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Structural investigation and thermal stability of new extruded wheat flour based polymeric materials

Nathalie Leblanc[a,*], Redouan Saiah[b], Eric Beucher[c], Richard Gattin[a], Michel Castandet[a], Jean-Marc Saiter[b]

[a] *Laboratoire Génie des Matériaux (LGMA), Esitpa, Rue Grande, BP 607, 27 106 Val de Reuil Cedex, France*

[b] *Laboratoire «Polymères, Biopolymères et Membranes», Unité CNRS 6522, équipe L'ECAP, Avenue de l'Université, BP 12, 76 801 Saint Etienne du Rouvray Cedex, France*

[c] *Centre Régional d'Innovation et de Transfert de technologie Analyses et Surface, Site industriel des Jonquets, 2 chemin du Roy, 27400 Louviers, France*

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Abstract

In this study, we compare physical properties of wheat starch and wheat-flour based materials. The comparison has been done using thermogravimetric, calorimetric, X-ray diffraction, mechanic and morphologic experiments conducted on a series of wheat-flour extruded materials. The wheat flour used here can be understood as a by-product of the farm-produce wheat flour. All data obtained by means of these experimental methods allow us to conclude that, basically no significant difference exists between our wheat-flour based and wheat-starch based materials. Only one clear difference occurs for the strain to break value which decreases by about 30% for wheat-flour based materials.

Keywords: Cereal flours; Biodegradable material; Thermoplastics; Extrusion; SEM; Thermogravimetry; DSC; X-ray diffraction

1. Introduction

Looking back over the four last decades, we may without any doubt claim that the use of plastic materials has increased drastically such that today the existence of plastic waste becomes one of the most urgent problems to solve in many countries. Do plastics exhibit more or less risk for the health of the human and mammal population and create further environmental problems? Many studies are performed, but whatever their results, it is clear that in the very near future it will be of prime importance to have substitution materials. To find these new materials, many different ways can be explored as described in Fig. 1, which depicts four categories of biodegradable polymers.

The first one concerns natural polymers, derived from renewable raw materials. In their native state, these polymers are biodegradable. Nevertheless, their stability is not constant and depends on many parameters difficult to control. In this group, we may distinguish proteins and hydrocarbonate molecules coming from plants. The most known material derived from these polymers is caoutchouc. It concerns principally polyosides and their derivatives, i.e. cellulose and starch. When starch is incorporated at low concentrations (6–15%) in traditional plastic, biofragmentable plastic is produced. Starch can equally give thermoplastic materials in specific conditions, exhibiting properties close to polystyrene ones, but remains water-sensitive. Among these materials, some have shown very promising hope (Miller & Krochta, 1997; Petersen et al.,1999; Savary, Colonna, & Della Valle, 1993), as for instance biodegradable market bags and golf tees produced from cornstarch, or bags produced from paprika.

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[*] Corresponding author. Tel.: +33232597071; fax: +33232596621. *E-mail address:* nleblanc@esitpa.org (N. Leblanc).

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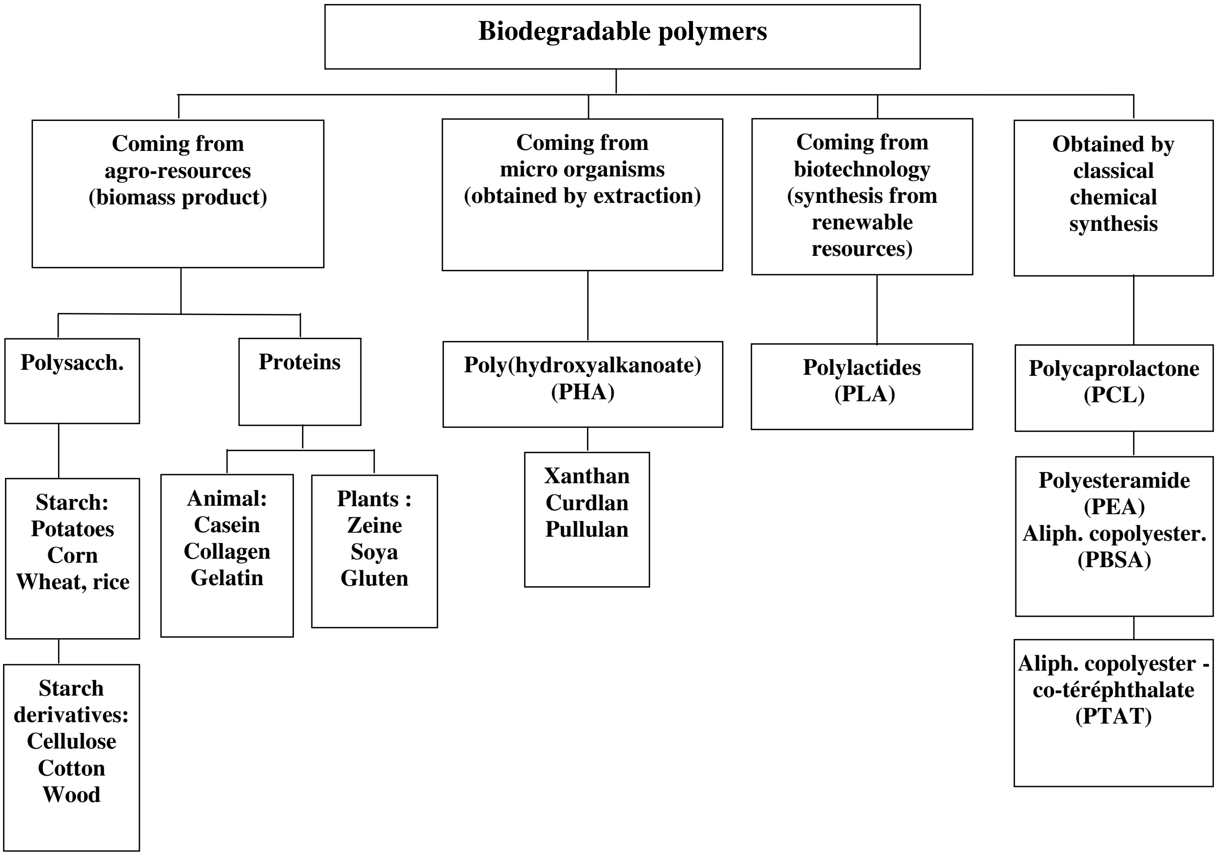


Fig. 1. Classification of biodegradable polymers.

The second category groups polymers coming from micro-organisms. These polymers are of bacterial origin. They are produced from biomass based on a fixed carbon source, such as glucose, methanol or starch. The choice of fermentation conditions and of microbial original cell governs the polymers composition and production yield (Steinbüchel, 1991). Many works concern polyhydroxyalkanoate and in particular poly(β-hydroxybutyrate) (PHB) (Brand, Bachofen, Mayer, & Wintermantel, 1995). In this way, we may notice the existence of the poly-3-hydroxybutyrate-poly-3-hydroxyvalerate copolymer (PHBV), named «Biopol» manufactured by Monsanto using polysaccharides fermentation protocol.

The third and fourth categories concern synthetic polymers. Among them, aliphatic polymers exhibit the best reactivity for a biodegradable process. In this polymer family, we find the well-known polycaprolactone (PCL) and polylactic acid (PLA). These polymers are synthesised from monomer acids, obtained either by biotransformation of renewable raw materials, or by chemical synthesis of petroleum derivatives. PCL is used as a copolymer, manufactured by BASF. Another family is polyvinyl polymers as polyvinyl alcohol (PVA), soluble in water. In presence of activated mud, secondary hydroxyls undergo enzymatic oxidation and involve the break of chains during hydrolysis (Hocking, 1992). Finally, we shall present amide polyester families synthesised from caprolactame, butanediol and adipic acid, as BAK, manufactured by BAYER. Its biodegradation in stamping is complete and can only occur "under" humidity bacterial and fongic-species exposition.

In addition to these four categories, the description will not be complete if nothing is said concerning new composite materials. In this category starch composites, such as starch-PCL, exhibit good water-resistance. We may present the commercial product Mater-Bi® developed by Novamont, whose mechanical properties are comparable to LDPE.

Today, it appears that one of the best-known biopolymers is starch, which exhibits good faculties to give film (De Bock & Van Den Broecke, 1994; Van Soest, Hulleman, de Wit, & Vliegenthart, 1996). The major advantage of such material, coming from agricultural sources, is the great amount of available and renewable raw materials. The great drawbacks are, generally a large dispersion of properties because of the natural origin leading to poor data reproducibility, and a great sensibility to water molecules (hydrophilic materials) leading to poor material durability (this can be also regarded as an advantage if the durability is limited by the ability to be totally degraded). Another drawback is that, whatever its botanical origin, the extraction of starch generates a significant energetic and thus economic cost, limiting by this way the profitability.

Thus, are alternative methods available? Is the extraction of starch compulsory? In this work, we present our latest results concerning the feasibility of plastic materials obtained directly from wheat flour without any prior starch extraction, which is quite a costly process. Then we propose a comparison between the physical performances of these new materials and those carried out from starch.

2. Materials and methods

The wheat flour is provided by Grands Moulins de Paris (France). After a dry division of the cereal, the flour was separated into two categories. One rich in protein, that will be used by the food industry, the second one, used in this work, has a low protein content, less than 12% w/w and contains 85% w/w starch. This second flour can be understood as a by-product of wheat-flour production. The wheat starch is provided by Roquette (France). Additives present in final materials, such as glycerol, sorbitol, silicium dioxide and magnesium stearate have laboratory quality.

The wheat flour, with different additives, was placed in a thermo-regulated turbo-mixer (Kaiser, Germany) for 3 min and mixed with a rotating speed of 750 tr/min. Water mixed with glycerol is introduced slowly through a valve fixed on the lid. Then with a single-screw extrusion machine (Scamex, S0262, France), the mixture is extruded under the following conditions: heated up to 120 °C with a screw-rotating speed of 40 rpm. In this way pellets are obtained (Fig. 2). Then, a stress-relaxation and stabilisation are performed by maintaining the pellets at room temperature for a few hours. A second extrusion using the same temperature and screw-speed is performed to obtain the final film (Fig. 2), which will immediately be put into dessicators and kept under a controlled atmosphere (rh = 75%, room temperature for one week). In this way a wheat-flour based sample called A and a wheat-starch based sample called B have been prepared and Table 1 gives the details of the sample composition. The choice of the additive has been investigated and patented (Leblanc & Dubois, 2001). This choice allows us to obtain high quality film though good performance. To compare the physical performance of wheat-flour based materials and wheat-starch based material the same protocols have been used to prepare the samples and to analyse their characteristics. The thickness of extruded films is about 400 μm and the width is about 100 mm.

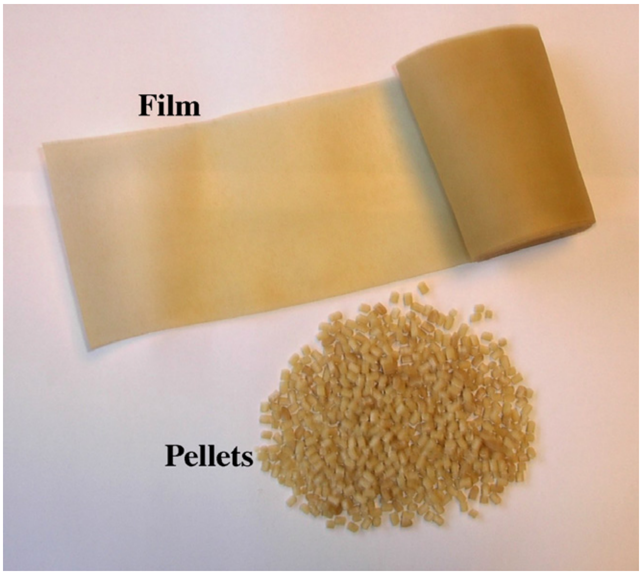


Fig. 2. Examples of wheat-flour based films and pellets, obtained by extrusion.

SEM micrographs were obtained with a scanning electron microscope LEO 1530 FEG. Each sample was cryogenically fractured in liquid nitrogen and then coated with gold palladium. The thickness of coating was lower than 4 nm.

The thermal stability of the films was analysed by thermogravimetric measurements, using a Netzsch TGA 209 balance (Germany). Measurements have been performed at 10 °C/min under a nitrogen atmosphere (15 ml/min). A sample mass of about 10 mg has been used to perform this test.

The thermal properties have also been estimated by means of calorimetric measurements performed with a differential scanning calorimeter (DSC 2920 TA Instruments, USA). Measurements were carried out under a nitrogen ambience (100 ml/min) with a heating rate of 10 °C/min by scanning a temperature range from −80 °C to 180 °C. Calibrations in energy and temperature of the calorimeter have been achieved by measuring the fusion of pure indium. For these measurements, the sample ($m \sim 10$ mg) was placed in an aluminium pan.

The structures of the samples were tested with X-ray diffraction experiments using a Rigaku miniflex wide angle X-ray diffractometer. The X-ray diffraction patterns were performed with the Cu Kα radiations ($\lambda = 154$ Å) scanning 2θ angles from 5° to 35° with a step of 0.02° and a counting time of 5 s.

Tensile tests of samples A and B were carried out on a universal testing machine (Instron 4301). The tests were performed using a load cell of 1 kN at a cross head speed of 2 mm/min. The sample has been taken in the center of extruded film and in the extrusion drawn direction. The sample geometry is standard traction specimen as described on Fig. 3. Determination of tensile modulus (E) is provided to tangent at origin of the curve stress–elongation. For each sample, values of the mechanical characteristics were the arithmetic mean of at least five different specimens.

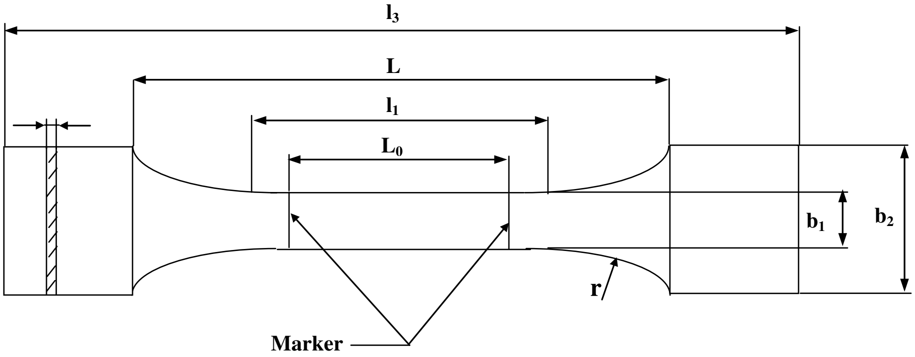
3. Results and discussion

To compare the appearance of wheat flour to wheat starch, at a microscopic level, we used the SEM photos displayed on Fig. 4. Fig. 4a and b obtained on wheat starch for two different magnifications shows intact starch granules which are smooth, free from pores, cracks, or fissure around to oval shapes and which are relatively thick. The

Table 1
Composition of samples A and B (w/w percentages)

	Based material	Plasticizer	Sorbitol	Silicium dioxide	Magnesium stearate
Sample A : wheat flour content (% w/w)	68.2	21.8	7.2	1	1.8
Sample B: wheat starch (% w/w)	68.2	21.8	7.2	1	1.8

The plasticizer is a mixture of 58.7% glycerol with 41.3% water.
Percentages are weight by weight.



b_1 = 10 mm ± 0,2mm
b_2 = 20mm ± 0,5mm
h $\leq$ 1 mm
L_0 = 50 mm ± 0,5mm
l_1 = 60 mm ± 0,5mm
L = 115 mm ± 5mm
l_3 $\geq$ 150 mm
r $\geq$ 60 mm

Fig. 3. Description of the geometry of standard traction specimen.

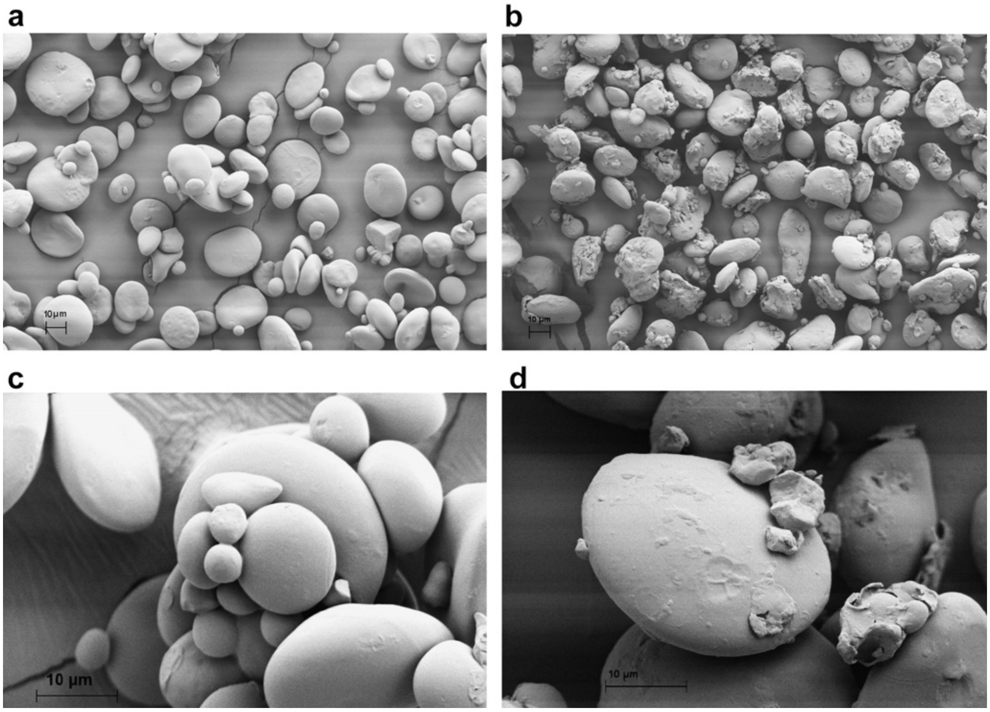


Fig. 4. SEM micrographs of native wheat starch (a, b) and wheat flour (c, d).

wheat starch used in this work exhibits the expected structure as reported by Charles, Kao, and Huang (2003). The same experiments performed on wheat-flour lead to Fig. 4c and d. At these scales the oval shapes of granules are still observed, but the surfaces of the granules are now coarse. Keeping in mind the origin of this wheat flour (by-product of wheat-flour production), this shape is due to the existence of proteins, lipids, pentosane molecules which have not been eliminated during the flour-milling extraction and also of remaining impurities located at the surface of the granules. The global amount of impurities has been estimated to be close to 15% w/w. This amount has been determined by measuring protein and lipid contents and by waste calcination method. Finally, for both starch granules we notice the existence of a wide distribution of granule size. This wide distribution is a common feature of cereal starches (Buleon, Colonna, Planchot, & Ball, 1998; Charles et al., 2003).

The molecular organisation of the granules can be investigated by X-ray diffraction. This technique is known to be able to reveal the existence and to quantify the amount of crystalline and amorphous phases in such materials. The X-ray diffraction patterns obtained for initial wheat flour and initial wheat starch are displayed in Fig. 5 (Panels a and b for initial wheat flour and initial wheat starch, respectively). In this figure, the signal obtained for these two samples are quasi identical. Diffraction rays superimposed on a diffusion halo prove the semi-crystalline nature of these materials (one volume fraction is amorphous and another crystalline). The diffraction peaks are obtained for 2θ values equal to 11.3°, 15.2°, 17.3°, 18.1°, 23.3° and 26.7° implying that these raw materials present an A-type structure, characteristic of cereal starches as already observed in many other works (Buleon et al., 1998; Myllärinen, Buleon, Lhtinen, & Forssell, 2002; Van Soest et al., 1996). This structure is a double helix organised in a monoclinic unit cell ($a = 2.124$ nm, $b = 1.172$ nm, $c = 1.069$ nm, $\gamma = 123.5°$, space group B2), where, as demonstrated by Zobel, eight water molecules are located between the double helix (Zobel, 1988). From a molecular aspect, the native starch crystallinity is linked to amylopectin molecules which act as the constituting elements (Morris, 1990). The diffusion halo proves the existence of a disordered structure (amorphous) which contains linear amylose and branching points of amylopectin as proposed by Jouppila and Roos (1997). It is possible to have a quantitative evaluation of each constitutive phase. This is obtained by fitting the obtained X-ray signal by a set of Gaussian curves. This fitting procedure is performed by subtracting first the diffusion halo by using for each diffraction peak a Gaussian law, then by superimposing all the curves to obtain the experimental data. By doing so, we get the curves presented on Fig. 5c and d, leading us to conclude a degree of crystallinity of 40% w/w for starch and of

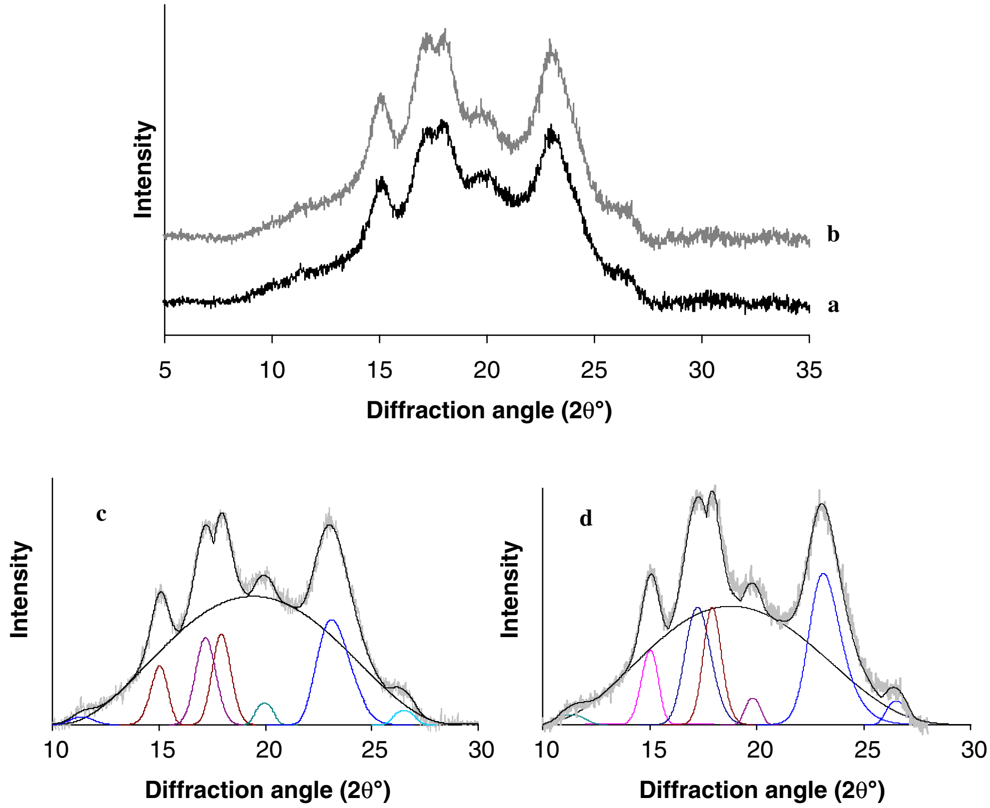


Fig. 5. XRD curves for wheat flour (a) and wheat starch (b). Fig. 4c and d corresponds to computer calculations for wheat flour and wheat starch, respectively.

30% w/w for the flour. Assuming that wheat gluten is a highly amorphous multipolymer system (Gontard & Ring, 1996; Hoseney, Zeleznak, & Lai, 1986; Kalichevsky, Jaroszkiewicz, & Blanshard, 1992) and also that crystallinity occurs in the starch fraction for both raw materials, and using the precedent results showing a quantity of impurities of 15% w/w for wheat flour, it is found that the degree of crystallinity for both materials based on the content of starch are quasi identical (30% of crystallinity for 85% of starch in wheat flour). We may conclude that basically the impurities observed previously for the wheat flour are located at the surface of the granule and that the intimate structure of the granules are the same for the two raw materials.

The same experiments have been performed on extruded samples and the X-ray diffraction patterns obtained are displayed in Fig. 6 (Panels a and b for samples A and B, respectively). Samples A and B exhibit the same signals. Using the previous procedure, Fig. 6c and d give the fitting results. Diffraction peaks superimposed on an amorphous halo are still observed, but the 2θ values are now 7.2°, 12.9°, 19.8°, and 22.6° characteristics of a Vh crystalline type structure (Buleon et al., 1998; George, Frederick, & Randal, 2002; Le Bail, Bizot, Pontoire, & Buleon, 1995). According to these authors, this structure is formed by amylose and lipids complex, leading to a single helix structure packed in an orthorhombic unit cell ($a = 1.37$ nm, $b = 2.37$ nm, $c = 0.80$ nm) with the space group P212121 and with 16 water molecules within the unit cell. Thus, the same structural modifications are obtained for samples A and B. The peak located at $2\theta = 17.3°$ of very small magnitude proves the existence of a residual A-type crystalline structure in the extruded materials. A very small fraction of granules is not transformed in the extrusion process (Van Soest et al., 1996; Willett & Doane, 2002). The quantitative analysis of this data leads to a calculated degree of crystallinity of 14% w/w for both systems. It is difficult to compare this last data obtained on extruded materials with those obtained on raw materials because the crystalline structures are different and to date we have no information concerning the density of each crystalline fraction. Nevertheless, the decrease of crystallinity and thus the concomitant increase of the amorphous phase opens up the question of the thermal stability (physical ageing) of the extruded materials. Indeed, it is well established today that the existence of a disordered structure allows molecular relaxation able to change the physical properties of the materials during their use and ageing. In particular, the kinetics of ageing depends on the temperature of use compared to that of the glass transition. One way to determine the glass transition temperature consists of performing calorimetric measurements.

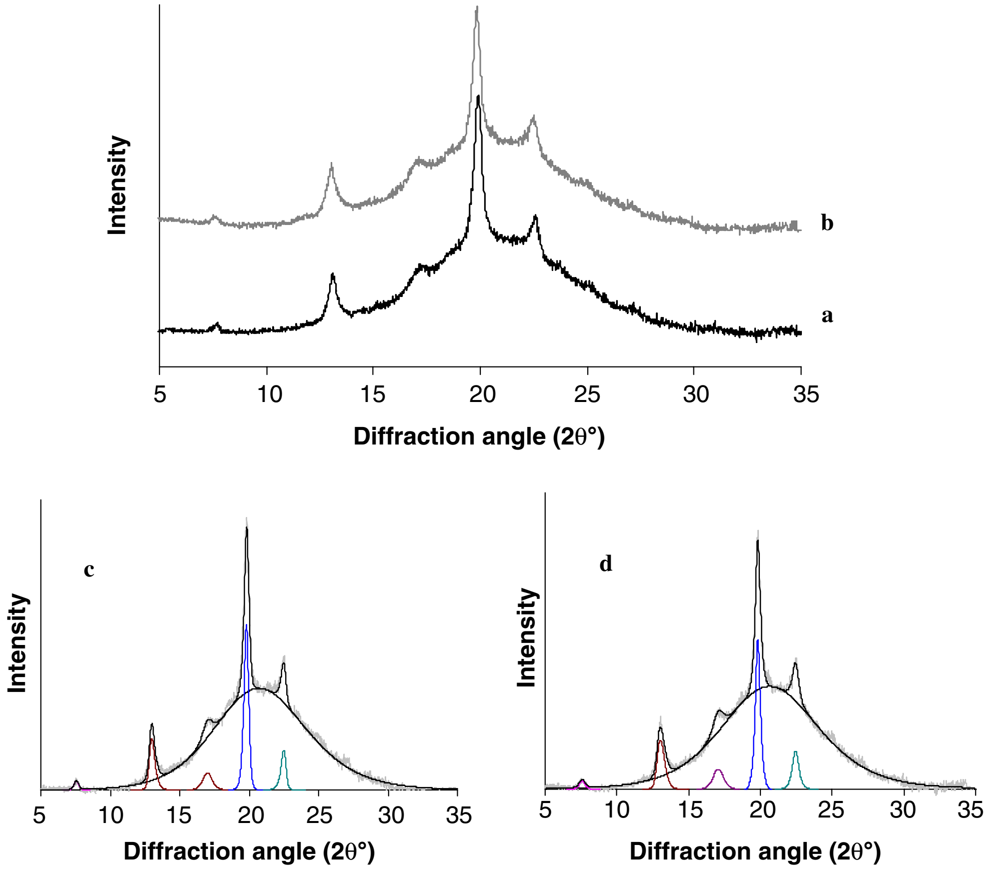


Fig. 6. XRD curves for sample A (a) and sample B (b). Fig. 5c and d correspond to computer calculations for samples B and A, respectively.

For this purpose, we have performed DSC measurements and the curves obtained are presented in Fig. 7. Basically the same curves are obtained for the wheat-flour based and starch based material. At low temperature ($T \approx -73$ °C) an endothermic heat capacity step of $\Delta Cp_{(T=-73\,°C)} \approx 0.15$ J/g K is observed. This signal is characteristic of a glass transition. For temperatures higher than 100 °C a second endothermic reaction of very large magnitude appears for the two samples. We notice that this transition is concomitant with a mass loss observed by means of thermogravimetry. A zoom of this curve in a temperature range between 40 °C and 120 °C shows the existence of a second small endothermic signal, close to 70 °C with an endothermic capacity step $\Delta Cp'_{(T=-70\,°C)} \approx 0.11$ J/g K. This second signal seems to be the signature of a second glass transition temperature. The glass transition observed at low temperature is related to the presence of the glycerol-rich phase (T_g glycerol = −81 °C) and as demonstrated by Lourdin, Bizot, and Colonna (1997), this glass transition is influenced by the presence of a β-relaxation of starch. The same behaviour has been observed by De Meuter, Rahier, and Van Mele (1999) for also some starch-based materials. The second glass transition observed at high temperature by Biliaderis (1992) and Biliaderis, Page, Maurice, and Juliano (1986) on starch systems seems to be linked to the heterogeneous nature of the amorphous phase engaged in granular starches. The existence of a remaining granular structure after extrusion of our samples is concordant with the X-ray diffraction data obtained previously. Thus, depending on the temperature of use $T \leqslant -70$ °C, $-70\,°C \leqslant T \leqslant +70$ °C, $T \geqslant 70$ °C, the kinetics of molecular relaxation will be different.

The high-temperature thermal stability of these materials have been analysed by means of thermogravimetry. The mass loss as a function of the temperature for initial wheat flour and wheat starch is reported in Fig. 8a. The curves obtained show that these materials exhibit a first mass loss of 11% w/w for temperatures from 50 to 200 °C. Then for temperatures from 200 °C to 500 °C, the main degradation process occurs and finally at high temperature ($T > 500$ °C) some residues exist, 17% w/w for wheat flour and 11% w/w for wheat starch. Thus, it is found that the raw materials exhibit a poor thermal stability because a mass loss occurs at low temperature (70 °C) but both systems exhibit exactly the same behaviour. That remains true in terms of kinetics of decomposition as proved by the derivative curves presented in Fig. 8b. The same results and thus the same conclusions were obtained, by doing the same measurements on extruded materials as presented in Fig. 8c. Nevertheless, when comparison is performed between raw materials and extruded materials some differences have to be pointed out. A direct comparison of the data displayed in Fig. 8b and d, shows that the kinetics of mass loss degradation are different. The extrusion process acts on the thermal stability of the materials. To have a better view on the different events able to occur during this analysis, we studied the thermal behaviour of each constituting element used to prepare samples A and B, which are presented in Table 1. Fig. 9 gives the thermogravimetric curves obtained for all these constitutive materials. In Fig. 9, curves “d” and “e” are, respectively, thermal behaviour of wheat starch and wheat flour. Curve “h” corresponds to the thermal behaviour of the silicium dioxide compound and as expected with such mineral oxide, no mass loss is observed. On the contrary, curve “a” gives the behaviour of water and as soon as the heated program started, the water evaporates. Curve “c” is the behaviour of glycerol, for which a mass loss begins at 100 °C and as expected with a very fast evaporation kinetics. Curve “b” is the result obtained for a mixture water–glycerol and the signal obtained which exhibits a plateau shows that the beginning of mass loss is due to evaporation of water

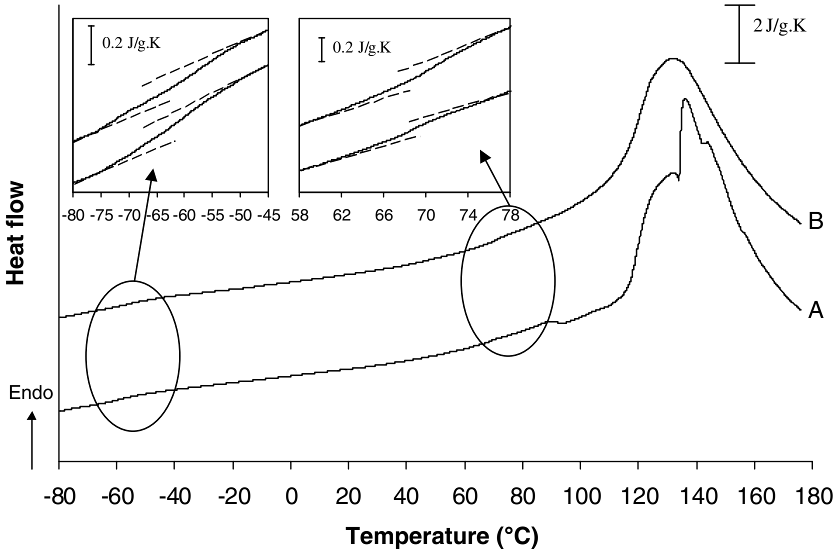


Fig. 7. DSC heat flow measured at 10 °C min^{-1} of samples A and B. A detail of the heat flow signal between [−80 °C, −45 °C] and [58 °C, 78 °C] is shown.

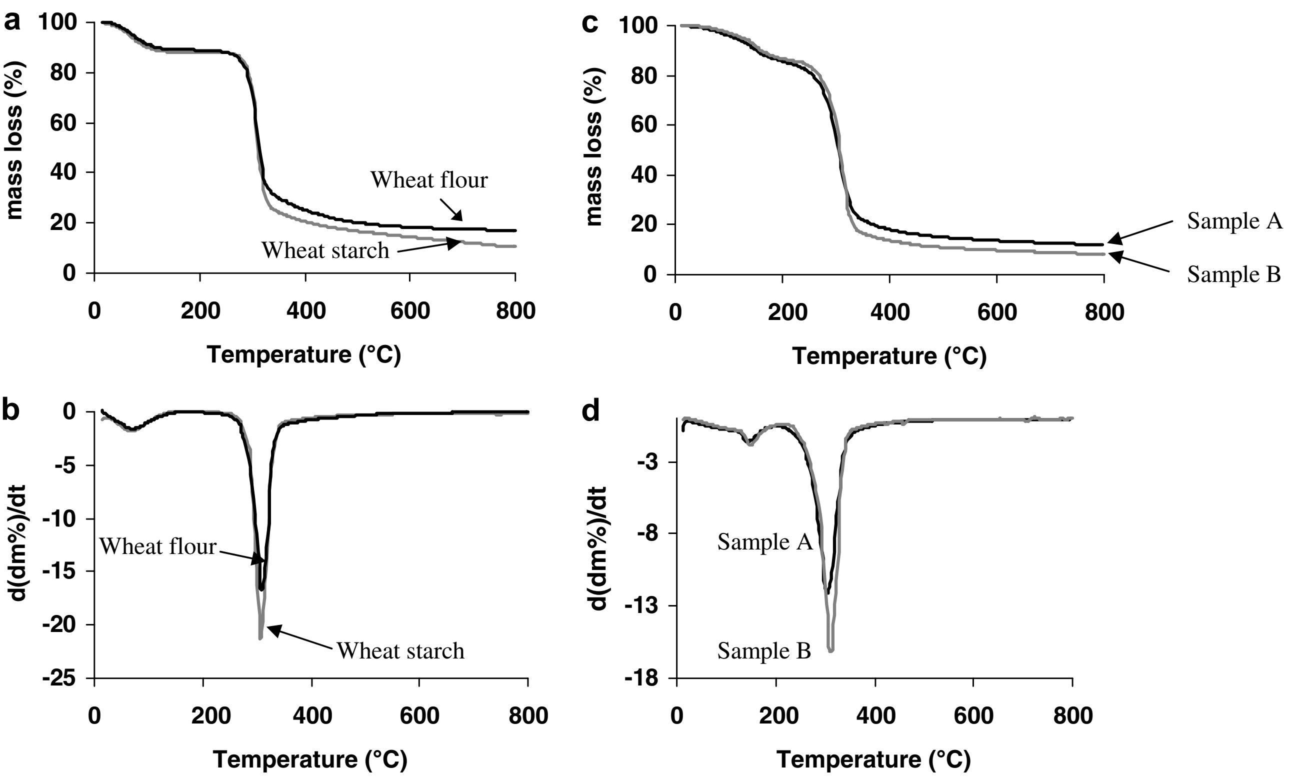


Fig. 8. Comparison of thermal stability between wheat flour and wheat starch (Fig. 7a and b) and between samples A and B (Fig. 7c and d).

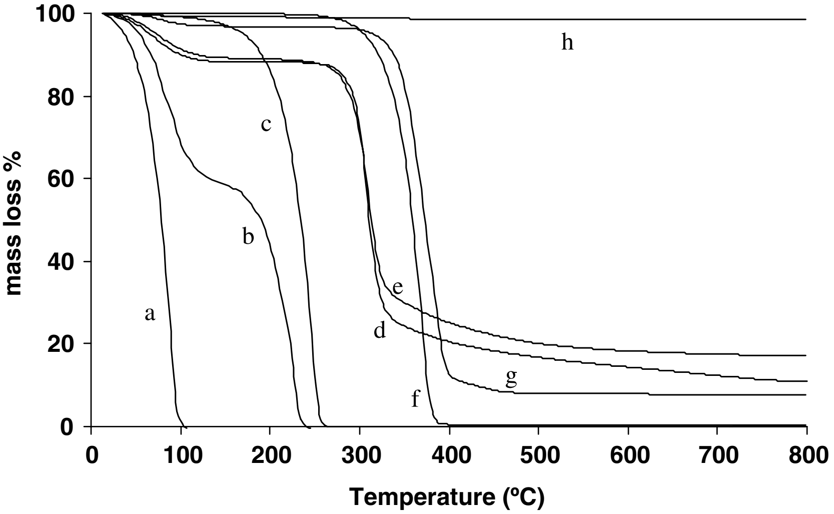


Fig. 9. Thermogravimetric curves of all the constitutive elements of samples A and B.

(we find 41% which corresponds to the initial composition). Curves “f” and “g” are the thermal behaviours of sorbitol and magnesium stearate. Degradation temperatures for both these additives are respectively, 340 and 346 °C. For magnesium stearate a first mass loss is observed at low temperature indicating the possibility of water molecules desorption. At 346 °C (T_{donset}), the main degradation is observed as a one-step phenomenon and some shares remains at high temperature. Sorbitol is degraded at 340 °C (T_{donset}) and the degradation is completed.

The values of the different parameters available from these measurements are reported in Table 2. Coming back now to the curves 8a and c, we may conclude that the first mass loss observed is due to water and glycerol evaporation, while the mass loss beginning at 280 and 289 °C is mainly due to the degradation of flour and starch, respectively. The comparison of curves for each individual constituent and for samples A and B, shows that a very good agreement exists if each individual constituent is added according to the samples A and B

Table 2
Different parameters obtained from thermogravimetric analysis for samples A and B and for each constitutive element of samples A and B

	T_{donset} (°C)	T_{m} (°C)	dm (%)	dm_1 (%)	dm_2 (%)	$\mathrm{dm}_{\mathrm{residue}}$ (%) at 800 °C
Sample A	280	306	88	14	74	12
Sample B	289	311	92	14	78	08
Wheat flour	291	310	83	11	72	17
Starch flour	294	308	89	11	78	11
Sorbitol	340	369	99	99	–	1
Mg Stearate	346	371	92	3	89	8
Silicium dioxide	–	–	–	–	–	100
Glycerol	216	246	100	100	–	0
Water	65	88	100	100	–	0
Plasticizer	–	–	100	41	59	0

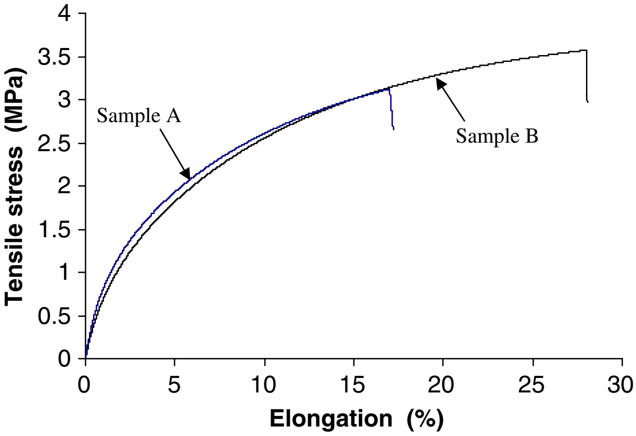


Fig. 10. Evolution of tensile strength versus elongation for sample A and B.

compositions. This comparison shows that the additives do not create drastic modifications (chemical bounds) in the sample structures.

Finally, the intense endothermic peak observed by DSC described as a melting reaction in fact cannot be interpreted correctly because of the concomitant mass loss as proved by our thermogravimetric measurements.

The tensile test results obtained for samples A and B are reported in Fig. 10. The curves presented in this figure correspond to the average curves obtained from at least five different specimens. The values of the different parameters available from these measurements are reported in Table 3. It appears that the same correlation is observed for samples A and B which differ only for the stress break which is observed for a deformation of 17% for wheat-flour based sample (sample A) and 28% for wheat starch based sample (sample B). Surprising results in regard to the nature of the sample, is the relatively good reproducibility of the data and the associated low data dispersion.

The calculation of the tensile modulus (*E*) leads to a value of about 110 MPa, which is in good agreement with other data, when comparison is performed for the same moisture constant, presented in the literature.

Table 3
Different parameters obtained from tensile tests for samples A and B

	$\sigma_{\max}$ (MPa)	$\varepsilon_{\max}$ (%)	*E* (MPa)
Sample A	3.2 ± 0.1	17 ± 1	125 ± 6
Sample B	3.6 ± 0.1	28 ± 1	101 ± 4

4. Conclusion

We have performed thermogravimetric, calorimetric, X-ray diffraction, mechanic and morphologic experiments on a series of wheat-flour extruded material, using wheat flour that can be understood as a by-product of the farm-produce wheat-flour.

Comparison of all these data with a reference wheat starch sample of the same composition allows us to conclude that for all the tests performed, no drastic differences exist between wheat-flour based and wheat-starch based materials. The only one clear difference occurs for the strain to break value which is diminished by about 30% for wheat-flour based materials. This decrease is probably due to the greater number of impurities content in wheat flour, which makes sample A less homogeneous in comparison to sample B (wheat starch content).

Acknowledgements

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