 DOI: 10.1002/masy.201050415

Biodegradable Materials from Agro-Based By-Products

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Summary: A new biodegradable thermoplastic material based on a wheat flour by-product has been developed. The influence of various additives (glycerol, silica) and fibers (flax, cotton, hemp) on the mechanical properties of the material has been investigated. The development of expanded materials is also presented.

Keywords: agro-based materials; composites; mechanical properties; natural fibers; wheat flour

Introduction

Concern for the environment over the past decade has led to extensive work aimed at replacing petrochemical-based plastic materials by renewable polymers. Starch is one of the most important carbohydrate obtained from plants. Due to its availability as a renewable resource, it has been investigated for the successful usage as a raw material for the preparation of biodegradable thermoplastics.[1]

Non food use of agricultural resources is of undisputable interest for the replacement of synthetic plastics; however it must not compete with food production. It is thus essential to make use of surplus or by-products of the agricultural production. In accordance with these ethics, our group has developed a new biodegradable thermoplastic material based on a wheat flour by-product. In previous works, we showed that wheat flour having low protein content and high starch content can also be successively used for the formulation of biodegradable thermoplastic polymers;[2] with the advantage of saving the cost of starch extraction.

Our current concern is the improvement of the time-dependent and use properties of this new material. We are working on both chemical and physical ageing. On one hand this implies understanding the role of the various components of the thermoplastic matrix in order to optimize the composition for a better stability of our material. On another hand, to reinforce the mechanical properties, we have also investigated the incorporation of various natural fibers in the thermoplastic matrix, thus developing natural agro-composites. We present here the recent developments of our research.

Materials and Methods

Wheat flour, having protein content less than 12% w/w and starch content 85% w/w, which is a by product of the flour industry, was provided by Grands Moulins de Paris (Paris, France). Glycerol, sorbitol, silica and magnesium stearate of the laboratory quality, were used as additives for the preparation of the polymeric matrix. More details concerning the composition of this matrix by N. Leblanc et al. have been patented.[3] The flax fibers provided by Agy Lin Société Coopérative Agricole (France) have been cut into short fibers of approximately 1 mm length by société Pierret (Belgium) with guillotine (FP2600). The waste cotton fibers were provided by the French Textile and Apparel Institute

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(IFTH, France). The length of the cotton fibers varied from nanometre to millimetre scale. Hemp fibers were provided by Chanvrière de l'Aube (France) and were sieved to separate fibers of approximately 1 mm for sample preparation.

The wheat flour with different additives and fibers were weighed using a balance (Denver Instrument, XP 3000, USA), placed in a thermo-regulated turbo mixer (Kaiser, Germany) and mixed at a rotating speed of 750 rpm over 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 extrusion machine (Scamex, S0262, France) at a temperature of 110 °C and at rotating speed of 40 rpm. By this method pellets of materials are obtained. After the homogenization, the pellets were extruded again at 110 °C with a rotating speed of 70 rpm to get the final film that was kept under controlled atmosphere.

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 2mm/min having a strain gauge extensometer with gauge length of 12,5 mm. Average values of the five different specimens were reported.

DMA measurements were performed with a TA Instruments Q800, from −100 °C to 120 °C at 3 °C.min^{-1} (frequency 5Hz, tension-compression mode).

Wheat-Flour Matrix

In order to improve the time-dependent and use properties of our agro-based material, we first studied the influence of the various additives on the properties of the material.

Glycerol

The effect of glycerol on the structure of the matrix has been investigated[4] and it appears a decrease of cristallinity from 14 to 11% when the glycerol content varies from 12,8 to 20% in the matrix. The average intermolecular distance increases from 4,28 to 4,35 Å and the average density (or specific volume) decreases. As a consequence, it is expected that the amount of free volume linked to existence of an amorphous or a vitreous phase increases in the extruded materials.

For mechanical properties of the matrix (Figure 1) the increase of glycerol content in the material from 12,8% to 20% gives a decrease in the stress at break of 34%, an increase in the strain at break of 35% and a decrease in the Young Modulus of 54%. These results indicate that the ductility of material increases and, as expected, a plasticization effect is obtained by introducing glycerol in the sample composition. It means that plasticization gives more mobility in the matrix and there is therefore a decrease of the mechanical resistance.

These plasticization effects due to glycerol have been observed in materials made of starch.[5] In this latter system, introducing plasticizer reduces direct interaction between starch chains, thus facilitating movement of starch chain under tensile forces. The same scenario occurs with wheat-flour-based materials.

The study of the molecular relaxations in the matrix for different contents of glycerol (Figure 2) shows that there are two phases in the material: one at lower temperature region corresponding to a glycerol rich phase; another at higher temperature region corresponding to a starch rich phase.

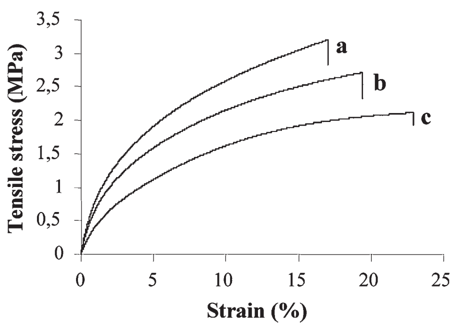

Figure 1.
Stress-strain curves for wheat-flour based materials with **a**: 12,8%; **b**: 16,5%; **c**: 20% of glycerol (w/w).

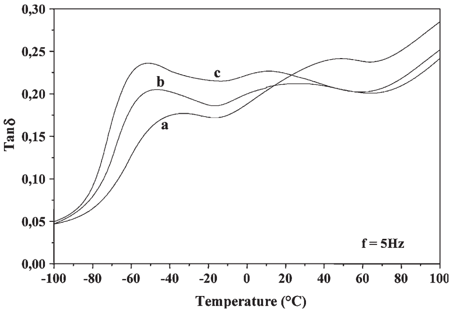

Figure 2.
Differential mechanical analysis wheat-flour based materials with **a**: 12,8%; **b**: 16,5%; **c**: 20% of glycerol (w/w)

The percentage of glycerol in the matrix modifies the characteristic temperature of these two phases.

Silicon Dioxide

Silicon dioxide is added for the preparation of the matrix and it appears that when one percent is added, the mechanical properties of the matrix are affected (Figure 3) with an increase in the stress at break of 129%, also a great increase in the Young's modulus (247%) and a little decrease in the strain at break (20%).

This great change in mechanical properties when a small amount of silica is added indicates a reinforcement effect of this mineral charge.

Silicon dioxide also affects the molecular relaxations of the matrix (Figure 4), but only the second phase transition of the material, the starch rich phase. Maybe the silica particles act like obstacles in this phase, making the mobility of starch chains difficult.

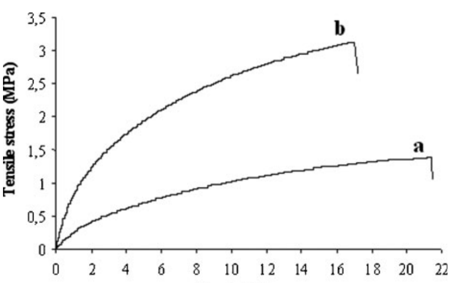

Figure 3.
Stress-strain curves for wheat-flour based materials with **a**: 0%; **b**: 1% of silicon dioxide (w/w).

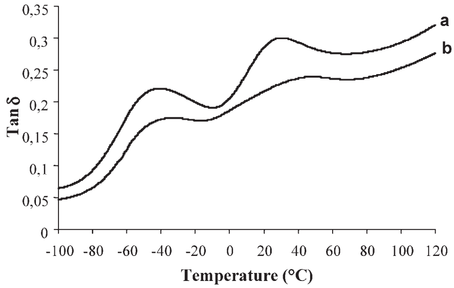

Figure 4.
Differential mechanical analysis wheat-flour based materials with **a**: 0%; **b**: 1%; of silicon dioxide (w/w).

Agro-Composites

To reinforce the mechanical properties of agro-based materials, the incorporation of various natural fibers in the matrix was investigated, thus developing natural agro-composites. We present here some results with flax and cotton fibers.

Flax Fibers

Morphological studies show a good dispersion and adhesion of the fibers in the matrix.[6]

Stress–strain curves for the composite material with different content of treated fibers ranging from 0 up to 20% were performed and the resulting average values of stress and strain at break are presented in Figure 5 as a function of flax fibers content.

The fiber content decreases the strain at break of the composites (from 17% to 6%). The drastic decrease was observed for the composite having 5% w/w of flax fibers (from 17% to 8%). When the fiber content increased further from 5% to 20% w/w a slight decrease was observed from 8% to 6%. This indicates that addition of fibers to the matrix decreases the ductile nature of the polymer. It is also found that when the fiber content increases from 0% to 20% w/w, stress at break and tensile modulus

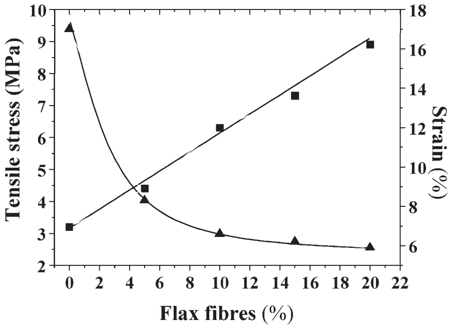

Figure 5.
Average stress at break (▲) and strain at break (■) of agro-composites as a function of the flax fibers content (% w/w).

increases from 3,2 MPa to 8,9 MPa and 125 MPa to 465 MPa, respectively. As the fiber content increases, because of good fibers dispersion, the stress transfer between fiber and matrix occurs properly, as a result the tensile strength and modulus increase.

Cotton Fibers

We also made composites with cotton waste fibers.[7] Stress-strain curves for agro-composites with varying amounts of cotton fibers are shown in Figure 6.

When the fiber content varies the entire behavior of the composite changes and become less ductile. As the fiber content increases, the percentage of elongation value decreases: for the 15% composite, the percentage of elongation decreases from 56 to 12%, i.e. a decrease of 78% when compared to the pure matrix, indicating that the composite becomes more rigid in nature.

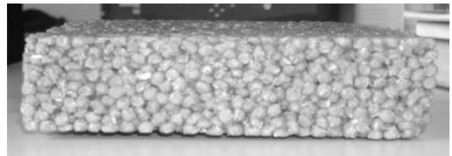

Figure 7.
Panel of compressed expanded balls.

The tensile strength and Young's modulus increase as a function of fiber content.

As for flax fibers, when the fiber content increases, good fiber dispersion occurs in the matrix and stress transfer occurs properly between the fiber and the matrix. Also due to the chemical similarity between the starch and cellulose fibers, the intrinsic adhesion of the fiber/matrix interface will be enhanced which ultimately leads to the increase in the tensile properties.

Expanded Agro-Materials

Another topic in our group is the development of expanded materials. By varying the composition of additives, we managed to obtain expanded balls that can be assembled together by compression in a mould (Figure 7). The aim was to develop an insulating material. The panel obtained displayed a thermal conductivity 0,083 $W.m^{-1}.K^{-1}$ for a density of 250 $kg.m^{-3}$.

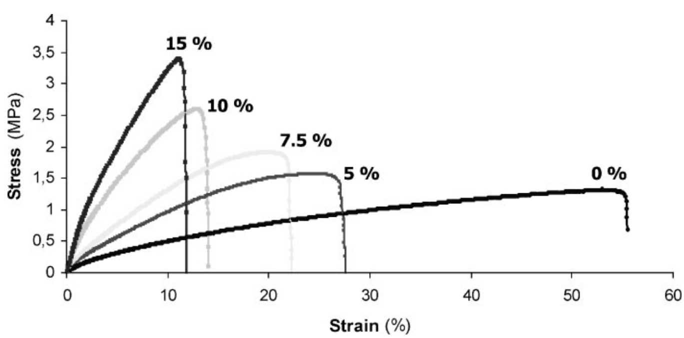

Figure 6.
Stress-strain curves for wheat-flour based materials with various contents of waste cotton fibers (w/w).

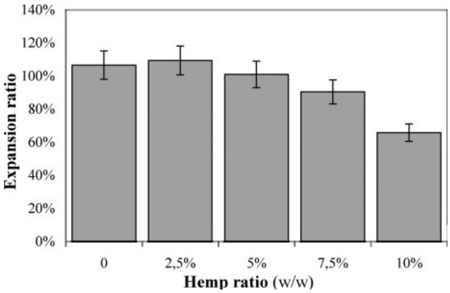

Figure 8.
Influence of fiber ratio on the expansion ratio of expanded balls.

Composite expanded balls were prepared. The results obtained with hemp fibers are presented in Figure 8. Expansion ratio (defined as the diameter of the balls divided by the diameter of the die) varies with the fiber ratio. Beyond 2,5% w/w of fibers, expansion decreases.

Conclusion

Food production by-products can be used to develop interesting agro-based materials. We developed a set of materials from wheat flour by-products and investigated the influence of additives (glycerol, silica) and natural fibers (flax, cotton, hemp) on the mechanical properties. The aim is to understand the relationships between composition, structure and properties in order to be able to design a specific material for a defined application.

[1] F. Vilaseca, J. A. Mendez, A. Pèlach, M. Llop, N. Cañigueral, J. Gironès, X. Turon, P. Mutjé, *Process Biochemistry* **2007**, *42*, 329.

[2] N. Leblanc, R. Saiah, E. Beucher, R. Gattin, M. Castandet, J. M. Saiter, *Carbohydrate. Polymers* **2008**, *73*, 548.

[3] N. Leblanc, M. Dubois, (**2001**), Matériaux Biodégradables, Patent FR 01 15451

[4] R. Saiah, P. A. Sreekumar, N. Leblanc, M. Castandet, J. M. Saiter, *Cereal Chemistry* **2007**, *84*, 276.

[5] S. Mali, M. V. E. Grossmann, M. A. García, M. N. Martino, N. E. Zaritzky, *Journal of Food Engineering* **2006**, *75*, 453.

[6] R. Saiah, P. A. Sreekumar, P. Gopalakrishnan, N. Leblanc, R. Gattin, J. M. Saiter, *Polymer Composites* **2008**, in press

[7] L. Dobircau, P. A. Sreekumar, R. Saiah, N. Leblanc, C. Terrié, R. Gattin, J. M. Saiter, *Composites: Part A* **2009**, *40*, 329.

