



Thermoplastic Starch Modification by Reactive Extrusion: Hydrolysis with Organic Acids During Processing

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Abstract: The melt processing of glycerol-plasticized starch in the presence of a carboxylic acid resulted in a progressive loss of its molecular weight because the residual moisture in the mixture induced an acid-catalyzed hydrolysis of the ether linkages in the polysaccharide chains. The study of this reaction can lead to a useful means of adjusting its course and thus of preparing starch materials with controlled properties.

Keywords: Starch; Plasticization; Hydrolysis; Carboxylic acids

Introduction

Starch can be chemically modified into several derivatives, through oxidation, esterification, etherification and hydrolysis. These derivatives are usually manufactured by reacting starch in an aqueous suspension or by direct treatment of the dry starch granules followed by heating at temperatures up to 150°C [1]. A very attractive process for the synthesis of polymers or their chemical modification is reactive extrusion. Extrusion is commonly used in starch processing for its physical modifications [2], such as the desestructuration, which is an alternative to gelatinization processes that require a large amount of water. Controlled hydrolysis of starch as a thermoplastic material can find numerous applications, such as adhesives, coatings, or for thermoplastic starch modifications and the hydrolyzed starches can be used for further chemical modifications.

Thermoplastic starch (TPS) is obtained by processing native starch in the presence of plasticizers or water, under conditions of high shear and temperatures, to give amorphous thermoplastic materials [3]. A very convenient way to study the reactive extrusion of starch is by processing it, in the presence of plasticizers, in an intensive batch mixer rheometer, which provides accurate melt viscosity measurements during the actual processing.

As we showed in a previous paper, shear-induced macromolecular scissions during the melt processing of TPS can cause appreciable changes in its molecular weight and molecular weight distribution [4]. This problem has been the subject of several studies, which were devoted to minimize it, especially because it can cause losses in the mechanical properties of the final material [5,6].

However, it can be argued that a *controlled* decrease in the average molecular weight of starch could be beneficial in certain contexts. The aim of the present study was precisely to investigate a way to master this phenomenon by melt processing starch-glycerol plasticized compositions in a controlled manner, using carboxylic acids, such as ascorbic acid and salicylic acid as catalysts for the *controlled hydrolysis* of starch.

Experimental

Materials

The starch used in this investigation was conventional cornstarch containing 28% of amylose. Its average moisture content was 11% w/w. Commercial reagent grade ascorbic acid, salicylic acid and twice distilled glycerol were used as received. All samples contained 30 wt % of glycerol on a starch dry basis.

Processing

Starch, 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 pre-heated mixer chamber preheated at 160°C. The rotors were operated at 50 rpm and the mixing time was varied from 6 to 15 min. The compositions of these materials and the processing conditions are shown in Table 1.

High-performance size exclusion chromatography.

HPSEC analyses were conducted at 35°C with a high-performance liquid chromatograph equipped with a refractive index detector, as previously described [4]. The three linear columns used for SEC separation were Ultrahydrogel (7.8 mm i.d. x 300 mm length) and the eluent was a 0.1 M NaNO₃ solution adjusted at pH 11.5. The standards utilized were Pullulan (polymaltotriose) with molar masses of 180; 738; 5,800; 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 2h),

which were then filtered through a 1µm glass fiber filter.

Results and Discussion

The compositions and the processing conditions for all the thermoplastic starch mixtures prepared are presented in Table 1. The two relevant variables here were the carboxylic acid content and the mixing time.

Table 1. Compositions of the TPS/acid mixtures and mixing times. All samples presented 30 wt % glycerol on starch dry basis.

Experiment #	Carboxylic acid	Content of Carboxylic acid (wt %)	Mixing time (min)
0	-	-	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

During processing, the melt viscosity decreased appreciably, as shown in Figure 1a, and the molten materials displayed increased tack or adhesive character. The evolution of torque as a function of processing time and composition (Figure 1a), clearly suggested that the molecular weight of the starch samples containing a carboxylic acid was affected and the extent of its decrease depended on both the amount of added acid and the processing time, whereas the blank sample was much less affected. These observations indicated that the reaction responsible for the macromolecular fragmentation was not due to mechanical shearing, but, instead to acid-catalyzed hydrolysis.

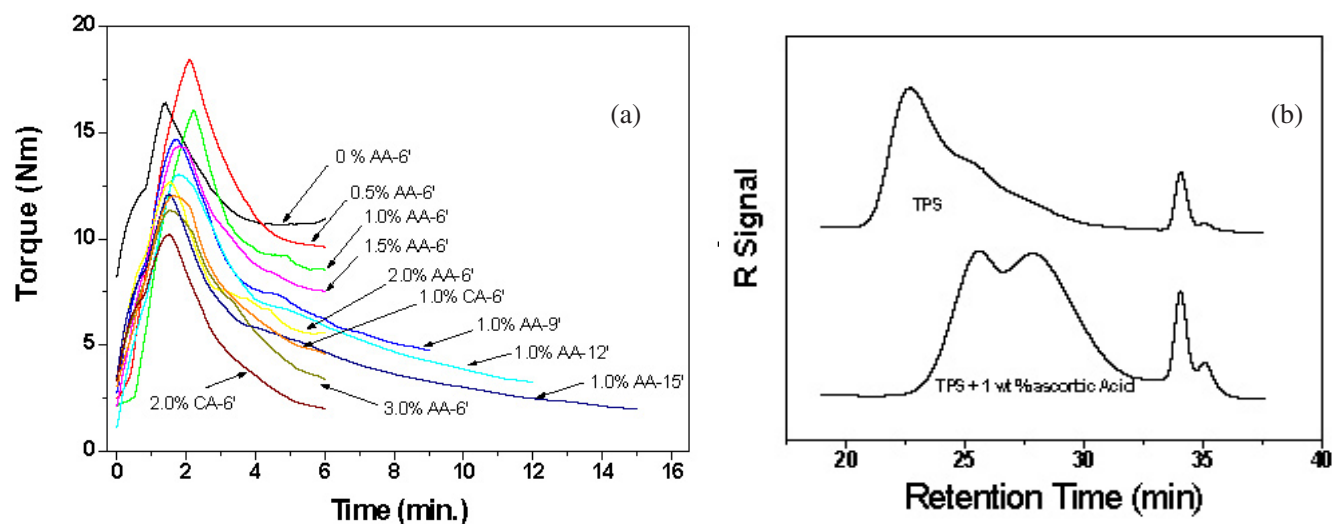


Figure 1. (a) Plots of torque versus processing time for the various samples TPS mixtures with ascorbic and citric acid. (b) Chromatography profiles of TPS without and with 1 wt % of ascorbic acid, processed at 150°C for 6 min. All samples were prepared with 30 wt % glycerol.

These viscosity-related results were confirmed by direct molecular weight measurements which showed a progressive decrease.

Thus, for example, the effect 1 wt% of ascorbic acid on the starch molecular weight and its distribution was quite severe. As calculated from Figure 1b \overline{M} and \overline{M} values of the processed plasticized starch *without* added acid were 160,000 and 770,000, respectively, whereas with 1 wt% ascorbic acid they had decreased to 41,000 and 130,000, respectively.

After processing, the ensuing mixtures were clear and colorless, i.e. with no signs of degradation or oxidation, other than the chain scission.

Conclusion

Melt hydrolysis of thermoplastic starch, arising from the residual moisture and catalyzed by carboxylic acids, was successfully conducted in an intensive batch mixer. No oxidation or other type of degradation accompanied this process. Work is in progress to study this process in more details in order to optimize its exploitation and to prepare starch-based materials with properties controlled by the molecular weight of the polysaccharide.

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