Influence of Proteins on the Mechanical Properties of Agro-Based Materials

C. Terrié,[1] V. Constantinescu,[1] N. Leblanc,[1] J.-M. Saiter[2]*

Summary: A new biodegradable thermoplastic material based on a wheat flour by-product has been developed. The influence of protein content in wheat flour on the mechanical properties of the material has been investigated. For protein content between 4% and 10%, no influence of the protein content was evidenced, whereas beyond 10% w/w of proteins in the wheat flour, the mechanical properties of agro-based materials decrease, thus confirming the advantage of using a wheat flour by-product (i.e. with protein content below 8% w/w).

Keywords: agro-based materials; mechanical properties; proteins; starch; wheat flour

Introduction

Non food use of agricultural resources is of undisputable interest for the replacement of synthetic plastics. In this field, starch has attracted considerable attention due to its natural abundance, and its ability to be made thermoplastic by various processing techniques[1] (such as extrusion). However, non food use of agricultural resources must not compete with food production. It is thus essential to restrict non food use to surplus or byproducts of the agricultural production. In this way, our group has developed a new biodegradable thermoplastic material based on a wheat flour byproduct. Flour is obtained through a milling process that may include an air classification step in a turbomill, where flour is separated into several fractions differing from granulometry and protein content. Fraction of low protein content (6.5% w/w) is considered as a byproduct and is available for new applications. It was shown that agro-based material prepared with this byproduct displays after extrusion similar properties as thermoplastic starches,[2] with the advantage of saving the economic and energetic costs of starch extraction. Like starch-based materials it could be used in short-term applications such as packaging.

Compared with other biodegradable materials such as PHAs and PLAs, an agro-based material displays the advantage of being obtained directly from a raw material or byproduct, without any biological or chemical synthesis. However, as a starch-based material, its major drawbacks are its water sensibility and low mechanical properties; hence our current concern is the improvement of the time-dependent and use properties of this new material. The influence of various additives (glycerol,[3] lipids[4]) and fibers (flax,[5] cotton,[6] hemp, sisal) on the thermal and mechanical properties of the material has been investigated. In this study we focused on the influence of protein content in wheat flour on the mechanical properties of the wheat flour based material.

Materials and Methods

Wheat flour fractions were provided by Grands Moulins de Paris (France). The nitrogen contents of the wheat flours fractions were determined using the Kjeldahl[7] method. Then the protein contents were calculated using a protein conversion

[1] LGMA – Esitpa, 3 rue du Tronquet, BP 40 118, 76 134 Mont Saint Aignan cedex, France
E-mail: cterrie@esitpa.org
[2] LECAP – EA 4528 Université de Rouen - Avenue de l'Université, B.P. 12, 76801 Saint Etienne du Rouvray cedex, France

factor of 5.7[8] currently used for wheat flour. At least 3 measurements were performed for each flour sample, and the resulting protein content was obtained with a relative uncertainty of 5%.

Additives used were glycerol (12.8% w/w), water (9% w/w), sorbitol (7.2% w/w), silica (1% w/w) and magnesium stearate (1.8% w/w) that were of laboratory quality. The different proportions for each constituent were chosen in agreement with previous work.[9]

The wheat flour (68.2% w/w) and the additives (except water and glycerol) were placed into a thermo-regulated turbo mixer (Kaiser, Germany) and mixed at a rotating speed of 750 rpm for 3 min. A mixture of plasticizers (water, glycerol) was introduced slowly through the valve fixed on the lid. The mixture was then extruded with a single-screw extruder (Scamex, S0262, France) at a temperature of 110 °C and at rotating speed of 40 rpm. By this method pellets of materials are obtained. Then a second single-screw extrusion is performed with the pellets, at 110 °C with a rotating speed of 70 rpm, using a flat die to get the final film. The materials had a final humidity of about 3% w/w (determined by oven drying at 130 °C until the weighed mass is constant).

Tensile tests were carried out by using a universal testing machine (Instron model 4301, France). The tests were performed using a load cell of 5 kN at a speed of 5 mm/min having a strain gauge extensometer with gauge length of 12.5 mm. The samples have been taken in the center of extruded film and in the extrusion drawn direction. The samples geometry is a standard traction specimen.[2] Prior to analysis, the samples were conditioned at 75% relative humidity at 20 °C for 48 hours, and the tests were performed at room temperature and humidity, under atmospheric pressure. Data were collected with Instron BlueHill 2 software. The results obtained with a material made from a 6.5% proteins wheat flour is given as an example in Figure 1.

For each agro-based material, values of stress at break and strain at break were taken at the break point on each curve, and the reported values are the arithmetic means of at least 6 different samples. Determination of tensile modulus (E) is provided to tangent at origin of the mean stress-strain curve.

Results and Discussion

In a previous study we compared a wheat-flour based byproduct and a wheat-starch based material from thermogravimetric, calorimetric, X-ray diffraction, mechanical and morphological experiments.[2] For all the tests performed, no drastic difference between the two materials was evidenced. The only clear difference occurs for the strain at break value which is diminished by about 30% for the wheat-flour based material. This decrease was attributed to the greater number of impurities in wheat flour, making the resulting material less homogeneous.

This first study led us to conclude that the wheat-flour byproduct is an interesting raw material for the development of biodegradable material, with the advantage of saving the process and cost of starch extraction, while displaying similar properties as thermoplastic starches.

However, as a difference in mechanical properties was noticed, and since the major difference between pure starch and wheat flour is the presence of proteins (mainly gluten) in flour, we wanted to investigate further the influence of proteins on the mechanical properties of wheat-flour based materials.

In order to study the influence of wheat proteins on the mechanical properties of wheat-flour based agro-material, a set of agro-based materials from 7 different wheat flour fractions was prepared, with protein contents of 4.4, 6.5, 8.3, 10.1, 12.2, 13.7 and 16.6% w/w (only the 4.4% and 6.5% fractions are byproducts). The same formulation and process (previously developed for a wheat flour byproduct with 6.5% of proteins) were used for all samples, and in each case a proper material was

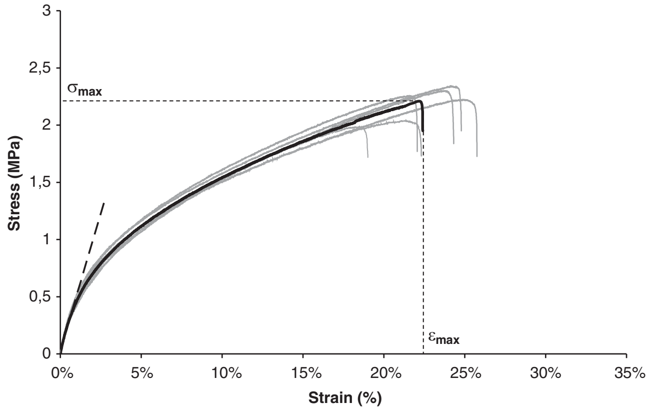

Figure 1.
Stress-strain curves for the material made from a wheat-flour containing 6.5% proteins (w/w). Grey curves show the full set of measurements, black curve is the calculated mean curve. – – –: tangent at origin of the mean curve.

obtained. The first observation is thus that in this range of protein content (up to 16.6%) there is no negative effect of proteins on the processing of agro-based materials by extrusion.

To investigate the mechanical properties of the materials, tensile tests were performed and the values of mechanical characteristics were determined from stress-strain curves for each sample. The values of the tensile modulus as a function of protein content were dispersed in a range of 15-40 MPa without any significant difference. The values of stress at break and strain at break are given in Table 1.

Figure 2 shows the evolution of stress at break as a function of the protein content in flour. Up to 10% w/w of proteins, there is no clear evolution of the stress at failure. At higher protein contents (12–17%), the tensile strength decreases with protein content, indicating that the materials become less resistant to failure.

Table 1.
Values of mechanical characteristics of agro-based materials made from wheat flour fractions with different protein contents (values are average ± standard deviation).

Proteins (% w/w)	σ_{max} (MPa)	ε_{max} (%)
4,4	1,7 ± 0,11	27 ± 1,2
6,5	2,1 ± 0,25	23 ± 2,7
8,3	1,8 ± 0,29	26 ± 2,7
10,1	1,9 ± 0,16	25 ± 2,1
12,2	1,2 ± 0,15	14 ± 2,3
13,7	1,4 ± 0,10	11,6 ± 0,86
16,6	1,0 ± 0,20	7 ± 2,4

The variations of the strain at break as a function of protein content are shown in Figure 3. No significant evolution of the strain at break is observable for protein contents in wheat flour between 4.4 and 10.1%. For higher protein contents, the strain at failure obviously decreases. This indicates a decrease in the ductile nature of the material when the protein content increases.

From those experiments, it can be concluded that in the range 4–10%, no significant influence of proteins on the mechanical properties was evidenced. When wheat flour of higher protein contents are used (12–17%), an increase in protein content leads to a decrease of the mechanical properties of the wheat-flour based materials. Low quality flours or flours byproducts, with protein contents below 8% w/w, are thus best raw materials for the development of agro-based materials, compared to flours of higher protein content.

The main protein in wheat flour is gluten (80–85%), which is also known and studied for its film forming properties, also in the

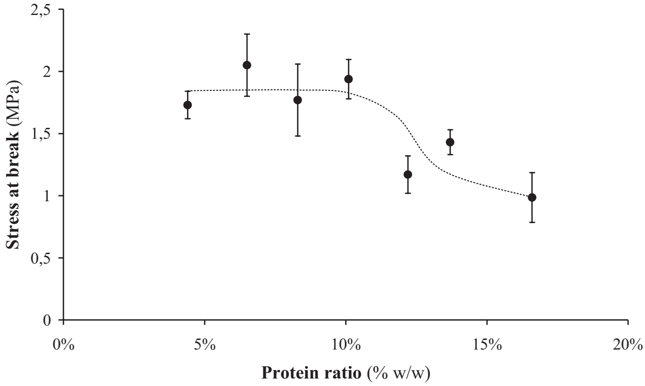

Figure 2.
Evolution of the stress at break as a function of protein ratio in wheat flour (The curve is merely drawn to guide the eye and has no theoretical basis).

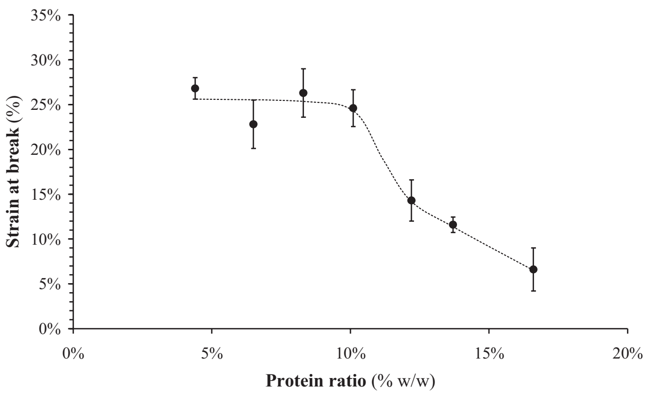

Figure 3.
Evolution of the strain at break as a function of protein ratio in wheat flour (The curve is merely drawn to guide the eye and has no theoretical basis).

presence of water and glycerol.[10] However, in the present study the results suggest that gluten do not participate to the starch network (unlike a plasticizer) but rather behaves like an incompatible filler dispersed in the starch matrix.

Similar observations were reported by Chanvrier *et al*[11] for corn flour and starch-zein based materials, from three-point bending tests. The behavior of starch-zein blends with one component at low concentration was similar to the behavior of the pure major component. When zein content increases up to 15% for strain at failure and 30% for stress at failure, the mechanical properties of the blends decrease. This fragility was attributed to the phase separation between starch and zein; and zein was compared with particles which fill a continuous polymer matrix.

In the referred study,[11] further increase in zein content (from 50% up to 100%) led to an increase in mechanical properties, because starch-zein blends have then a continuous zein phase and exhibit behavior similar to glassy zein materials. According to those results we can suppose that if we increased protein concentration beyond 17% and further, we would also observe a minimum in the mechanical properties, then an increase at high protein content when the material would become a gluten matrix with dispersed starch. However flour fractions usually do not contain more than 18% protein.

Conclusion

This preliminary study shows that low protein content in flour fraction do not significantly influence the mechanical properties of wheat-flour based materials, leading to materials displaying similar properties as starch-based materials. However, when the protein content in wheat flour increases beyond 10%, the mechanical properties decrease. This confirms the interest of using a wheat-flour byproduct, which have low protein content (below 8% w/w).

On another hand, we could take advantage of the presence of proteins in wheat-flour based materials to decrease their water sensitivity: proteins may indeed be crosslinked with a naturally occurring molecule, genipin. Genipin-crosslinked materials display lower surface tension and decreased moisture absorption.[12]

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