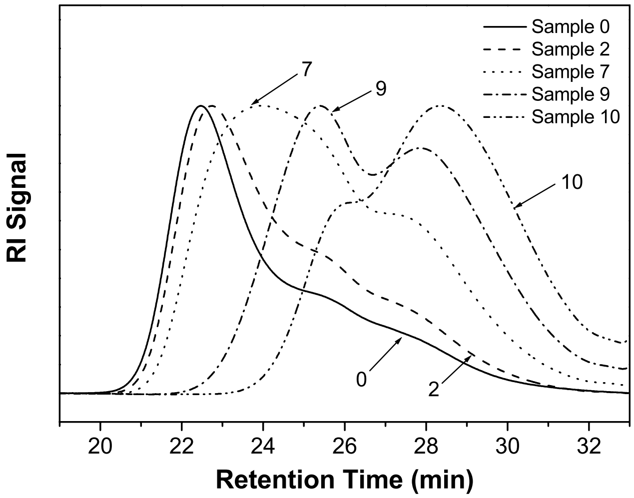

Fig. 2. HPSEC tracings comparing the effect of the two acids (see Table 1).

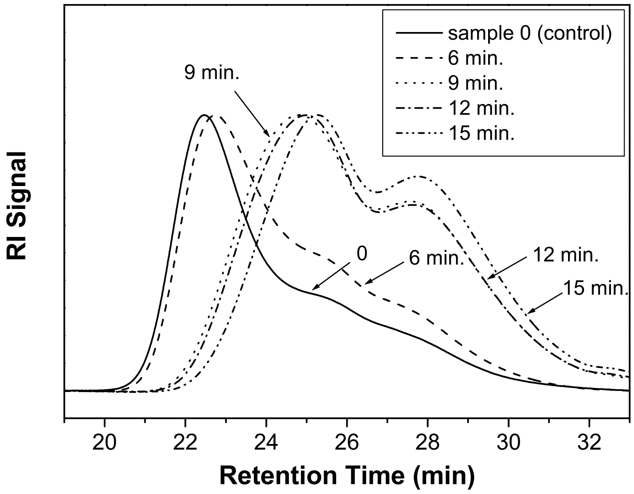

Fig. 3. HPSEC tracings showing the effect of the processing time for samples containing 1% of ascorbic acid (see Table 1).

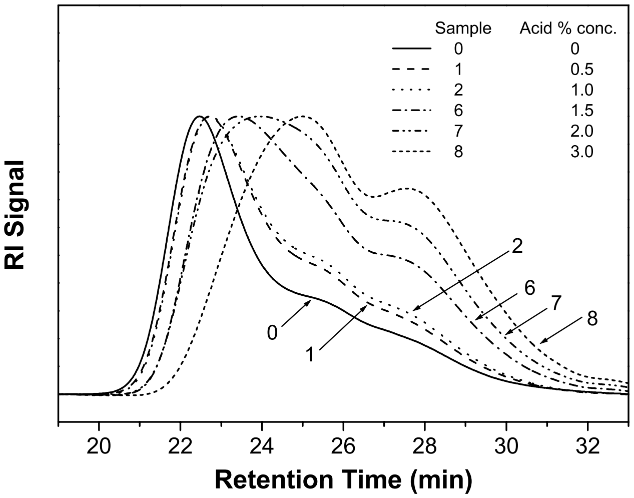

Fig. 4. HPSEC tracings showing the effect of ascorbic acid concentration (see Table 1).

the limits of the experimental conditions adopted in this investigation. Notwithstanding the fact that the molar mass decrease caused a decrease in the melt viscosity and an increase in tack, such intrinsic properties as crystallization and water absorption were not changed appreciably.

The titration of the free acid remaining in the samples revealed that in all instances most of the added acid was present as such after processing, i.e. that its consumption in other reactions was not a relevant issue under the present experimental context.

The evidence gathered in this study points unequivocally to the occurrence of random hydrolytic scission of the starch macromolecules induced by the residual moisture and catalyzed by the presence of the carboxylic acid (Tomasik & Schilling, 2004, & Tomasik et al., 2004). The extent of this reaction, reflected by the actual decrease in the average starch chain length, depended, as expected, on the acid strength, its concentration and the duration of the process. As for the essential role of water, its large excess in the starch samples ($>$ 10 wt%) at the beginning of each processing experiment, insured the occurrence of the hydrolysis, i.e. the water concentration was not a limiting factor for this reaction. However, as the treatment proceeded, moisture was released from the samples and it appears that, in the present conditions, its residual concentration after about ten minutes became low enough to become a limiting factor to the rate of hydrolysis, as indicated by the modest extent of chain scission after that time (Fig. 3).

If all the ether moieties of the starch macromolecules had the same probability of being cleaved, the longer polymer chains would be more attainable and thus the reaction would yield a product with a narrower molar mass distribution, as indeed observed. The occurrence of this partial hydrolytic degradation did not affect the recrystallization process following the processing, as suggested by both the DSC results and the X-ray evidence.

4. Conclusions

The possibility of fine-tuning the decrease of the molar mass of starch polysaccharides over a wide range of values by the judicious use of small amounts of carboxylic acids, as additives during melt processing, constitutes a novel and promising way of preparing biodegradable TPS materials with controlled properties. Moreover, the use of non-volatile and *non-toxic* acids as catalysts, provides the additional advantages of health safety and food compatibility in, e.g. packaging applications for these materials. Work is in progress to extend the range of these additives in order to widen the scope of this original approach.

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