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Extrusion blow molding of a starch–gelatin polymer matrix reinforced with cellulose

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ABSTRACT

This work investigated the possibility of using hydrolyzed corn starch–gelatin as a base matrix and cellulose as reinforcement, to produce containers by extrusion blow molding. First, the compounds were characterized by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) to determine their viscoelastic behavior and thermal stability. The results showed that the most suitable processing temperature should be less than 120 °C to avoid degradation. Furthermore, the addition of cellulose decreased the viscosity of the starch–gelatin polymer matrix allowing the compounds to be processed at temperatures as low as 100 °C. Then, parisons were obtained by extrusion blow molding and presented suitable processing characteristics. Overall, the best containers were found to have 44% higher energy at break and better dimensional stability when cellulose was added.

1. Introduction

Natural polymers processed by extrusion have been investigated for different applications like packaging [1–5]. One readily available natural polymer is starch which is known to behave as a thermoplastic material under specific shear and temperature conditions [6,7]. This is why several investigations were devoted to develop different starch-based products such as extrusion foaming [8–10], compression molding [11–13], injection molding [3,14,15], sheet forming [16–18], and blown films [2,19–21]. In all cases, some additives like water, glycerol, sorbitol, and ethanol, were used to improve melt processability.

However, extrusion blow molding has not been studied yet for starch-based materials because high shear stress lead to degradation (molecular bond break-up) and increasing gelatinization even at low moisture [6,22]. Usually, a polymer can be processed by extrusion blow molding if it has good melt strength, thermal stability, and limited swelling since the parison must withstand its own weight before being captured by the mold [23]. When the mold closes, the parison is cut for air to be injected and parison expansion occurs to be in contact with the mold walls and be cooled [24]. The parison wall thickness determines the thickness of the final part, but other parameters like mold geometry are important where complex relations

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between different forces (gravity, viscosity, elasticity, etc.) are acting on the material itself. Up to now, only synthetic polymers like high density polyethylene, low density polyethylene and polyvinyl chloride have been processed by extrusion blow molding [23,25–28].

To improve the performance of starch under shear and temperature conditions, proteins have been shown to be effective, especially when the material is extruded [29–33]. Also, gelatin was shown to have good film forming capacity as well as good barrier properties, making it useful for packaging applications like sheets or blown films [34–37]. Gelatin was also shown to improve the elongational [30,32,38] and tensile strength [32] of starch when blended. On the other hand, the addition of cellulose was reported to improve the dimensional stability of conventional plastics [39]. In starch-based polymers, it has been shown to increase the mechanical performance (reinforcing effect) of extruded materials [13,40–42]. Lately, it was reported, using acoustic atomic force microscopy, that recycled cellulose addition in starch–gelatin blends can increase the modulus by chemical interaction between OH groups [43]. In the same way, has been reported that mechanical properties of starch–gelatin blends are in function of starch concentration [38].

Based on the information available in the literature, the main objective of this work is to determine if hydrolyzed starch–gelatin polymer blends, with or without cellulose as a reinforcement, can be processed by extrusion blow molding. To do so, the processing conditions (limited degradation and gelatinization) were first estimated using dynamic mechanical analysis and thermogravimetric analysis. Then, from the results obtained, blown containers were successfully produced and characterized in terms of tensile properties.

2. Experimental

Hydrolyzed corn starch–gelatin pellets, with or without 5% cellulose (Whatman®) were processed using a single screw extruder. The cellulose content was limited at 5% to avoid agglomeration and to obtain good tensile characteristics according to previous results reported for the work group for similar materials and same polymer matrix [44,45]. After some preliminary trials, the extruder (L/D ratio of 20:1) was operated at a temperature profile of 35–40–50 °C and 30 rpm to produce the compounds before being pelletized (die diameter = 3 mm). The samples for characterization were produced by compression molding (Carver Mini C press, Wabash, USA), with 2 tons of force for 10 min at 100 °C. The samples were then cut form the plates (115 × 115 × 3 mm) for analysis.

Moisture content was determined using a thermobalance (MX-50) operated at 100 °C to record mass as a function of time.

Dynamic mechanical analysis (DMA) was performed on a TA Instruments RSA3 (New Castle, USA). A three-point bending geometry was used with rectangular samples having dimensions of 40 mm × 25 mm × 1.35 mm. Temperature ramps were performed between 35 and 120 °C at a rate of 2 °C/min. From the data obtained, the storage modulus (E') associated with the elastic properties (stiffness) and the loss modulus (E'') associated with the viscous properties (energy dissipation) were determined [46]. Also, the loss factor or Tan δ, which represents the ratio E''/E', was used (especially the presence of a peak) to characterize the samples.

Thermogravimetric analysis (TGA) was made on a TA instruments Q5000 (New Castle, USA) between 50 and 800 °C at a heating rate of 10 °C/min using platinum crucibles. All the measurements were done in a nitrogen environment.

Extrusion blow molding was carried out on a Vulcano machine (Mexico), with L/D ratio of 20 and a 30 mm vertical die. Screw compression was 17° as the thread angle and the mold shape was a bottle of 500 mL volume. Mold closing and opening, as well as its horizontal displacement, were performed automatically through a control panel.

Scanning electron microscope (Philips X130 ESEM, Eindhoven, Holland) was used to examine blown materials, by an ESEM XL-30 software and micrographs were taken at 1000×.

Finally, the extrusion blow molded specimens were cut to get samples to perform tensile mechanical testing. Measurements were performed following ASTM D638 [47] for films with 10 repetitions using a Texture Analyzer TA-XT2® (Texture Technologies Corp., Scarsdale, NY/Stable MicroSystems, Haslemere, Surrey, UK) with 1 mm/s as the strain rate.

3. Results and discussion

3.1. Thermogravimetric analysis

From the TGA analysis, the derivative of the curves were calculated and presented in Fig. 1. For the hydrolyzed corn starch, degradation mostly occurs around 287 °C, while for cellulose the peak is close to 345 °C. For gelatin, several transitions are observed. The first at 95 °C is associated with water content. The second transition at 285 °C corresponds to long chains breaking, while at 590 °C denaturation occurs. For the starch–gelatin polymer matrix reinforced with cellulose, a peak at 125 °C was associated to the glycerol content in the matrix, while the peaks at 220 °C, 233 °C, and 281 °C were associated to the degradation of, starch, and cellulose, respectively. Finally, gelatin degradation continued up to around 600 °C. The addition of cellulose in a starch–gelatin polymer matrix exhibited a thermal behavior that was previously reported in the literature [12,48]. From these curves, it can be concluded that the most suitable temperature to process the starch–gelatin polymer matrix reinforced with cellulose is less than 120 °C to avoid thermal degradation.

Fig. 2 presents the thermal behavior of the starch–gelatin polymer matrix for the extruded pellets and the parison form. After extrusion, the peak around 233 °C decreased and the thermal stability of the material decreased by about 10 °C for the