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Material Properties

Evaluation of enzymatic degradation based on the quantification of glucose in thermoplastic starch and its characterization by mechanical and morphological properties and NMR measurements

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ABSTRACT

Biodegradable polymers represent a promising solution to the environmental problem of plastic waste disposal. Among the candidate polymers, starch, a low-cost natural polymer, can be processed as a thermoplastic. In this work, thermoplastic starch containing glycerol (20, 30 or 40 wt%) was prepared by extrusion. The mechanical properties of the blends were assessed by tensile stress at break, elongation at break and Young's modulus. Nuclear magnetic resonance (NMR), through proton spin-lattice relaxation (T_1 H) measurements, was used to understand the molecular dynamic of the samples. The morphology of the films was assessed by electron scanning microscopy (SEM). The susceptibility to enzymatic degradation was assessed in films incubated with α -amylase in acetate buffer. The loss of mass was determined after 1, 2, 3, 6, 9, 12 and 24 h of enzymatic digestion. The results obtained showed that all of the mechanical properties were improved by the addition of 20% glycerol, but decreased with higher concentrations of glycerol. The amount of free glucose released into the solution during digestion was quantified using a commercial glucose kit. Starch containing 40% glycerol degraded faster than the other blends, because it facilitated the efficiency of the gelatinization process and also the phase separation, as shown by the proton spin-lattice relaxation time. The amount of glucose released was directly proportional to the glycerol content of the samples. These results suggested a short lifetime for this blend, which is in agreement with the values of the T_1 H relaxation parameter that suggests a decrease of the average molecular weight.

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1. Introduction

The indiscriminate discarding of plastics has increased and the waste does not degrade rapidly because synthetic polymers are inert to the immediate attack of microorganisms [1]. The use of biodegradable polymers provides

a promising solution to this problem and this theme has been an objective of many researches. A biodegradable polymer is defined as a plastic that is degraded primarily by the action of naturally occurring microorganisms, such as bacteria, fungi and algae [2].

In particular, starch and its derivatives could provide a substitute for synthetic polymers in industrial processes [3]. Starch, a low-cost, biodegradable polymer [3], is abundant in plants, where it is stored in granule form and functions as an energy reserve. Starch is composed of two polymers, amylose and amylopectin, both of which

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contain α -D-glucose units. In amylose, the linkage between units is (1 \rightarrow 4) with the ring oxygen atoms all on the same side, whereas in amylopectin approximately one residue in every 20 also has a (1 \rightarrow 6) linkage that forms branch points. The hydrophilicity of these polymers is responsible for their incompatibility with most hydrophobic polymers [1,4–9].

Amylose is linear and its composition is around 25% in the starch. Amylopectin is branched and has a higher molar mass than amylose; it is found to be around 75% in the starch composition. The linear portion of amylopectin forms double helical structures stabilized by hydrogen bonds between the hydroxyl groups and forms the crystalline region of starch granules. The amorphous region is composed of amylose and amylopectin chains [6,8–11].

Starch is currently used in the development of thermoplastic materials [3,12,13]. The addition of starch to synthetic polymers enhances the microbiological degradation of the blend. Starch can be processed as a thermoplastic and also can be incorporated as a filler in traditional plastics or associated with plasticizers [14]. However, starch is not a thermoplastic in its natural state and must therefore be plasticized. Thermoplastic starch (TPS) is obtained by the disruption and plasticization of native starch with the help of plasticizing agents (glycerol, water and other polyols) [15,16]. The addition of plasticizers to polymers can modify the final characteristics and improve the processing conditions. Glycerol is particularly useful for this purpose.

The biodegradation of plastics can be determined by various methods, ranging from a simple assessment of the degradation of plastics discarded directly in landfills that contain a large variety of microorganisms to tests in synthetic cultures with well-defined microorganisms [16]. Biodegradation is initiated by the action of bacteria or fungi on the polymer surface, with these microorganisms secreting an extracellular depolymerase that degrades the polymer. However, with the exception of the enzymatic biodegradation of collagen and cellulose [17,18], there is considerable debate about the involvement and relevance of enzymatic activity in the biodegradation of modified natural and synthetic polymers.

Starch is highly biodegradable because of its elevated glucosidic bond content that can be cleaved by specific enzymes [1,19]. The main enzyme involved in the degradation of starch is amylase, which is an extracellular protein that hydrolyzes the glycosidic bonds (1, 4) to produce oligosaccharides, with the release of glucose (predominantly), maltose and maltotriose [1,7].

In this work, we examined the mechanical and morphological properties of starch plasticized with different glycerol percentages, and assessed the extent of enzymatic degradation by quantifying the amount of glucose produced during degradation. In addition, the proton spin-lattice relaxation time, determined by nuclear magnetic resonance, was determined because this parameter provides useful information on blend homogeneity, filler dispersity and components interaction [20,21], which will help us to evaluate the samples behavior before enzymatic degradation.

2. Experimental

2.1. Materials

- *Corn starch (Amidex 3001) (A₁)*: Regular corn starch was supplied in powder form by Corn Products Brazil Ingredientes Industriais Ltda. (Jundiá, SP, Brazil) and contained 27 wt% amylose and 73 wt% amylopectin, with a Mw of 486,000 g/mol, 4–6 wt% water content and a gelatinization temperature of 90–95 °C.
- *Glycerol* (lote 58878 from Synth, Diadema, SP, Brazil).
- α -*Amylase* (Termamyl), supplied by Corn Products Brasil.
- *Kit for the enzymatic determination of glucose* (LABORLAB, Guarulhos, SP, Brazil).

2.2. Processing of thermoplastic starch

Starch was mixed with glycerol in a MH-100 homogenizer (Mecanoplast[®]) with a capacity of 2 kg. Initially, the powdered starch was shaken for 3 min at 800 rpm. Liquid glycerol was added to the starch at 1 min intervals, with stirring. Starch and blends containing glycerol were passed through a single screw extruder with a diameter of 25 mm and length of 250 mm and threaded with a compression ratio of 3.5:1. The thermal profile was 110 and 120 °C (zones 1 and 2, respectively) and the screw speed was 200 rpm. Table 1 shows the composition of the formulations.

2.3. Molding

The compositions were compression-molded into sheets (180 mm \times 180 mm \times 1 mm) using a model MA 098 Marconi press (Marconi Equipamentos e Calibração para Laboratórios, Piracicaba, SP, Brazil). The mold containing the sample was initially placed in the press and heated for 5 min without applying any pressure to ensure uniform heat flow through the material. For all of the formulations, the temperature was kept at 100 \pm 5 °C for 5 min at 5 t. The resulting sheets were removed from the press after cooling to room temperature.

2.4. Mechanical properties

Specimens for tensile measurements (ISO 527/ASTM D638 – Type III [22]) were cut from each sheet. The samples were kept at 23 \pm 2 °C and 40% humidity for 24 h before test. The tensile tests were done using an EMIC Universal Testing Machine – DL 2000 Model. Five samples of each blend were strained at a rate of 50 mm min⁻¹ at room temperature, using a grip separation of 115 mm. The

Table 1
Formulation studied in this paper

Formulation	Amount of starch (%)	Amount of glycerin (%)
80S/20G	80	20
70S/30G	70	30
60S/40G	60	40

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