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# New Natural Injection-Moldable Composite Material from Sunflower Oil Cake

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## **Abstract**

Through a twin-screw extrusion process the native structure of sunflower oil cake was completely transformed (globular protein denaturation/texturization and husk fiber defibration) into a simpler matrix-fiber structure, as could be seen on SEM micrographs. Further chemical reduction of protein disulfide bridges greatly reduced the melt viscosity of the moistened composite that it could be injection-molded. The molded specimens were tested and their tensile and flexural properties and water absorption calculated. Their water resistance appeared to be particularly high, and could be enhanced further after a thermal treatment (N<sub>2</sub>, 200°C). The proteic matrix seemed to behave like a natural thermoset resin. Sunflower oil cake could be used without any additives to make biodegradable, water resistant and exceptionally cheap materials.

## **Key words**

Biodegradable, injection-molding, protein texturization, thermoset, thermal treatment

## **Introduction**

The consequences of the extensive use of plastics (dumpsite congestion, maritime environment pollution) and the difficulties in setting up their recycling (sorting, greenhouse effect) promote the development of agro-materials. Obtained from raw materials of agricultural origin and shaped thanks to tools developed for plastics, those which are marketed today are always composite materials. Their matrix is generally constituted by a "thermoplastic" biopolymer, the most common being starch, to which is added lubricating and/or water repellent agents and a filler, generally cellulose fibers (Rouilly and Rigal, 2002).

Sunflower oil cake (SFOC), the residue of the oil extraction of the seed, consists of approximately 40% highly lignified husk lignocellulosic fibers (characteristic of the secondary vegetable cell walls) and approximately 35% protein (Table 1). Sunflower proteins possess appropriate physicochemical properties for manufacture of polymer materials as demonstrated by a number of publications concerning the study of their glass transition (Rouilly et al., 2001), their film-forming abilities by casting (Ayhllon-Meixueiro et al., 2000) or thermo-molding (Orliac et al., 2002) and of their rheological behavior in injection-molding (Orliac et al., 2003). Sunflower oil cake could thus be an interesting raw material for the manufacture of agro-materials; it contains by nature matrix and fibers. In spite of a world production oscillating around 10 Mt/year, it has few outlets in cattle feeding because of lower nutritional properties than those of its competitors, rapeseed and soybean oil cake (Gonzalez-Perez et al., 2002; Schroeder et al., 1996). It is thus available in large amounts, concentrated on a small number of sites and is particularly cheap, 0.09 € / kg.

In its raw state, the SFOC cannot be shaped by injection-molding without addition of another thermoplastic compound (Baganz et al., 1999). The objective of this work was to show that, knowing its structure exactly, it is possible to transform it by a thermo-mechanical process of twin screw extrusion involving protein texturization and husk fragment defibration followed by a chemical reduction. Its rheological properties were greatly improved and it could be shaped by injection-molding. The resulting materials had interesting properties, in particular a low sensitivity to water which could be improved further by thermal treatment.

### **Materials and Methods**

**Materials.** Sunflower oil cake (SFOC) was provided by the company “Toulousaine de Céréales” (Toulouse, France). The sodium sulphite used as a reducing agent was of “reagent” grade and was purchased from Aldrich (St Quentin Fallavier, France). This agent was used as received.

Extruded sunflower oil cake (ESFOC), water and an appropriate amount of sodium sulphite were mixed using a Perrier 32.00 mixer (Montrouge, France). The mixture was then conditioned in an airtight container for 12 hours at 25°C. The equilibrated mixtures were then used randomly in rheological analysis or to make injection-molded objects.

**Optical microscopy.** Samples at their equilibrium moisture content were analyzed with a binocular microscope (Nikon SMZ1500) equipped with a digital camera (Nikon DMX 1200).

**Scanning electronic microscopy.** These observations were made with a scanning electron microscope LEO 435VP (Cambridge, UK). All the samples were dried at 60°C in a desiccator under vacuum for 48 hours before being metallized and observed with an accelerating voltage of 15 kV.

Twin-screw extrusion. The treatment of the cake by extrusion was conducted with a twin screw extruder BC45 (Clextral, Firminy, France). Six types of screw element, 52 mm in diameter, made up the screw profile used for this study (the number following the screw element corresponding to the pitch value): T2F: Trapezoid direct pitch screw with double fillets, C2F: Direct pitch screw with double fillets, CF2C: Reverse pitch screw with double fillets and perforated at 120°, MAL0: Simple mixing paddle.

Following the first attempts made with SFOC (Leyris, 1998), mixing paddles were present in the chosen screw profile to homogenize the solid/liquid mixture and crush the biggest particles and a reverse screw was used to apply a strong shear stress. The use of a die was more restricting than effective and was thus not retained. Because of an important number of different interactions, proteins do not undergo a "melted" state (Arêas, 1992). The optimized screw profile for the SFOC treatment is described in Figure 1.

The extrusion conditions are summarized in Table 2. The entrance inputs of solid and liquid were set in such a way that the moisture content (MC) of the mixture inside the extruder was 30%.

Rheological study. A Rheomex single screw extruder (Haake PolyLab System, Karlsruhe, Germany) equipped with a capillary die ( $L/D = 10$ ;  $D = 3\text{mm}$ ) was used for rheological studies. The temperature of the die was between 100°C and 150°C. The temperature of each unit of the barrel was 10°C lower than that of the previous unit or die. The temperature of the supply tank was fixed at 50°C for all measurements. The screw speed was between 20 and 200 rpm. The compression rate of the rheometer screw was 1.8.

The die was equipped with pressure and temperature sensors. The mass flow rate was calculated with a balance which integrated the mass for the duration of the measurement.

The Rheomex was controlled by computer with on-line acquisition of the system characteristic units (output, temperature and pressure).

Modeling experimental curves of viscosity. The apparent shear rate ( $\gamma$ ) for Newtonian fluids is calculated as follows:

$$\gamma = 4Q/\pi R_c^3 \quad (1)$$

Where Q is the volumetric flow rate in cm<sup>3</sup>/s and R<sub>c</sub> is the radius of the capillary die in cm. The shear stress of the wall ( $\tau_p$ ) is expressed as a function of: the difference between the pressure at the beginning of the capillary and the atmospheric pressure ( $\Delta P$  expressed in Pa), the length of the capillary L<sub>c</sub> and the radius of the capillary R<sub>c</sub>, both of which are expressed in cm:

$$\tau_p = R_c \Delta P / 2L_c \quad (2)$$

If the fluid is pseudo plastic, the shear rate ( $\gamma$ ) must be corrected by using the following equation, known as the Weissenberg-Rabinowitch equation:

$$\gamma_p = \gamma(3m+1)/4m \quad (3)$$

$$\text{with } m = d(\log \tau_p) / d(\log \gamma) \quad (4)$$

In the present study, this correction was directly applied by the rheometer.

For most thermoplastics, the shear stress is linked to the shear rate by a power law-type model:

$$\tau_p = K \gamma_p^m \quad (5)$$

The shear rate ( $\dot{\gamma}_p$ ) and shear stress ( $\tau_p$ ) can be used to obtain a curve showing the viscosity at the wall ( $\eta$ ) of the material tested by applying the following equation, known as the Ostwald de Waele equation:

$$\eta = \tau_p / \dot{\gamma}_p = K \dot{\gamma}_p^{m-1} \quad (6)$$

The values of  $m$  are between 0 and 1 for thermoplastic materials, which explains their shear thinning behavior. The values of the  $K$  (consistency) and  $m$  (pseudo-plasticity index) coefficients are obtained by linear regression of  $\log_{10}$  values of the real viscosity as a function of the  $\log$  values of the shear rate. This measurement, carried out in a single capillary, does not take edge effects into account and does not allow calculation of absolute values of viscosity. All of the viscosity values ( $\eta$ ) reported herein are therefore apparent viscosity values, calculated from equation (6).

**Thermal study.** The study was performed on a Pyris 1 power modulation Differential Scanning Calorimeter (Perkin Elmer), equipped with an Intracooler. The measurement cells were purged with dry nitrogen. The temperature was calibrated by use of indium ( $T_f = 156.6^\circ\text{C}$ ) and distilled water ( $T_f = 0^\circ\text{C}$ ). The capsules used for this study were airtight, steel capsules with an O-ring seal. They resisted high pressure (40 bars) and were therefore well adapted for studying weakly hydrated proteins at high temperatures. The SFOC and ESFOC were equilibrated at 60%RH before being tested. The samples weighed approximately 10 mg. Each mixture was tested in triplicate. The measurements were taken during the first scan, between 50 and 200°C. The heating rate was 20°C/min. This high heating rate was used because pans do not always withstand internal pressure (Rouilly et al., 2002).



Production of injection-molded samples. The equilibrated mixtures were injected with a Billion H280/90TP injection press (Oyonnax, France). The temperature of the die was between 110°C and 130°C. The temperature of each unit of the barrel was 10°C lower than that of the previous unit or die. The temperature of the supply tank was fixed at 50°C for all experiments. The resulting materials were in the form of standardized rectangular bars (80 mm x 10 mm x 4 mm) and standardized dumbbells (150 mm x 10 mm x 4 mm) . After conditioning in humidity-controlled chambers until equilibrium (15 days at 60% RH; 25°C), the bars were subjected to flexural strength tests. The standardized dumbbells were used to measure the mechanical properties of the materials during tension tests .

Mechanical properties. A TA-XT2 texture analyzer (RHEO Stable Micro Systems, London, UK) was used to assess the flexural properties of the test specimens. The test samples were 80 mm long and 5 mm wide. Their dimensions were measured at five points with a digital micrometer (model IDC-112B, Mitutoya Corp., Tokyo, Japan) and the mean value recorded to calculate their volume and section. All specimens were weighed to calculate mean apparent density. These bars were then used to measure flexural properties of the material (flexural strength at break ( $\sigma_{max}$ ) and elastic modulus ( $E_f$ )) and for the water uptake experiments. The grip separation was 50 mm and the test speed was 5 mm/min.

An MTS 1/M (MTS Systems France, Créteil, France) apparatus was used for tensile tests. The crosshead speed was 5mm/min and the initial grip separation was 110 mm. The measurement of the force exerted by the apparatus as a function of elongation was used to determine the tensile strength at break ( $\sigma_t$ ) and the Young's modulus ( $E_y$ ) of the injected dumbbells.

Thermal treatment. Four series of five test specimens obtained by injection-molding of extruded and 5% sulfite treated sunflower oil cake (ESTOC) were submitted to a thermal treatment at 200°C, under nitrogen atmosphere, for periods of 5, 15, 30 and 60 minutes. Their mechanical and water resistance properties were then tested.

Water uptake. Rectangular injection-molded bars (80 mm x 10 mm x 4 mm) were weighed and immersed in demineralized water at 25°C. At defined times, the specimens were taken out of the water, their surfaces were dried mechanically and the samples were weighed in a Petri dish to minimize water exchange with the atmosphere. The difference between the initial mass of the dried sample and the mass after immersion was used to calculate the water uptake.

## **Results and Discussion**

Structural analysis. At a macroscopic scale, only coarse fragments of husks were observable (Figure 2A). The husk represents approximately 22% of the mass of the seed while this one consisted of more than 40% oil, localized essentially in the kernel. The husk content of the cake was thus approximately 40% (Table 1). The heterogeneous fragments had a brilliant aspect which could be related to the presence of sugar crystals on their surface, which is in agreement with the important amount of short sugars found by Bach Knudsen (Bach Knudsen, 1997).

By studying these fragments in scanning electron microscopy, the remaining compounds of the kernel (fine parietal fibers, shapeless fragments and protein corpuscles) could be seen on the surface of the strongly organized structure of the husk fragments (Figure 2B). Increasing the magnification to 2500X, two types of protein corpuscles could be highlighted. The isolated protein corpuscles (Figure 2C) had a well-defined spherical shape and a diameter in the range between 2 and 6  $\mu\text{m}$  while other plastids were agglomerated in a non-well-defined-shape

aggregate and had elongated forms (Figure 2D). If the first ones can be identified as spare globulin, the others could be globulins too, but bound to complexes constituted by some denatured albumins and some phenolic compounds formed during the extraction of oil (Shahidi and Nazck, 1992), corresponding then to the definition given by certain authors for sunflower glutelins (Gueyasuddin et al., 1970; Schwenke et al., 1979).

Structural modification. The small and hard particles of SFOC (Figure 3A) were transformed during extrusion into small and soft fiber aggregates (Figure 3B). The bulk density of the extruded sunflower oil cake (ESFOC) decreased from 0.45 after the grinding of the granules to 0.29 after extrusion. The softness of the ESFOC can be attributed to the moistening of the initial mixture and to the defibration of the fibrous fragments of hull.

This forming of the fibrous aggregates could be credibly connected to a complex process of association of the non-cellulosic compounds of the mixture. The globulins were effectively denatured by this treatment (Figure 4). On the differential scanning calorimetry analyses the peak corresponding to the globulin denaturation (at about 160°C for SFOC samples) disappears on the DSC thermogram of the ESFOC. Nevertheless, the temperature of the extruder (Table 1) was lower than the temperature of denaturation measured in DSC for a 30% moisture content (Rouilly et al., 2002). Two reasons could explain this phenomenon: the local temperature rise in zones of higher stress (Micard et al., 2001) and the influence of the shear rate on the phenomenon. Besides, further to the denaturation, the temperature can promote a set of association reactions involving the other protein fractions, the phenolic compounds, possibly the ligneous by-products released by the defibration of the husk fragments and sugars (Maillard reactions) (Arêas, 1992).

In this case, the temperature was too low to allow the formation of numerous covalent bonds such as cysteine bridges. But several weak interactions can occur during cooling, notably hydrophobic interactions involved in protein aggregation (Sanchez and Burgos, 1997) and in the associations of phenolic compounds, which could explain the apparent homogeneity observed on the scanning electron micrographs (Figure 3D). The protein corpuscles of the raw sunflower oil cake (Figure 3C) disappeared after the treatment and the fibers were embedded in a continuous matrix.

The structural modification of SFOC resulted in a substantial reduction in its apparent viscosity (Figure 5). So, after the defibration of the husk fragments and the "fusion" of the protein corpuscles, the ESFOC viscosity at 25%MC was equivalent to the SFOC viscosity at 30%MC. This is really advantageous for the injection-molding process. Firstly, the flow of the mixture being easier, the mold filling is better; and secondly, the less the raw material is wet, the less injection-molded samples will deform during drying.

Like starch (Willett et al., 1995), the hydrated sunflower oil cake was shear-thinning and its viscosity followed a power law model. The improvement of the rheological behavior of the SFOC after extrusion resulted in a significant decrease of the consistency coefficient and in an increase of the pseudo-plasticity index (Table 3). But this index remained low in comparison with those obtained for starch (Parker et al., 1989), resulting from the strong interactions within the polypeptide entanglements. In spite of the increase in temperature, the decrease of the moisture content led to a decrease of the index  $m$ .

Disulfide bond reduction. Cysteine bridges are the only non-peptidic covalent bonds in proteins. Formed by the oxidation of cysteine-thiol groups, they contribute to the stabilization of the three-dimensional structure of proteins. Cysteine bridges of sunflower albumins have been mapped

(Egorov et al., 1996) but those of the globulins have not yet been directly studied. As most of the dicotyledonous globulins have similar structures (Marcone et al., 1998), their concentration must be close to those measured for linseed globulins, that is to say 61.4  $\mu\text{mol/g}$  of proteins (Li-Chan and Ma, 2002). On the whole protein fraction, their concentration is probably close to that measured on the soybean protein isolate, that is to say approximately 70  $\mu\text{mol/g}$  (Kalapathy et al., 1996).

Although the reduction of disulfide bridges also involves decreases in the temperature and the denaturation enthalpy (Li-Chan and Ma, 2002), the treatment was only carried on the ESFOC. The evolution of the ESFOC viscosity according to the amount of reducing agent was similar to that observed in a previous study of the rheological properties of sunflower protein isolate (Orliac et al., 2003). The increase of the sodium sulphite ratio with regard to the mass of protein (Table 1) from 0 to 5% resulted in a progressive decrease of the apparent ESFOC viscosity. Then, when the addition was increased above 5%, the viscosity did not decrease any more, and was even higher when a low shear stress rate was applied to the mixture. This result was attributed to the consequence of the structural changes in proteins during the chemical attack but the mechanism governing this phenomenon has not yet been elucidated.

Extruded sunflower oil cake treated with 5% sodium sulfite (ESTOC) had an optimal rheological behavior. The addition of reducing agent led to a large decrease of the consistency coefficient  $K$  and an increase of the pseudo-plasticity index  $m$  (Table 3). At a moisture content of 25% and a temperature of 120°C, the coefficients of consistency and pseudo-plasticity were, respectively, 310958 and 0.04 for the ESFOC and 9145 and 0.54 for the ESTOC. The rheological behavior of ESTOC is particularly interesting and it would be possible to decrease its moisture content

further. So, while the treatment by extrusion resulted in a 5% decrease in the moisture content of the cake, the treatment with sodium sulphite decreased it at least as much (Figure 5).

Injection-molding. The SFOC with 30% moisture content could be formed by injection-molding. However, due to its lack of "plasticity", the use of a screw without back flow stop valve was necessary. The mechanical constraint engendered by this valve resulted in a local temperature rise and consequently water evaporation. Materials obtained from injection of the SFOC were fragile and needed to be handled with care (Table 4).

The thermo-mechanical and chemical treatments improved the flow of the SFOC (Figure 5) and decreased the amount of water necessary for forming. Materials injection-molded from the ESTOC were denser and more resistant than those obtained from SFOC and from ESFOC (Table 4). In addition, they could be formed in normal conditions used for the injection of thermoplastic materials, with the back flow stop valve.

The mechanical characteristics obtained, and notably the tensile and flexural stress at break values, respectively 12.5 MPa and 37 MPa, were slightly lower than those of commercial starch-based composite materials (Krajewsky and Patzschke, 1999). These materials were brittle when no external plasticizers were used, like all agro-materials (Rouilly and Rigal, 2002).

ESTOC, however, presents a particularly important advantage. Molded samples from ESTOC did not disintegrate when immersed in water at 25°C and reached a maximum of absorption lower than 60% in 24 hours, while the samples injected from ESFOC could not be handled after the same time (Figure 6). The protein matrix seems to have had a thermoset-like behavior rather than a thermoplastic behavior. Heat and shear induced aggregation of proteins involving hydrophobic interactions and disulfide bridges results in the formation of a three-dimensional network (Meng

et al., 2002; Redl et al., 2003). This phenomenon was also responsible for the low proportion of water soluble material in sunflower protein-based films obtained by thermo-molding (Orliac et al., 2002).

This essential property can be used in injection-molding only because the cellulosic fibers contained in the sunflower oil cake prevent the complete cross-linking of the proteins in the injection screw, as occurs during the forming of sunflower protein isolate when a temperature higher than its denaturation temperature is used (Orliac et al., 2003; Wang and Chen, 2002).

Thus, the ESTOC can easily be formed by injection-molding (Figure 7) and the resulting materials are quite water-resistant and can be even less sensitive after a thermal treatment.

Thermal treatment. When a thermal treatment is applied to wood or proteic films, their hygroscopicity can be decreased. In the first case, the treatment is based on the crosslinking of hemicelluloses and ligneous compounds at high temperature and under inert atmosphere (200°C, under nitrogen flow) (Guyonnet, 1998). Above the glass transition temperature of the amorphous biopolymers, this crosslinking reaction is allowed by the mobility of the biopolymer chains and the reactivity of phenolic compounds. The main consequence is the transformation of hemicelluloses, the most hydrophilic polymers, into a network with a more or less hydrophobic character. The amount of crosslinking is low, but the improvement of the physical properties of the material is marked (Tjeerdsma et al., 1998).

In the case of protein films (Gennadios et al., 1996; Micard et al., 2000), the treatment is carried out at lower temperatures than those used in the present study (95-125°C), allowing the denaturation and the coagulation of proteins and the forming of new interactions (hydrophobic and cysteine bridges) in the loose network of films obtained by casting.

When applied to the ESTOC, the thermal treatment should have an influence only on fibers, because the protein network is well established after the forming. However when phenolic compounds interact with proteins, they may form new bonds at higher temperature, even in an inert atmosphere.

The first consequence of the thermal treatment was a loss of mass, which reached 6.4% of the initial mass after equilibration at 25°C and 60% R.H., associated with a decrease of volume. Finally, the apparent density decreased by about 0.1 during the first minutes of treatment (Table 5). In those first minutes, the evaporation of water at this temperature resulted in an irreversible modification of the treated samples.

Overall, thermal treatment led to a decrease of the mechanical resistance of the test pieces; the stresses at break in flexion and in tension decreased by 30% (Table 5), with an increase of their rigidity in the axis perpendicular to fibers, while the module of flexion increased during the treatment. The same consequences were observed during the treatment of the wood (Guyonnet, 1998). This is related to the replacement of water plasticizing molecules by interactions between polymeric chains.

The mechanical resistance loss (Table 5) seemed to stabilize for a cooking duration higher than 3 min/g. For shorter times, the treatment involved first of all the disappearance of a part of the equilibrium absorbed water: at 1.25 min/g, the apparent density after equilibrium at 25°C and 60% R.H. had already fallen to 1.2 and the mechanical resistance decreased greatly (Table 5). On the other hand, the kinetics of water absorption were practically unmodified (Figure 6), indicating that the treatment duration was not sufficient to form new covalent bonds, but only new secondary interactions between chains. Above 3.75 min/g, the mechanical properties did not



seem to be affected further while the water absorption decreased; the plateau absorption was then lower than 40%. It would seem thus advantageous to make a long treatment.

However, from a qualitative point of view, pieces that underwent the treatments of 7.5 and 15 min/g begin to degrade, with darker color and higher water dissolution rate. A duration close to 3 min/g would improve the materials' durability and reduce the probability of their decomposition by biological agents without deterioration of their appearance. This finding has been applied to a practical application: the manufacture of planting out flowerpots from sunflower oil cake (Rouilly et al., 2000).

### **Conclusions and Perspectives**

Sunflower oil cake constitutes a particularly interesting natural composite base for agro-materials manufacture. Cheap raw material and its structure can be modified by thermo-mechanical-chemical treatment, causing defibrillation of the husk fragments and denaturation/coagulation and reduction of the proteic fractions. The resulting composite has interesting flow properties and can be shaped by injection-molding. Its behavior is of thermoset type, as during the molding new disulphide bonds are formed.

The materials obtained are water resistant and this property can be improved further by thermal treatment. However several points still require further research to improve their setting for practical applications:

Firstly, it would be interesting to decrease the quantity of water necessary for injection-molding to its equilibrium value at 25°C and 60% R.H. The use of organic plasticizers would then be necessary.

The thermal treatment has to be optimized. The use of a temperature gradient should make it possible to control the evaporation of gas products, which caused blistering of some of the test pieces. In addition, the temperature of the treatment will have to be studied in relation to the degradation reactions of the components.

The relationship between water absorption in immersion correlated with the heat treatment and soil degradation could be studied. Control of the biological breakdown of the material would be particularly advantageous for the manufacture of planting out pots.

## References

- Arêas, J. A. G., 1992. Extrusion of food proteins. *Critical Reviews in Food Science and Nutrition*, 32 (4), 365-392.
- Ayhllon-Meixueiro, F., Vaca-Garcia, C., Silvestre, F., 2000. Biodegradable films from isolate of sunflower (*Helianthus annuus*) proteins. *Journal of Agricultural and Food Chemistry*, 48 (7), 3032-3036.
- Bach Knudsen, K. E., 1997. Carbohydrate and lignin contents of plant materials used in animal feeding. *Animal Feed Science and Technology*, 67, 319-338.
- Baganz, K., Lang, H., Meissner, G., 1999. Industrial use of oilseed meal : a reasonable injection moulding compound. *Fett/Lipid*, 101 (8), 306-307.
- Bonjean, A. (1993). *Le Tournesol: Les Editions de l' Environnement*.
- Egorov, T. A., Odintsova, T. I., Musolyamov, A. K., Fido, R., Tatham, A. S., Shewry, P. R., 1996. Disulphide structure of a sunflower seed albumin : conserved and variant disulphide bonds in cereal prolamin superfamily. *FEBS Letters*, 396, 285-288.
- Gennadios, A., Ghorpade, V. M., Weller, C. L., Hanna, M. A., 1996. Heat Curing of Soy Protein Films. *Transactions of the ASAE*, 39 (2), 575-579.
- Gonzalez-Perez, S., Merck, K. B., Vereijken, J. M., Van Koningsveld, G. A., Gruppen, H., Voragen, A. G. J., 2002. Isolation and Characterization of Undenatured Chlorogenic Acid Free Sunflower (*Helianthus annuus*) Proteins. *Journal of Agricultural and Food Chemistry*, 50, 1713-1719.
- Gueyasuddin, S., Cater, C. M., Mattil, K. F., 1970. Preparation of a colorless sunflower protein isolate. *Food Technology*, 24, 242-243.
- Guyonnet, R., 1998. Method for treating wood at the glass transition temperature thereof. WO 98/04392.
- Kalapathy, U., Hettiarachchy, N. S., Myers, D., Rhee, K. C., 1996. Alkali-Modified Soy Proteins : Effect of Salts and Disulfide Bond Cleavage on Adhesion and Viscosity. *JAOCS*, 73 (8), 1063-1066.
- Krajewsky, P., Patzschke, H., 1999. Biologisch abbaubar. *Kunststoffberater*, 44 (9), 35-37.
- Leyris, J., 1998. Valorisation du tourteau de tournesol. PhD Thesis, Laboratoire de chimie Agro-Industrielle, INP Toulouse.
- Li-Chan, E. C. Y., Ma, C.-Y., 2002. Thermal analysis of flaxseed (*Linum usitatissimum*) proteins by differential scanning calorimetry. *Food Chemistry*, 77 (4), 495-502.

- Marcone, M. F., Kakuda, Y., Yada, R. Y., 1998. Salt-soluble seed globulins of dicotyledonous and monocotyledonous plants II. Structural characterization. *Food Chemistry*, 63 (2), 265-274.
- Meng, G.-T., K.-M. Ching, and C.-Y. Ma, 2002, Thermal aggregation of globulin from indigenous Chinese legume, *Phaseolus angularis* (red bean). *Food Chemistry* 69, 93-103.
- Micard, V., Belamri, R., Morel, M. H., Guilbert, S., 2000. Properties of Chemically and Physically Treated Wheat Gluten. *J. Agric. Food Chem.*, 48, 2948-2953.
- Micard, V., Morel, M. H., Bonicel, J., Guilbert, S., 2001. Thermal properties of raw and processed wheat gluten in relation with protein aggregation. *Polymer*, 42, 477-485.
- Orliac, O., Rouilly, A., Silvestre, F., Rigal, L., 2002. Effects of additives on the mechanical properties, hydrophobicity and water uptake of thermo-moulded films produced from sunflower protein isolate. *Polymer*, 43 (20), 5417-5425.
- Orliac, O., Silvestre, F., Rouilly, A., Rigal, L., 2003. Rheological Studies, Production, and Characterization of Injection-Molded Plastics from Sunflower Protein Isolate. *Ind. Eng. Chem. Res.*, 42, 1674-1680.
- Parker, R., Ollett, A.-L., Smith, A. C., 1989: *Starch Melt Rheology : Measurements, Modelling and Applications to Extrusion Processing*. COST 91 bis.
- Redl, A., S. Guilbert, and M.H. Morel, 2003. Heat and shear mediated polymerisation of plasticized wheat gluten protein upon mixing. *Journal of Cereal Science*, 38(1), 105-114.
- Rouilly, A., Orliac, O., Silvestre, F., Rigal, L., 2001. DSC study on the thermal properties of sunflower proteins according to their water content. *Polymer*, 42, 10111-10117.
- Rouilly, A., Orliac, O., Silvestre, F., Rigal, L., 2002. Thermal denaturation of sunflower globulins in low moisture conditions. *Thermochimica Acta*, 398, 195-201.
- Rouilly, A., Rigal, L., 2002. *Agro-Materials: A Bibliographic Review*. *Journal of Macromolecular Science, Part C-Polymer Reviews*, 42 (4), 441-479.
- Rouilly, A., Silvestre, F., Rigal, L., Caruel, H., Paux, E., Silvestre, J., Morard, P. (2000): Utilisation de tourteau de tournesol pour la fabrication de pots de repiquage biodégradables. 15th International Sunflower Conference, pp. B-59.
- Sanchez, A. C., Burgos, J., 1997. Gelation of Sunflower Globulin Hydrolysates : Rheological and Calorimetric Studies. *Journal of Agricultural and Food Chemistry*, 45, 2407-2412.
- Schroeder, G. E., Erasmus, L. J., Meissner, H. H., 1996. Chemical and protein quality parameters of heat processed sunflower oilcake for dairy cattle. *Animal Feed Science and Technology*, 58, 249-265.
- Schwenke, K. D., Pahtz, W., Linow, K.-J., Raab, B., Schultz, M., 1979. On seed proteins. Part 11. Purification, chemical composition, and some physico-chemical properties of the 11S globulin (Helianthinin) in sunflower seed. *Die Nahrung*, 23, 241-254.

- Shahidi, F., Nazck, M., 1992. An overview of the phenolics of canola and rapeseed : chemical, sensory and nutritional significance. *J. American Oil Chemists Soc.*, 69, 917-924.
- Tjeerdsma, B. F., Boonsta, M., Pizzi, A., Militz, H., 1998. Characterisation of thermally modified wood : molecular reasons for wood performance improvement. *Holz als Roh- und Werkstoff*, 56 (3), 149-153.
- Wang, S. H., Chen, C.-H., 2002. Soy protein-based chewable pet toy. US 6,379,725.
- Willett, J. L., Jasberg, B. K., Swanson, C. L., 1995. Rheology of thermoplastic starch : effects of temperature, moisture content and additives on melt viscosity. *Polymer Engineering and Science*, 35 (2), 202-210.
- Yu, L., Christie, G., 2001. Measurement of starch thermal transitions using differential scanning calorimetry. *Carbohydrate Polymers*, 46, 179-184.

## Figure Captions

Figure 1. Screw configuration for the SFOC extrusion.

Figure 2. Micrographs of SFOC. A. (x10). B. SEM (x500). C. SEM of globulins (x2500). D. SEM of glutelins (x2500).

Figure 3. Micrographs of SFOC and ESFOC. A. SFOC (x30). B. ESFOC (x30). C. SEM of SFOC (x250). D. SEM of ESFOC (x250).

Figure 4. DSC thermogram of SFOC and ESFOC. Samples equilibrated at 60%RH and 25°C.

Figure 5. Apparent viscosity of SFOC, ESFOC and ESTOC samples at different moisture contents and temperatures.

Figure 6. Mass gain in water at 25°C of ESFOC and thermally treated ESTOC samples.

Figure 7. Examples of objects obtained from sunflower oil cake.

Figure 1. Screw configuration for the SFOC extrusion.

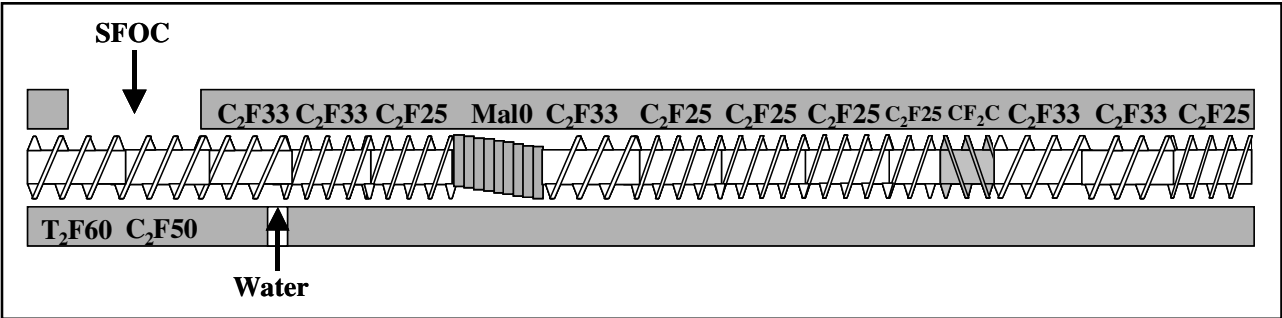


Figure 2. Micrographs of SFOC. A. (x10). B. SEM (x500). C. SEM of globulins (x2500). D. SEM of glutelins (x2500).

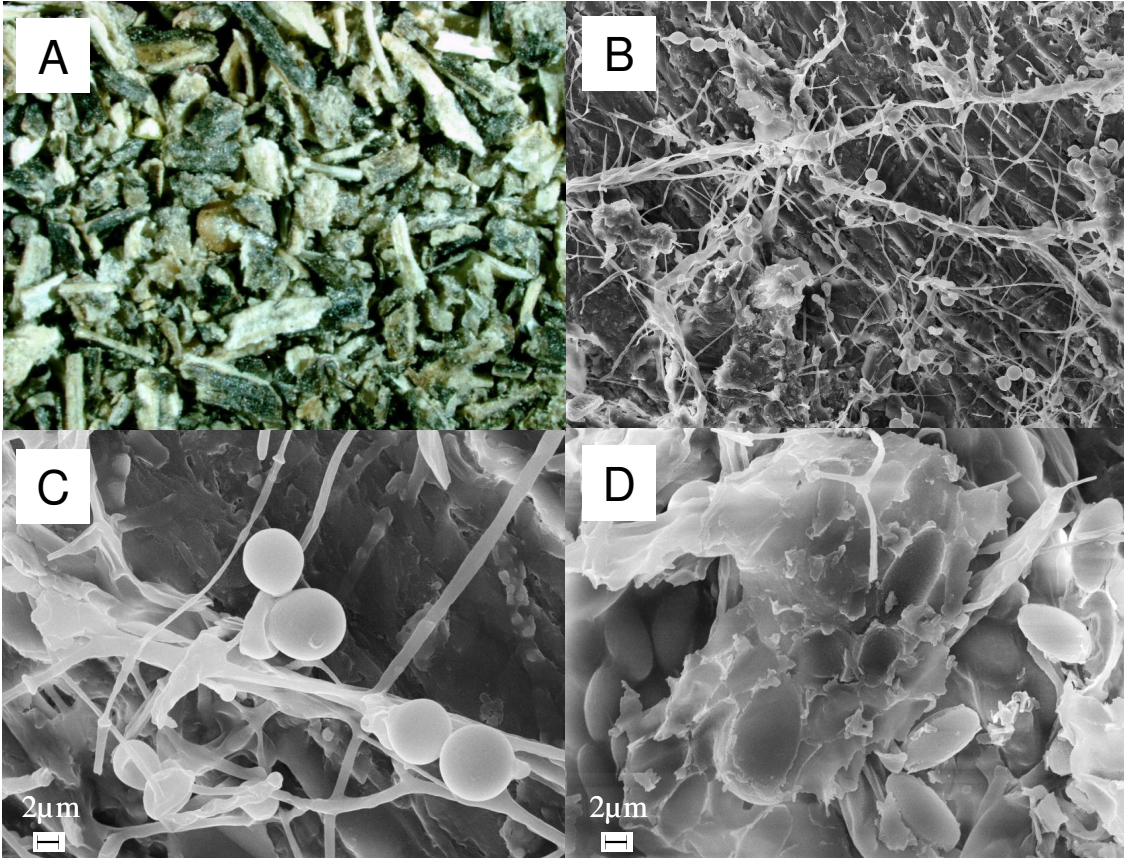




Figure 3. Micrographs of SFOC and ESFOC. A. SFOC (x30). B. ESFOC (x30). C. SEM of SFOC (x250). D. SEM of ESFOC (x250).

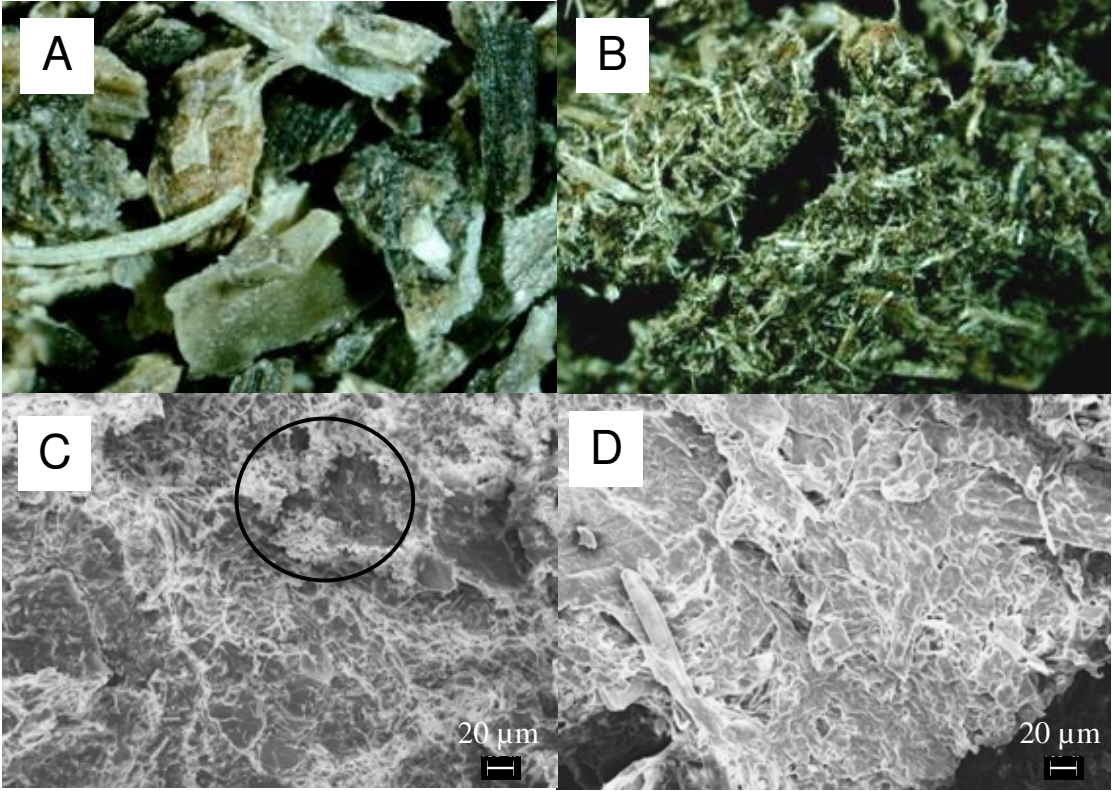


Figure 4. DSC thermogramm of SFOC and ESFOC. Samples equilibrated at 60%RH and 25°C.

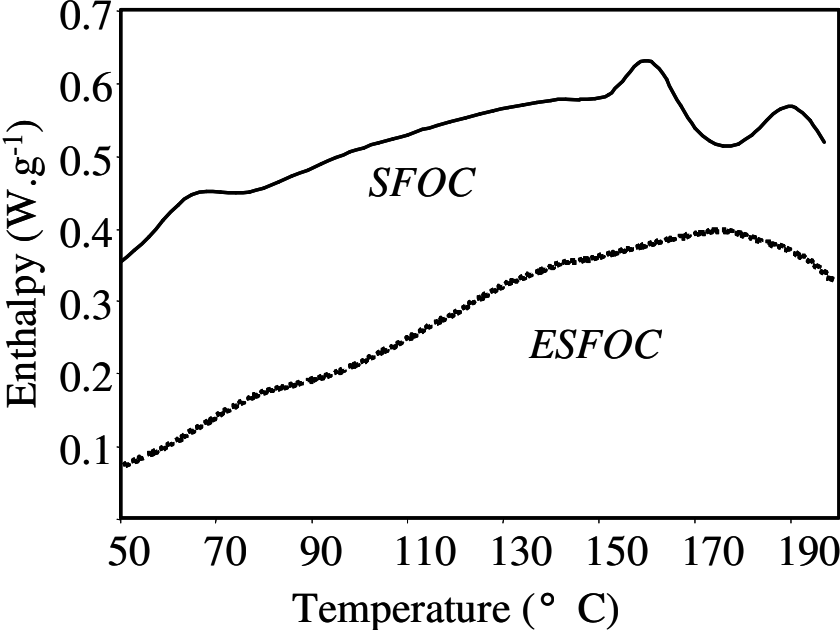


Figure 5. Apparent viscosity of SFOC, ESFOC and ESTOC samples at different moisture contents and temperatures.

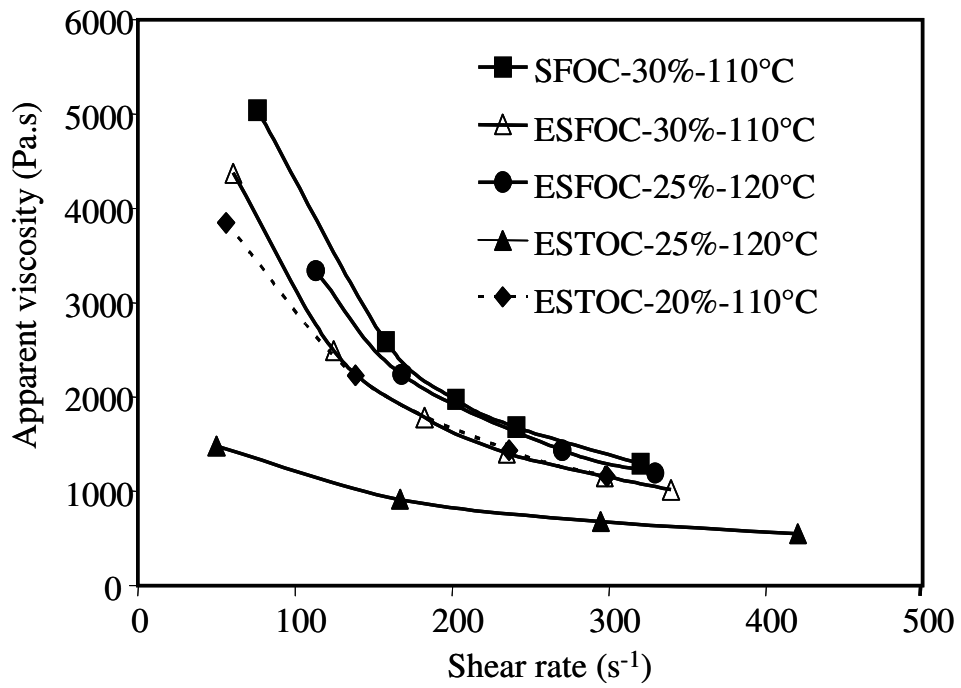


Figure 6. Mass gain in water at 25°C of ESFOC and thermally treated ESTOC samples.

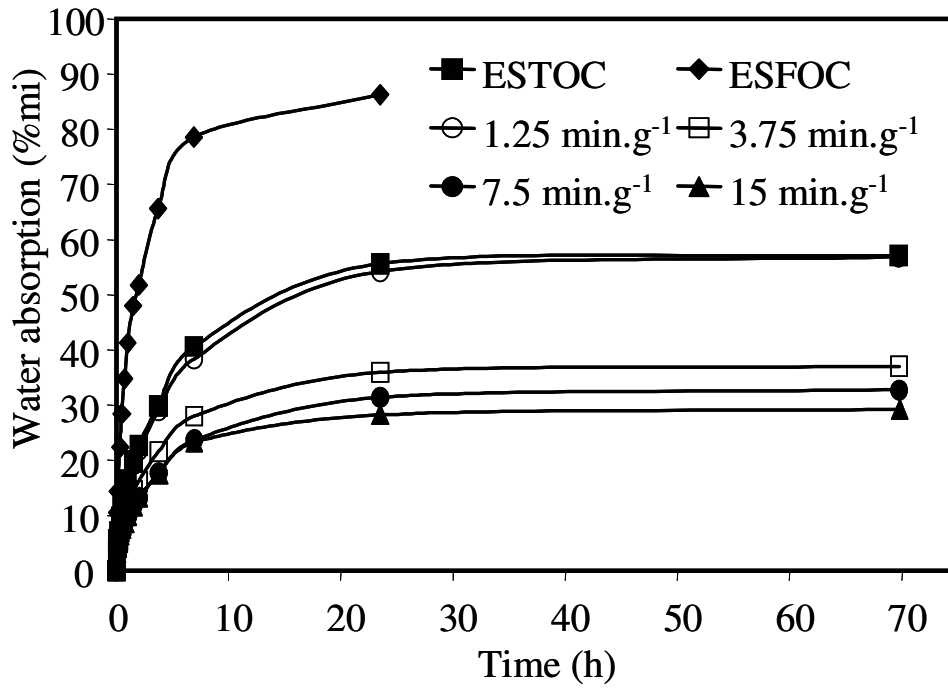


Figure 7. Examples of objects obtained from sunflower oil cake.



Table 1. SFOC composition. <sup>a</sup>(Leyris, 1998). <sup>b</sup>(Bonjean, 1993).

Ligno-cellulosic fibers <sup>a</sup>	37.3%
Cellulose	22.3
Lignin	5.2
Hemicelluloses	9.8
Proteins <sup>a</sup>	35.6%
Globulins <sup>b</sup>	55-60
Albumins <sup>b</sup>	17-23
Glutelins <sup>b</sup>	11-17
Prolamins <sup>b</sup>	1-4
Minerals <sup>a</sup>	7.6%
Phenolics compounds <sup>a</sup>	5.7%
Lipids <sup>a</sup>	1.0%
Water <sup>a</sup>	10.0%

Table 2. Twin-screw extrusion conditions of SFOC.

Parameters	Values
Barrel temperatures (°C)	100
Screw speed (t/min)	200
Solid feed rate (kg/h)	22.3
Liquid feed rate (kg/h)	6.5
Output (kg/h)	26.2
Output moisture content (%)	21.2
Specific mechanical energy (W.h/kg)	277.6

Table 3. Power law coefficients for SFOC, ESFOC and ESTOC viscosity measurements at different moisture contents and temperatures.

	K (Pa.s <sup>m</sup> )	m	R <sup>2</sup>
SFOC-30%-110°C	318640	0.04	0.9994
ESFOC-30%-110°C	147843	0.15	0.9988
ESFOC-25%-120°C	310958	0.04	0.9996
ESTOC-25%-120°C	9145	0.54	0.9923
ESTOC-20%-130°C	70097	0.29	0.9917



Table 4. Injection-molding conditions and mechanical properties in tension ( $\sigma_t$  : stress at break,  $E_y$  : Young modulus ) and bending ( $\sigma_f$  : stress at break,  $E_f$  : bending modulus) of SFOC, ESFOC and ESTOC molded specimens.

	SFOC	ESFOC	ESTOC
Moisture Content (%)	30	25	20
$T_{\max}$ barrel (°C)	50	120	130
T mold (°C)	100	ambient	ambient
Average density	1.09	1.20	1.34
Flexural properties			
$\sigma_{\max}$ (Mpa)	5	11.1 ± 1.4	37.0 ± 3.2
$E_f$ (Gpa)	0.73	1.8 ± 0.3	3.4 ± 0.3
Tensile properties			
$\sigma_{\max}$ (Mpa)	3.4 ± 0.4	9.8 ± 1.2	12.5 ± 2.7
$E_y$ (Gpa)	0.23 ± 0.02	2.0 ± 0.1	2.0 ± 0.1
Remarks	Without back flow stop valve	Teflon® mold cavity	Teflon® mold cavity

Table 5 Mechanical properties in tension ( $\sigma_t$  : stress at break,  $E_y$  : Young modulus) and bending ( $\sigma_f$  : stress at break,  $E_f$  : bending modulus) of thermally treated ESTOC samples .

Time (min/g)	0	1.25	3.75	7.5	15
Density	1.34±0.03	1.21±0.04	1.19±0.06	1.20±0.05	1.16±0.04
$\sigma_f$ (MPa)	37±3	34±4	24±4	27±5	25±2
$E_f$ (GPa)	3.3±0.3	4.4±0.6	3.8±0.6	4.4±0.2	4.2±0.3
Time (min/g)	0	0.55	1.67	3.33	6.67
$\sigma_t$ (MPa)	12.5±2.7	11.5±2.8	8.7±2.6	7.8±1.1	7.4±1.8
$E_y$ (GPa)	2.0±0.1	2.1±0.3	1.7±0.3	1.9±0.3	1.9±0.5