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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 → 4)-linked α-D-glucopyranose named amylose and its highly (1 → 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 Nestlè 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

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

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).

The wall apparent shear rate was calculated from the equation

$$\dot{\gamma}_{\text{app}} = \frac{3Q}{2B \times h^2}\,(\text{s}^{-1}) \tag{2}$$

where Q is the volumetric flow rate in the slit (mm^3/s), B is the width of the slit (mm) and h is the ½ of the slit height (mm).

The corrected shear rate was calculated according to the method of Rabinowitsch (Han, 1976) as follows

$$\dot{\gamma}_{\text{corr}} = \frac{(2n + 1/3n)}{(3Q/(2B \times h^2))}\,(\text{s}^{-1}) \tag{3}$$

where n is the flow behavior index, the rest of the symbols are the same as in Eq. (2).

The apparent viscosity was calculated from the power law equation

$$\eta = m \times \dot{\gamma}_{\text{corr}}^{n-1}\,(\text{Pa s}) \tag{4}$$

where m is the consistency index.

All samples after preparation and prior to their examination were stored for eight days at room temperature so that their moisture content to be equilibrated. Preliminary studies showed that this period of time was quite sufficient for sample stabilization as far as their functional characteristics are concerned.

2.5. Specific mechanical energy (SME)

The extruder was driven by a DC motor powered from 3-phase mains through controlled rectifier of thyristor for speed regulation. The SME provided by the motor of the extruder during the extrusion cooking process was calculated using the following equation:

$$\text{SME} = \text{ME} - \text{TE} = \frac{(V \times I) - (I^2 \times R)}{m}\,(\text{Wh kg}^{-1}) \tag{5}$$

where ME is the mechanical energy provided by the motor to the extruder, TE is the thermal loss due to electrical resistance in the motor (Joule effect), V is the voltage applied to the armature of the motor (Volts), I is the current (Amperes) and m is the feed rate supplied to the extruder (kg/h).Since, $(V - \text{IR})$ is proportional to the screw speed, it can be measured from the speed setting signal. The current signal was taken from the meter. Both signals were at mains potential, therefore were fed to the computer connected to the extruder, through opto-coupler for insulation and $V - F$, $F - V$ converter signal accuracy.

2.6. Moisture content

It was gravimetrically determined by heating the samples at 130 °C for 90 min.

2.7. Bulk density

It was determined using a volume displacement technique as follows: In a preweighed graduated cylinder, capacity 250 mL, 140 mL of n-hexane were added and the cylinder was reweighed. An approximately 12 cm in length of weighed extrudate sample was fully submerged inside the cylinder and by means of a positive displacement mechanical pipette the displaced volume of the n-hexane was carefully transferred to a dry preweighed beaker and the beaker was again weighed. Since the density of n-hexane is known to be 655 kg/m^3, the volume of the displaced n-hexane can be easily and accurately calculated.

2.8. Expansion ratio

The determination of the cross sectional area of the samples was quite difficult due to irregularities most of them exhibited on their surface. Hence, it was decided to use the following technique: The length of the samples was accurately measured using a digital vernier caliper. From bulk density determination the volume of the sample was known. Thus, dividing the volume by the length, the average cross sectional area of the sample was obtained. The expansion ratio was calculated by dividing the cross sectional area of the samples by the cross sectional area of the slit die.

2.9. Water solubility index (WSI)

WSI, defined as the water soluble fraction of the extrudate expressed as percentage of dry sample and being a measure of the dispersibility of the material was measured by the method of Anderson, Conway, Pfeifer, and Griffin (1969).

2.10. Adsorption isotherms

Extrudate samples were dried in a vacuum oven at 50 °C for at least 24 h, till constant weight. Quantities (~0.5 g) of the dried samples, contained in preweighed polypropylene dishes, were weighed in an analytical balance and placed over saturated (at 40 °C) salt solutions of known relative humidity values in hermetically sealed glass containers (capacity 800 mL). Then, the containers were stored in a thermostatically controlled chamber at 30 °C. The dishes were weighed, at regular time intervals, till constant weight. It was found that equilibrium was achieved after a week. The adsorption experiments were replicated three times. The adsorption isotherms were drawn using as coordinates the parameters, percentage relative humidity and water content i.e. the weight difference of the sample at the beginning of the storage period at a certain relative humidity environment and after the equilibrium in this environment was achieved, over the initial weight of the dried sample.

2.11. Modulus of elasticity and rheological glass transition temperature

Extrudate samples were cut into strips of dimensions 36 mm × 10 mm × 3 mm and were measured in a DMA rheometer Bohlin CVOR 150 (Malvern, UK), operated in the oscillatory mode under constant frequency 0.1 Hz, constant stress 150 Pa and programmed heating rate of 5 °C/min. The strain in all samples examined ranged from 10×10^{-7} to 10×10^{-5} which was well within the linear viscoelastic region. The parameters measured were the storage modulus G' and tanδ in relation to the temperature of heating. Glass transition temperature was determined from the position of tanδ peak observed for most extrudates.

2.12. Three-point bending test

Extrudate samples cut into strips were measured in an Instron UTM, table model 1140 (Instron, UK), equipped with a 50 kg maximum load force cell and operated in compression mode through a custom made software. A set of three point bending accessory was attached to the measuring unit of the instrument. The sample was held on two stationary bending supports 85 mm apart while being displaced at a central axis by the bending probe attached to the moving crosshead traveling at a speed of 0.083 mm/s. The final displacement was 10% of the sample thickness. The test was employed to determine Young's modulus of elasticity (E) using the following equation (Steffe, 1996):

$$E = \frac{Fa^3}{4d \times b \times h^3} \tag{6}$$

where a is the length between the stationary beams (supports), b is the width of the sample, h is the thickness of the sample and d is the displacement.

2.13. X-ray diffraction

Extrudate samples were immersed in liquid nitrogen and immediately were pulverised by means of a pestle and a mortar. The powder obtained was passed through a sieve with an aperture of 800 μm. X-ray powder diffraction measurements were carried out using a PANalytical X'Pert Pro diffractometer (Panalytical, Netherlands) with a Cu $\mathrm{K\alpha_1}$ radiation ($\lambda = 1.5405980$ Å). The diffractometer was operated in reflection mode at 45 kV and 40 mA. A divergence slit of 1°, an antiscatter slit of 2° and a receiving slit of 0.4 mm were used. Measurements were taken between 6 and 35° (2θ) with a step size of 0.04° and a scan speed of 0.008°/s.

For the determination of the relative crystallinity the data were normalised from 9 to 30° (2θ) and the background was determined using the X'Pert HighScore PANalytical software. The crystallinity index (X_c) was calculated according to the following equation (Stribeck, 2007):

$$X_c = \frac{I_{cr}}{I_{am} + I_{cr}} \tag{7}$$

where I_{cr} is the integrated area between the crystalline reflections and the amorphous halo and I_{am} the integrated area between the amorphous halo and the baseline. Crystallite size was determined according to Scherrer's formula (Brundle, Evans, & Wilson, 1992):

$$L \approx \frac{\lambda}{\mathrm{FWHM} \times \cos\theta} \tag{8}$$

where L is the crystallite size in Å, λ is the wavelength and FWHM is the Full Width at Half-Maximum.

3. Results and discussion

The use of pregelatinised starch as a raw material aimed at facilitating the interaction of amylose with the fatty acids during extrusion. The residence time of the feed material inside the extruder's barrel is fairly short (25–100 s) thus by using already gelatinised starch saves time, normally needed for native starch granule gelatinisation, to utilise it for speeding up the amylose–fatty acid interaction. Another asset is the use of lower processing temperatures than usually required for short time gelatinisation of starch which is beneficial to the quality attributes of the extrudates. In all extrusion experiments the quantity of fatty acids used was calculated to be 5% in excess to that needed to fully saturate the available amylose helices (Karkalas & Raphaelides, 1986), provided that all molecules of apparent amylose would be in position to interact freely with the fatty acid molecules. The fatty acids were added to starch as potassium soap aqueous solution in order their molecules to be in their most active form, i.e. as monomers. These precautions were taken since the available water in the starch system was limited and it was imperative to secure the best possible dispersibility of the fatty acid anions so to achieve the maximum degree of interaction between the starch molecules and the fatty acid anions.

3.1. Flow behavior of pregelatinised starch–fatty acid–glycerol extrudate melts

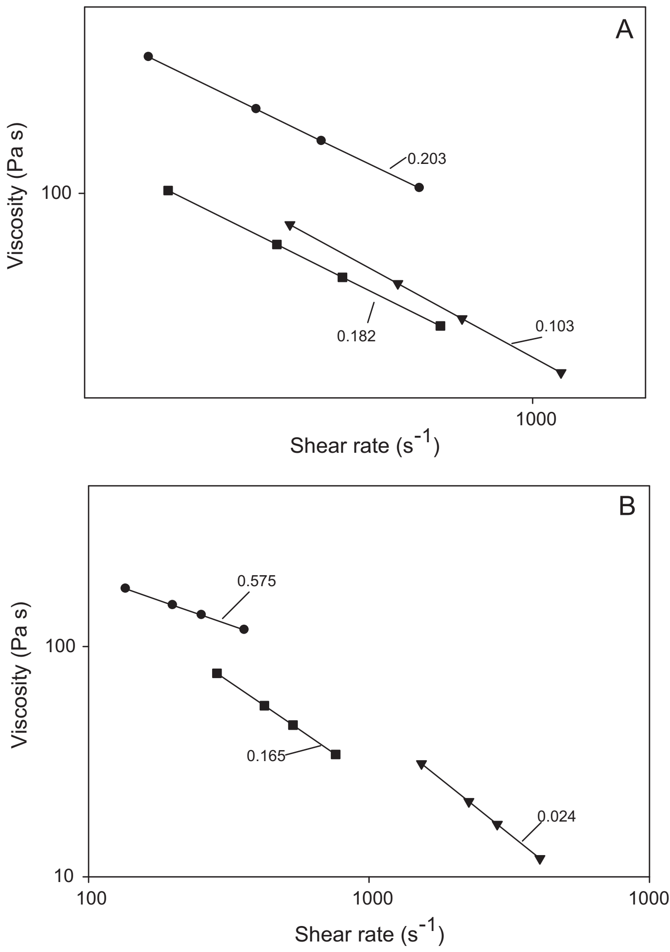

Fig. 1. Effect of heating temperature on the flow behavior of pregelatinised starch–fatty acid–glycerol extrudate melts. ●, control sample (no fatty acid added); ■, sample with added myristic acid; ▼, sample with added palmitic acid. (A and B) Heating temperatures of 80 and 100 °C, respectively. Numbers attached to the flow curves denote the flow behavior index of the individual curve.

Fig. 1 shows the changes taken place in flow behavior of the extrudate melt as influenced by the presence of fatty acids. It can be seen that the viscosity was dramatically reduced and the pseudoplastic character of the melt became even more pronounced due to the addition of the fatty acids. This can be attributed to the conformational transitions occurred to amylose molecules during complexation when the amylose molecular conformation changes from random coil to helix causing the reduction of viscosity (Karkalas & Raphaelides, 1986). The higher viscosity exhibited by the starch–palmitate system in comparison to that of the starch–myristate one could be attributed to the stiffer nature of amylose–palmitate helices in comparison to amylose–myristate helices. It is known (Karkalas & Raphaelides, 1986) that saturated, with fatty acid molecules, amylose helices accommodate in their cavity fewer palmitate ions than myristate ones per unit length because palmitate molecules are longer than the myristates. Thus, amylose–palmitate helices have fewer kinks than amylose–myristate ones and their conformation becomes stiffer whereas amylose–myristate helices are more flexible. Hence, the hydrodynamic volume of the amylose–palmitate helices retained its size during flow even at high shear rates to a greater degree, than that of the amylose–myristate ones did. It has to be noted that the pseudoplasticity (expressed by the flow behavior index) of starch–fatty acid extrudates was much higher (low index values) than that of the control especially at the higher extrusion temperature employed. This should be attributed to the orderly arrangement of the elongated amylose helices at high shear rates causing the steep reduction in viscosity.

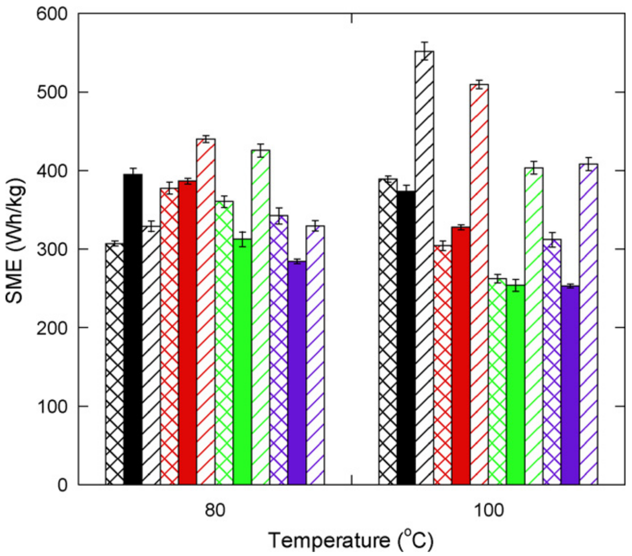

Fig. 2. Effect of screw speed and barrel temperature on the specific mechanical energy of pregelatinised starch–fatty acid–glycerol extrudates. Crossed line columns: control samples (no fatty acid added); filled columns: samples with added myristic acid; inclined line columns: sample with added palmitic acid. Column colors denote screw speeds: black, 80 rpm; red, 115 rpm; green, 145 rpm; blue, 210 rpm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. *Specific mechanical energy (SME)*

The amount of SME input during the extrusion process is considered as an indication of the severity of the structural modifications the feed material undergoes during extrusion. Fig. 2 shows the SME input at the specified barrel temperatures during extrusion of pregelatinised starch–glycerol systems with or without added fatty acids. It can be seen that for most of the cases the SME input for lipid containing samples was higher than that of the corresponding controls especially for samples containing palmitic acid. The higher SME values observed for the fatty acid containing samples could be attributed to significant conformational changes occurred to them as previously mentioned which caused the increase in energy consumption during their flow through the extruder's barrel possibly due to elastic forces developed during the amylose–fatty acid complexing process, especially in the case of the samples contained palmitic acid.

3.3. *Functional properties of pregelatinised starch–glycerol–fatty acid extrudates*

As far as the physicochemical parameters of the extrudates are concerned Table 1 shows that the moisture content of fatty acid containing extrudates was higher than the corresponding control ones. This might be due to topological and steric reasons of glycerol participating in the extrudate structure that could hold more efficiently water molecules in the case of the fatty acid containing samples than in the control samples. The bulk densities of the control samples appeared to be similar or lower than those of the fatty acid containing samples whereas the expansion ratio values of the control samples were substantially higher than those of the fatty acid containing samples indicating that a more open structure (i.e. less dense) was formed in the control samples in comparison to those of the fatty acid containing samples whose the more compact structure could be attributed to enhanced elasticity developed during amylose–fatty acid complexation, as previously mentioned, enabling the extrudates to overcome the shearing forces acting on them during extrusion and to retain their cohesiveness. It has been demonstrated (Raphaelides, 1992) that the addition of long chain fatty acids to starch solutions, in quantities sufficient to saturate the available amylose helices, increased the elasticity exhibited by starch systems in 0.01 N KOH aqueous solution, expressed in the form of normal force measurements during steady shear experiments. On the other hand the water solubility index of fatty acid

Table 1
Effect of screw speed and barrel temperature on the physicochemical characteristics of pregelatinised starch–fatty acid–glycerol–extrudates.

Sample	Screw speed (rpm)	Barrel temperature (°C)	Moisture content (%)	Bulk density (kg/m^3)	Expansion ratio	Water solubility index (%)	Crystallite size (Å)
Control	80	80	9.0 ± 0.1	1463 ± 5	2.40 ± 0.1	10.1 ± 0.2	298 ± 15
Starch + myristate			13.7 ± 0.2	1321 ± 2	1.25 ± 0.1	20.8 ± 0.2	164 ± 10
Starch + palmitate			14.4 ± 0.1	1367 ± 2	1.41 ± 0.0	18.7 ± 0.1	205 ± 8
Control		100	8.6 ± 0.3	1422 ± 5	2.03 ± 0.2	8.3 ± 0.2	309 ± 17
Starch + myristate			9.4 ± 0.2	1470 ± 2	1.19 ± 0.1	13.7 ± 0.1	195 ± 8
Starch + palmitate			12.2 ± 0.1	1485 ± 5	1.59 ± 0.2	14.2 ± 0.3	266 ± 12
Control	115	80	10.1 ± 0.3	1425 ± 3	2.82 ± 0.2	14.5 ± 0.2	252 ± 17
Starch + myristate			10.9 ± 0.2	1358 ± 4	1.62 ± 0.1	14.4 ± 0.2	222 ± 7
Starch + palmitate			16.1 ± 0.3	1390 ± 2	1.37 ± 0.0	16.9 ± 0.2	89 ± 5
Control		100	9.2 ± 0.2	1007 ± 8	5.32 ± 0.3	11.9 ± 0.1	296 ± 21
Starch + myristate			10.9 ± 0.1	1408 ± 4	1.31 ± 0.0	14.3 ± 0.2	247 ± 8
Starch + palmitate			12.1 ± 0.2	1482 ± 3	1.36 ± 0.0	13.4 ± 0.1	228 ± 6
Control	145	80	11.4 ± 0.2	1219 ± 1	2.92 ± 0.1	16.1 ± 0.3	288 ± 15
Starch + myristate			13.8 ± 0.1	1324 ± 6	1.49 ± 0.1	16.7 ± 0.3	239 ± 9
Starch + palmitate			15.8 ± 0.2	1334 ± 5	1.55 ± 0.2	15.8 ± 0.2	154 ± 8
Control		100	10.2 ± 0.2	1073 ± 4	2.18 ± 0.1	13.0 ± 0.1	251 ± 14
Starch + myristate			12.9 ± 0.1	1313 ± 7	1.43 ± 0.0	17.0 ± 0.2	215 ± 8
Starch + palmitate			11.7 ± 0.3	1387 ± 2	1.83 ± 0.1	14.7 ± 0.2	244 ± 8
Control	210	80	11.8 ± 0.1	830 ± 5	3.46 ± 0.3	17.0 ± 0.4	250 ± 15
Starch + myristate			12.5 ± 0.1	1336 ± 7	1.34 ± 0.0	18.4 ± 0.1	254 ± 9
Starch + palmitate			14.3 ± 0.2	1440 ± 5	1.42 ± 0.0	16.3 ± 0.3	258 ± 2
Control		100	9.4 ± 0.4	874 ± 5	3.65 ± 0.1	11.2 ± 0.3	241 ± 12
Starch + myristate			12.7 ± 0.1	1307 ± 3	1.41 ± 0,1	16.9 ± 0.2	253 ± 7
Starch + palmitate			10.9 ± 0.2	1337 ± 5	1.66 ± 0.0	10.5 ± 0.3	267 ± 8

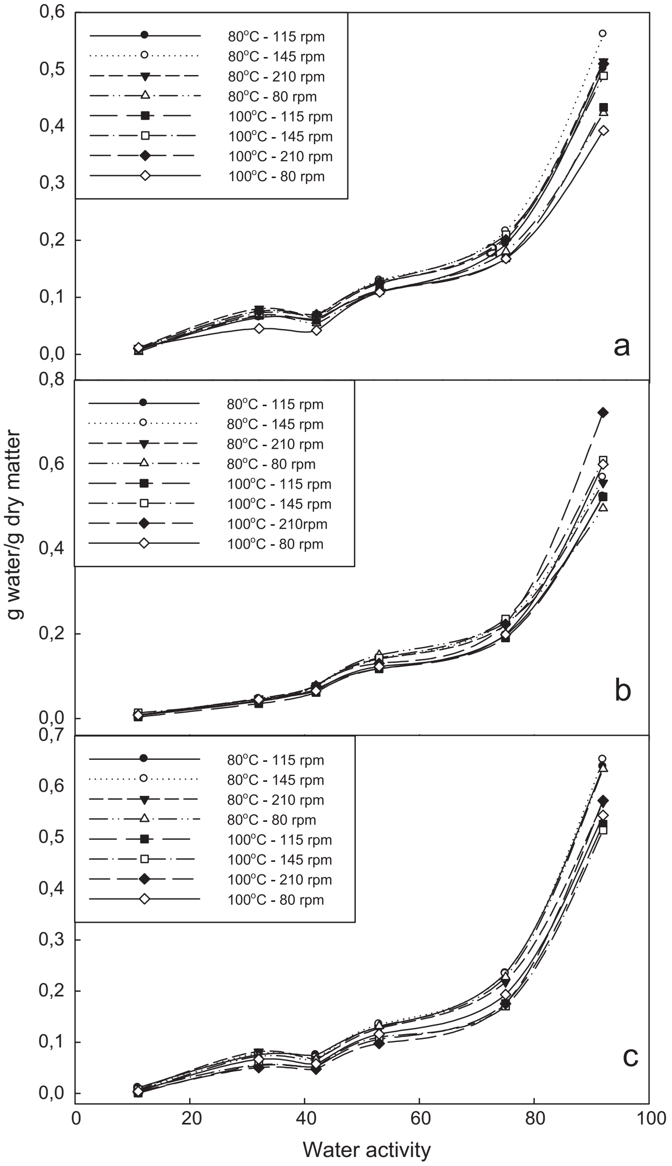

Fig. 3. Adsorption isotherms of pregelatinised starch–fatty acid–glycerol extrudates extruded at barrel temperatures: 80–100 °C and screw speeds 80–115–145–210 rpm. (a) Control samples (no fatty acid added). (b) Samples with added myristic acid. (c) Samples with added palmitic acid.

containing samples was rather higher than that of the control ones indicating that soluble material, possibly free glycerol, could be leached out more easily in the case of the former than of the latter due to steric reasons. That is, in the case of the control samples, glycerol molecules were more evenly distributed in the starch matrix in which either participated or were trapped more effectively than in the case of fatty acid containing samples where the amylose–fatty acid helical complexes formed crystallites from which glycerol was excluded thus it was less evenly distributed in the starch matrix and it could behave more independently.

3.4. *Adsorption isotherms*

Fig. 3 shows all isotherms obtained for the three sets of extrudate samples i.e. the control (a), the myristic acid (b) and the palmitic acid (c) containing ones. The shape of all curves appears to be bimodal i.e. for low relative humidity values (below 40%) limited moisture adsorption was observed up to approximately 40% relative humidity whereas at higher relative humidity values the adsorption capacity of the extrudates was progressing as the relative humidity was rising. It is noteworthy that at 92% relative humidity the adsorption capacity of the fatty acid containing samples was substantially higher than that of the corresponding control ones and this is in agreement with the previous statement that the fatty acid containing samples are more hydrophilic than the control samples. Similar shape of isotherms was also observed in the case of native maize starch–fatty acid–glycerol extrudate systems (Raphaelides et al., 2011). Attempts were made to employ the sorption isotherm GAB model to describe the isotherms, however it was found that one of GAB parameters had negative values for all isotherms examined thus it was rejected because of physical impossibility.

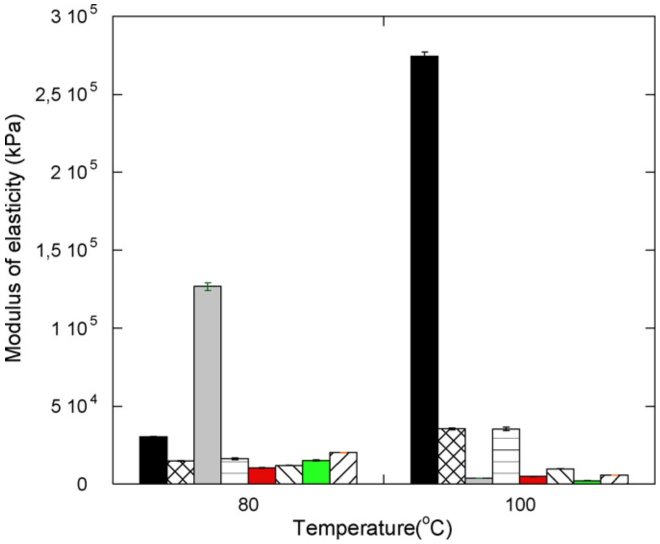

Fig. 4. Effect of screw speed and barrel temperature on the modulus of elasticity of pregelatinised starch–fatty acid–glycerol extrudates. Filled columns, control samples (no fatty acid added); inclined line columns, samples with added palmitic acid. Column colors denote screw speeds: black, 80 rpm; gray, 115 rpm; red, 145 rpm; green, 210 rpm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.5. *Three point bending*

As far as the rigidity, expressed as Young's modulus values, exhibited by the extrudates is concerned, Fig. 4 shows that control samples extruded at relatively low rotational screw speed i.e. 80 rpm appeared to be rigid compared with their palmitic acid containing counterparts which all of them were extremely flexible.

3.6. *Thermomechanical analysis*

Dynamic mechanical testing of starch extrudates under programmed heating confirmed the results previously reported concerning the three point bending test. That is, all the control samples appeared to be more rigid than their fatty acid containing corresponding samples. Nevertheless, the glass transition temperature (T_g) values of all extrudates were similar and barrel temperature depended. Thus, samples extruded at 80 °C regardless of whether they contained fatty acid or not showed T_g values ranged from 50 to 80 °C while those extruded at 100 °C exhibited T_g values ranged from 30 to 43 °C. This differentiation looks awkward and it is the opposite of what it would have been expected since the moisture content of the samples extruded at 100 °C was in general rather lower than that of the samples extruded at 80 °C (Table 1). It seems that glycerol played a more effective role as a plasticiser

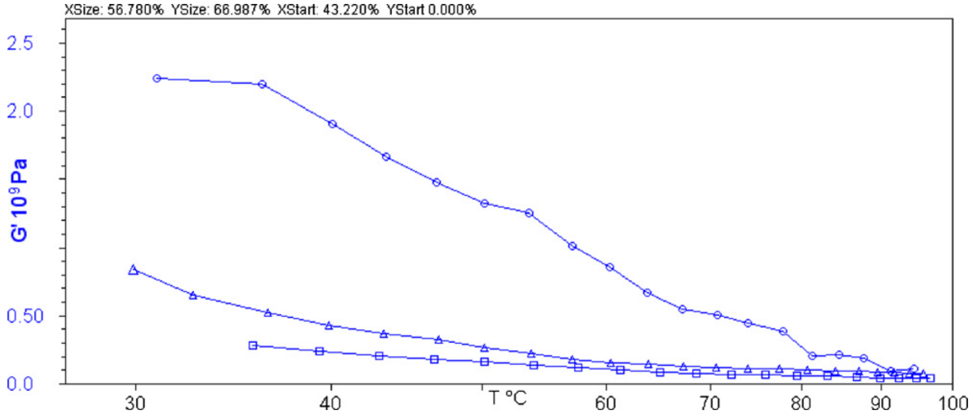

Fig. 5. Storage modulus (G') vs barrel temperature of pregelatinised starch–glycerol systems extruded with the addition of fatty acids or without (control). Symbols: ○, control; □, myristic acid; △, palmitic acid. Frequency of oscillation, 0.1 Hz; stress applied, 150 Pa; heating rate, 5 °C/min.

to the starch systems extruded at 100 °C than to those extruded at 80 °C. Fig. 5 shows typical storage modulus (G') vs temperature curves of samples with or without added fatty acids. It can be seen that the G' values of the control sample are higher than those of the samples contained myristic or palmitic acids.

3.7. X-ray diffraction

XRD analysis revealed the structural modifications undergone the pregelatinised starch–glycerol extrudates because of the addition of fatty acids. Fig. 6 shows typical XRD patterns of the extrudates where it can be seen the amorphous pattern of pregelatinised starch as well as the patterns of the samples containing fatty acids which are of the characteristic V-type with its well known peak at 19.7° (2θ) attributed to the amylose–fatty acid complexes and that of the control which exhibits apart from the characteristic peak at 19.7° corresponded to complex formation of amylose with endogenous lipids naturally present in maize starch, another peak at 16.9° attributed to the B-type pattern of retrograded amylose on aging (van Soest & Knooren, 1997). The results indicate that since the crystallinity exhibited by the starch matrix is almost solely due to amylose, then all available amylose molecules of the extrudates were crystallised either because of retrogradation on aging, forming double helices (B-type crystallinity) or because of complexation with fatty acids, forming single helices (V-type crystallinity). Moreover, it has been reported (Soest, Hulleman, de Wit, & Vliegenthart, 1996) that the formation of small amounts of B-type crystallinity increased the stiffness of extruded starch plasticised with glycerol, which explains the findings previously mentioned that the control samples appeared to be more rigid than the samples containing fatty acids.

As for the relative crystallinity exhibited by the extrudates, Fig. 7 reveals that the fatty acid containing samples were significantly more crystalline than the control ones and this reflects the effect of glycerol's presence in the starch matrix which contributed to its modification depending on the amylose's state in the matrix i.e. whether it was complexed with fatty acids or not. Determination of crystallite size showed (Table 1) that the crystallites of fatty acid containing extrudates had in general smaller size than the control ones. The amylose–fatty acid interactions taken place during extrusion cooking caused rapid formation of crystallites made of amylose–fatty acid helices with the result the structure of the starch matrix was quickly organised in a controlled and stable fashion with crystallites of small size. On the other hand in the control samples, most of the crystallites were formed after extrusion and during aging which is a rather slow process with the result the

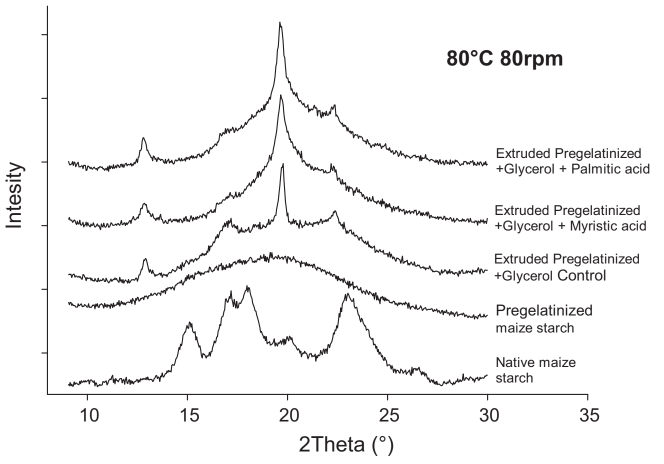

Fig. 6. X-ray diffraction patterns of pregelatinised maize starch extruded with the addition of glycerol and fatty acids or without at 80 °C barrel temperature and at 80 rpm screw speed.

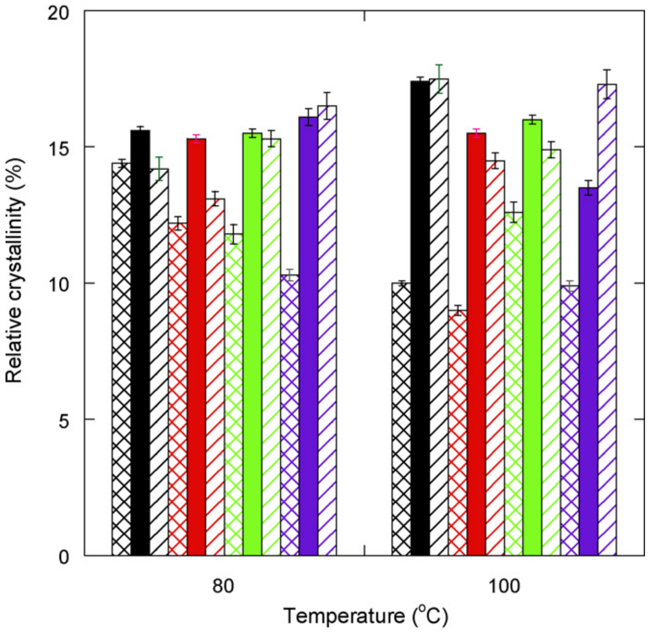

Fig. 7. Effect of screw speed and barrel temperature on the relative crystallinity of starch–fatty acid–glycerol extrudates. Symbols are the same as in Fig. 2.

crystallites which mainly consist of retrograded amylose helices to acquire bigger size than their fatty acid containing counterparts.

4. Conclusion

The present work revealed that the combined effect of fatty acid and glycerol addition to gelatinised maize starch systems during extrusion cooking caused significant changes in the structural characteristics of the extrudates which mainly influenced their mechanical properties. The results from the various physicochemical parameters studied, indicated that the starch matrix was considerably modified because of the presence of glycerol and the amylose–fatty acid complexes. It appears that glycerol molecules were more uniformly distributed in the starch system which did not contain added lipids whereas in the case of the lipids added to the system there was a different structural organisation possibly with patches rich in glycerol and others mainly occupied by the amylose–fatty acid crystallites formed. These changes could lead to products with tailor made functional properties suitable to be potentially utilised as biodegradable materials.

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