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Effect of processing conditions on the physicochemical and structural characteristics of pregelatinised starch–fatty acid–glycerol extrudates☆

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ABSTRACT

The possibility of using physically modified starch in combination with glycerol and fatty acids to produce biodegradable materials with tailor made functional properties was explored. For this purpose pregelatinised starch prepared by drying native maize starch aqueous dispersions in a pilot double drum drier, was extruded in the presence of glycerol with and without the addition of fatty acid potassium salts in a pilot twin screw cooker extruder equipped with a custom built slit die rheometer. The processing conditions employed were: heating at either 80 or 100 °C in all heated sections of the extruder and rotational screw speeds either 80 or 115 or 145 or 210 rpm. The in line melt viscosity measurements showed that the flow behavior of the starch–glycerol systems was significantly influenced by the addition of either myristic or palmitic acids. The examination of physicochemical properties of the extrudates indicated that the addition of fatty acids affected the functionality of starch–glycerol systems. That is, the moisture content, the bulk density and the water solubility index of the fatty acid containing starch–glycerol systems were higher than those of the corresponding control ones whereas the expansion ratio of the fatty acid containing extrudates was lower than that of the control ones. Three point bending tests revealed that the higher the screw speed the lower the modulus of elasticity attained by the samples. Structural studies carried out using X-ray diffraction analysis, indicated that the degree of crystallinity of starch–glycerol extrudates was lower than that of their starch–glycerol–fatty acid counterparts. The experimental results are discussed in the light of conformational changes occurring during extrusion due to starch–fatty acid interactions and their impact on the structural changes which have taken place in the starch matrix of the extrudates.

1. Introduction

Starch the major reserve polysaccharide of plants has been explored over the years as an alternative source for the development and production of biodegradable thermoplastic materials which can substitute for petroleum based plastics. It is fairly cheap as a raw material, abundant in nature and renewable. Starch is found in nature in the form of granules comprised of a biopolymer mixture of an essentially linear homopolymer of $(1 \rightarrow 4)$-linked α-D-glucopyranose named amylose and its highly $(1 \rightarrow 6)$-branched α-D-glucopyranose named amylopectin. Amylose is unique among the biopolymers having the ability to interact with polar and non polar compounds such as fatty acids, fatty alcohols, monoglycerides and others, to form helical inclusion complexes.

The potential development of starch based plastics involves a better understanding of the starch transformation using conventional polymer processing operations such as extrusion cooking. During extrusion of starch, the combination of shear, temperature and plasticisers makes possible the production of a molten thermoplastic material by disruption of the native crystalline granular structure. This material is susceptible to aging and starch retrogradation (crystallisation) rendering it unsuitable for use in packaging applications since its mechanical properties change with time and the extrudate becomes extremely rigid and easy to fracture.

When starch is extruded in the presence of lipids then, the crystallinity exhibited by these extrudates is due to amylose–lipid complex formation rather than starch retrogradation and for this reason is much more rapid and extensive than the crystallinity exhibited by starch extrudates contained no lipids which is solely due to starch retrogradation (Bhatnagar & Hanna, 1997; Colonna & Mercier, 1983; Mercier, Charbonniere, Grebaut, & de la Gueriviere,1980; Meuser, van Lengerich & Stender,1985; Raphaelides, Arsenoudi, Exarhopoulos & Xu,2010). Thus, starch–lipid interactions during extrusion cooking, in principle, could help in producing biodegradable materials with tailor

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made properties. However, this is not so since starch–lipid extrudates are extremely glassy due to the removal of water from their structure thus to become flexible it might be necessary to add a natural plasticiser such as glycerol to reduce the glass transition temperature. In a previous paper (Raphaelides, Dimitreli, Exarhopoulos, Kokonidis & Tzani, 2011) the effect of adding glycerol to granular normal maize starch, during extrusion, in the presence or absence of fatty acids was explored. It was shown that the control samples (contained no fatty acid) were much more rigid and glassy than the fatty acid containing samples. Moreover they exhibited different XRD patterns, that is the controls showed a mixture of V-type (amylose–fatty acid helical complexes) and B-type (retrograded amylose double helices) crystallinity whereas the fatty acid contained extrudates exhibited only V-type crystallinity. It was concluded that glycerol participated in a different way in the extrudate matrix of the control samples and the fatty acid containing samples.

The aim of the present study was to extend further the work reported above and to investigate what would be the effect of glycerol added to non granular starch prior to extrusion cooking in the presence or absence of fatty acids. To the best of our knowledge, the processing behavior and the functionality of pregelatinised starch–fatty acid extrudates plasticised with glycerol has not been investigated so far. Thus the study of their structural and functional characteristics will help to assess whether they exhibit technological characteristics suitable for industrial applications.

2. Materials and methods

2.1. Materials

Native maize starch was purchased from Nestlé Hellas, Greece. The apparent amylose and the total amylose contents of the starch were 21.5 ± 0.6% and 26.0 ± 0.3 respectively (determined using the method of Morrison & Laignelet, 1983). Myristic acid (purity > 98.5%) was purchased from Fluka, palmitic acid (purity > 95%) was purchased from Sigma Chemical Co and glycerol (purity > 90%) was obtained from Carlo Erba. Salts used to prepare solutions of known water activity were: LiCl (>99%), $MgCl_2{\cdot}6H_2O$ (>99%), K_2CO_3 (>99%), $Mg(NO_3)_2$ (>99%) purchased from Fluka, NaCl (>99%) obtained from Merck and KNO_3 (>99%) from Riedel-de Haën. All other reagents used were of analytical grade.

The starch was pregelatinised by drying a 10% aqueous dispersion of native starch by means of a pilot double drum drier (G.M.F. GOUDA, The Netherlands) heated at 160 °C. The rotational speed of the drums was 4 rpm. The formed dried sheet of gelatinised starch was comminuted by means of a high speed rotating cutter and the powder formed (9.7% moisture content) was stored in plastic barrels before being used in extrusion.

2.2. Extrusion conditions

Extrusion cooking was performed in a pilot co-rotating intermeshing twin screw extruder, Clextral model BC45, France. The barrel was 550 mm in length and 110 mm in diameter, with two heating zones heated with induction heaters and cooled with circulating tap water. At the barrel's end, a slit die rheometer was attached through a transition attachment. Both the attachment and the rheometer were custom made in a local workshop. The length of the attachment was 120 mm and that of the rheometer was 250 mm. The rectangular cross section of the slit die was 20 mm wide and the height was 1.5 mm. Both the attachment and the rheometer were equipped with centrally placed type K thermocouples. The rheometer was also equipped with high temperature Gefran, Italy (SP830 M series), pressure transducers, flush mounted along the length of the die with pressure range of 0–20 and 0–10 MPa, respectively.

All process variables, i.e. temperatures measured at every zone of the barrel, the neck and the rheometer, pressures from the pressure transducers, rotational speed of the screws, current and power input from the extruder's motor were continuously logged, in real time mode, on a PC through a data acquisition card constructed and programmed at our electronics workshop. The solid feed was transferred from a hopper, mounted on the extruder, through a controlled speed screw feeder to an opening located in the entrance of the barrel whereas the liquid feed was transported to the opening of the barrel's entrance by means of a metering diaphragm pump from a temperature controlled jacketed vessel equipped with a variable speed stirrer.

2.3. Experimental design

In all experimental runs the extruder was operated in the starve fed mode. The degree of fill, expressed as g of feed material/rpm of screw speed (van Lengerich, 1989) was kept constant at 1.53. As for the solid/liquid ratio of the feed material, it was 2:1 in all experimental runs.

Three series of samples were obtained from the respective experimental runs. That is,

1st run: the feed material was a mixture of starch (65%), water (14%) and glycerol (21%) (control)
2nd run: the feed material was a mixture of starch (65%), glycerol (20.3%), water (13.6%) and of myristic acid (1.1%).
3rd run: the feed material was a mixture of starch (65%), glycerol (20.3%), water (13.6%) and of palmitic acid (1.1%).

The experimental scheme applied in all three runs was the following

Sample	Throughput rate (solid + liquid) (kg/h)	Extrusion processing temperature (°C)	Screw speed (rpm)
1	7.35	80	80
2	10.83	80	115
3	13.69	80	145
4	19.46	80	210
5	7.35	100	80
6	10.83	100	115
7	13.69	100	145
8	19.46	100	210

In all heated sections of the extruder system and for each sample, the selected temperatures were the same. The feed solution (either with or without fatty acid) was kept, under continuous stirring (50 rpm), throughout the experiments at 60 °C to avoid lipid micelle formation in the feed vessel.

2.4. In line viscosity determination of the extrudate melts

Melt viscosity determination was based on the process parameters recorded on line throughout the course of the extrusion processing runs. The rheological equations used were obtained from Han's (1976) analysis.

That is, the shear stress was calculated from the equation

$$\tau = \frac{\Delta P \times H}{2 \times L}\ (\mathrm{Pa}) \quad (1)$$

where ΔP is the pressure drop between the pressure sensors, H is the height of the slit (mm) and L is the distance between the pressure sensors (mm).