MANUFACTURING PROCESS OF INJECTION-MOLDED AGROMATERIAL FROM SUNFLOWER OIL CAKE

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Abstract

The potential of transformation by injection moulding of sunflower cake depends on its thermomechanical or chemical treatments. Two types of extruder barrel were tested at the same temperature on raw sunflower cake (RSFC). Only one of them efficiently transformed RSFC into a "thermoplastic." The other one involved a too strong modification of the protein structure as indicated in the DSC data. When the sunflower cake was well extruded, a part of its protein was denaturated by the thermomechanical process and its apparent viscosity decreased. This phenomenon was more important after mixing with a plasticizer or a reducing agent. The lower the apparent viscosity was, the more the mechanical properties of injected test specimens were improved because the compaction of matter in the mould was better.

Introduction

During these last decades, the consumption of plastics has shown a huge increase, so their end-of-life has become a great ecological and economical problem. Consequently, the research devoted to the development of biodegradable materials has exploded in the last ten years. Moreover, fossil resources are not endless. It is important to develop new "plastics" from renewable raw materials. Polysaccharides such as cellulose and starch (Doane, 1992; Avérous, 2001) have been very often studied. Proteins have also been studied for many applications, among others a nonfood use as a thermoplastic (Borcherding, 1998). Oilseed meal was first used as a matrix of a thermoplastic polymer (Baganz, 1999). Considering biopolymers, a composite composed only of sunflower cake was created by extrusion (Rouilly, 2002). The purpose of our study was to determine, depending the conditions of extrusion, the physical and chemical modifications of proteins (the main part of sunflower cake) that are responsible for the potential transformation of sunflower cake by injection molding.

Materials and Methods

Sunflower oil cake as a raw material was provided by the company "Toulousaine de Céréales" (Toulouse, France). It is a by-product from the solvent extraction of oil. Sodium sulphite, as a reducing agent (reagent grade), and glycerol were supplied from Aldrich (St. Quentin Fallavier, France). Pellets of raw sunflower cake (RSFC) were ground on a grid plate of 6 mm diameter with an Electra hammer mill.

The initial extrusion treatment of RSFC was conducted with a co-rotating twin-screw extruder (model BC 45, Clextral, France). Six types of screw elements composed the screw profile used for this study. The extruder was built with seven modular barrels: three were heated by induction and all of them were cooled by water circulation. RSFC was fed into the extruder by a volume screw feeder (type 40, Clextral, France). Figure 1 shows the schematic modular barrel of the twin-screw extruder and screw profile tested. The Specific Mechanical Energy (SME) is calculated as follows:

$$SME\left(Wh.kg^{-1}\right)=\frac{\left(torque\times speed\right)}{massflow}=\frac{U\times I\times\cos\phi\times N}{N_{\max}\times Q}$$

where I is the intensity of engine (A), N is the speed of screw rotation (rpm), Q is the mass flow of RSFC feeding (kg/h), U = 460V, $\cos\phi$ = 0.95, and Nmax = 600rpm.

Mixtures of ESFC (extruded sunflower cake) were made using a Perrier 32.00 mixer (Montrouge, France) and they were conditioned in an airtight container until equilibration of moisture content.

Optical microscopy on a binocular microscope (Nikon SMZ 1500) equipped with a digital camera (Nikon DMX 1200) were used to obtain information about the level of structural modification of ESFC. Samples were analysed at their equilibrium moisture content.

Thermal analyses were performed on a Pyris 1 power modulated Differential Scanning Calorimeter (Perkin Elmer). The measurement cells were purged with dry nitrogen. Airtight steel capsules with an O-ring seal were used. The samples of sunflower cake (SFC) were ground on a 1-mm slotted plate of a Cyclotec cutting mill before being equilibrated at 60% relative humidity (RH). Approximately 10 mg of each sample was used and the samples were tested in triplicate. The measurements were taken between 50C and 180C. The heating rate was 10C/min.

A capillary rheometer (Rheomex, Haake PolyLab System, Karlsruhe, Germany) was used to determine the apparent viscosity of the thermoplastic-like material. It is a single-screw extruder equipped with a capillary die (diameter 3-mm, length/diameter 10). The apparent viscosity was calculated from measurable data: mass flow converted into volume flow rate knowing the density and the difference of pressure between atmospheric pressure and pressure in the capillary die.

Normalized test specimens were manufactured by injection moulding (ISO 527-2 for tensile test specimen, ISO 178 for flexural test specimen). Test specimens from ESFCs and RSFC were injected without a backflow stop valve and the mould was heated at 100C. For RSFC, ESFC1 and ESFC1RA, the temperatures of injection were 50, 120 and 130C, respectively.

Tensile tests were conducted with a MTS 1/M apparatus (MTS Systems France, Créteil, France). The crosshead speed was 5mm/min and the initial grip separation was 110 mm. The tensile strength at break (σt) and the Young's modulus (Ey) of injected standard dumbbells were calculated from the measurement of the force exerted by the apparatus as a function of elongation. Flexural tests were conducted with a TA-XT2 texture analyzer (RHEO Stable Micro Systems, London, UK). The grip separation was 50 mm and the test speed was 5mm/min. The flexural strength at break (σmax) and elastic modulus (Ef) were determined from the analysis of test specimens with standardized dimensions.

RSFC feeding

Zone 1		Zone 2		Zone 3		Zone 4		Zone 5		Zone 6			Zone 7	
.		.		100°C		100°C		100°C		100°C			100°C	
T2F60	C2F50	C2F33	C2F33	C2F25	Mal0	C2F33	C2F25	C2F25	C2F25	CF2C	C2F33	C2F33	C2F33	C2F33

water

Profile 1 ➢ $ESFC_1$

RSFC feeding

Zone 1		Zone 2		Zone 3		Zone 4		Zone 5		Zone 6				Zone 7	
.		.		100°C		100°C		100°C		100°C				100°C	
T2F60	C2F50	C2F33	C2F33	C2F25	Mal2	C2F33	C2F25	C2F25	C2F25	C1FT	CF2C	C2F33	C2F33	C2F33	C2F33

water

Profile 2 ➢ $ESFC_2$

Figure 1. Schematic configurations of the extruder barrel for treating RSFC. (Extruder BC 45, Clextral, France).

Results and Discussion

Extrusion treatment modified the structure of sunflower cake. Indeed a simple glance at raw and extruded sunflower cake (RSFC and ESFC, respectively) shows different appearances. That was confirmed by optical microscopy. RSFC is composed of many particles of hull: black on one side and white on the other. Pieces of kernels were also visible. The observations of ESFC show much more dark aggregates than hull particles. ESFC2 obtained under stronger conditions (profile 2, 100C) seems more destructured than ESFC1 (profile 1, 100C). Residual hull pieces are smaller and are less dense. ESFC1 aggregates look more homogeneous than the ESFC2 ones; they look like a paste that contains some little fragments of hull.

Those observations can be correlated with DSC results. For RSFC, the DSC analysis gave a thermogram with a denaturation peak around 152C for a moisture content of 8.5%. This peak corresponding to the denaturation of sunflower globulins (Rouilly, 2003), was still visible on an ESFC1 thermogram but its area was lower. Part of the sunflower protein should be denaturated by extrusion with profile 1 (Figure 1).

The denaturation peak disappeared on the thermogram of ESFC2. Nevertheless the temperature of the extruder was lower than this denaturation temperature. For a moisture content of 30% as during the extrusion, the temperature of denaturation should be around 120C (Rouilly, 2003). A localized self-heating in zone 6 with strong shear stress (CF2C, Figure 1) could explain those different values of temperatures.

Table 1. Physical data relative to the structural modification level of sunflower cake.

	SME ($Wh.kg^{-1}$)	DSC analysis		Rheological behavior	
		Temperature of denaturation (°C)	Peak area ($J.kg^{-1}$)	K (Pa.s)	m
RSFC	.	152	2.144	318640[a]	0.0006[a]
$ESFC_1$	153	153	1.388	147843[a] 295801[b]	0.0012[a] 0.0001[b]
$ESFC_2$	176	.	.	.	.

[a] rheological analysis at moisture content of 30%. [b] Rheological analysis at moiture content of 25%.

This thermal denaturation of SFC proteins during extrusion caused severe modification. Among other things, the rheological behaviour changed. Indeed, Figure 2 shows ESFC1 was less viscous than RSFC for the same humidity content. The capillary rheological analysis was impossible for ESFC2 because this material was too sticky and the feeding was irregular. Thus a plug was created in the die and ESFC2 burned into the plasticizing cylinder and into the capillary die. The modification of apparent viscosity indicated that less water is necessary to transform the ESFC by injection moulding. This is important information for the filling of a mould and the preservation of the form of pieces after stripping.

So, we can understand the importance of the apparent viscosity in injecting SFC with an injection press. Indeed this process is constituted by a plasticizing cylinder for the injection group and a mould. The knowledge of the rheological behaviour of the SFC is important to evaluate the possibility of injection because the material has to go through the injection nozzle and opening of the mould cavity in a molten phase, so it can go through the capillary die. In order to improve the preservation form of moulded pieces, the SFC humidity content should be as low as possible while keeping a viscosity sufficiently low enough for injection conditions.

Consequently to decrease the apparent viscosity, it might be interesting to decrease the water content of SFC. Yet we saw that extrusion allows a decrease in viscosity in the same conditions of moisture content and analysis temperature. Therefore we investigated several treatments of ESFC to improve the flow of this material with a moisture content as low as possible.

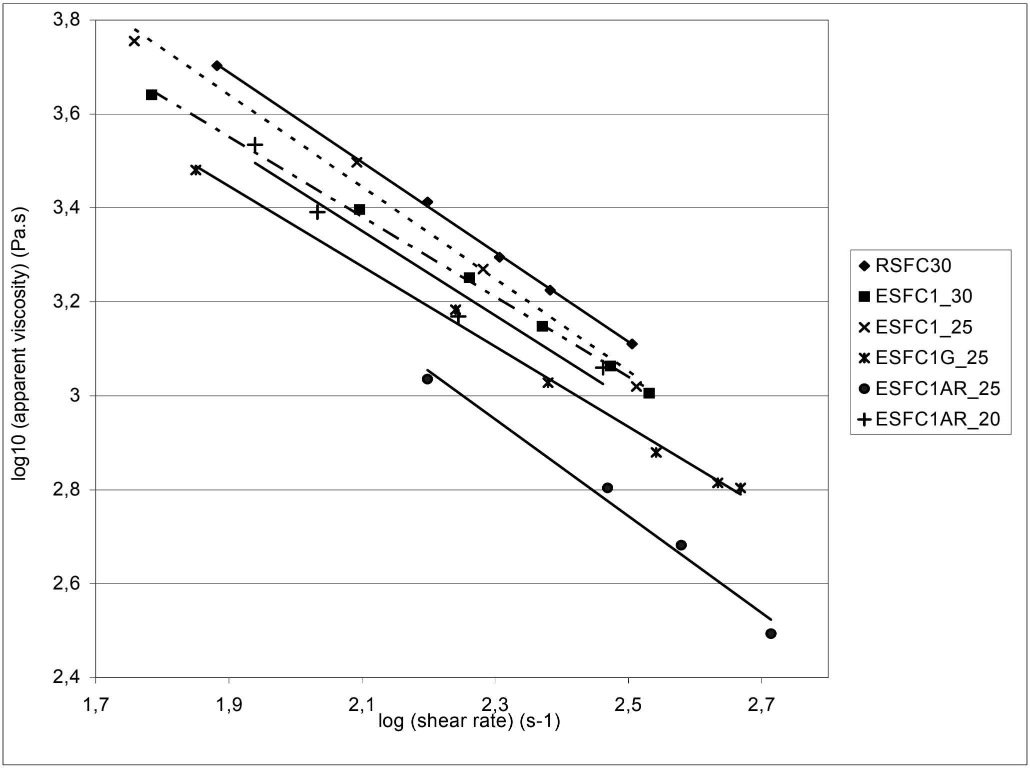

Figure 2. Apparent viscosity as a function of shear rate of sunflower cakes. Sunflower cakes at 30, 25 & 20% of humidity content were respectively analyzed at 110, 120 & 130C. ESFC1G contained 10% of glycerol and ESFC1AR were treated with 5% of sodium sulphite as a reducing agent.

Glycerol is often used as a plasticizer of biopolymers (Sala and Tomka, 1993; Di Gioia, 1998). An addition of 10% glycerol to ESFC1 improves its flow (Figure 2). But the most efficient treatment is the reduction of disulphur bonds with disulphide as a reducing agent. These anions induce a thiol/disulphide exchange reaction and the three-dimensional structure of protein changes (Morel, 2000). An optimum disulphide content of 5% exists to improve the flow of ESFC (Rouilly, 2002).

Table 2. Mechanical properties of injection-moulded test specimens from different sunflower cakes.

	Tensile properties		Flexural properties	
	σ_t (MPa)	E_y (GPa)	σ_{max} (MPa)	E_f (GPa)
RSFC	3.4 ± 0.4	0.23 ± 0.02	5	0.73
ESFC1	9.8 ± 1.2	2.0 ± 0.1	11.1 ± 1.4	1.8 ± 0.3
ESFC1AR	12.5 ± 2.7	2.0 ± 0.1	37.0 ± 3.2	3.4 ± 0.3

Test specimens made from RSFC are much more brittle than the ones from ESFC1 and ESFC1AR. In order to have a flow compatible with the transformation by injection molding, RSFC, ESFC1 and ESFC1AR need to reach a moisture content of 30, 25 and 20%, respectively. The RSFC is less “plastic” than ESFC1 and ESFC1AR (Figure 2), and its consistency is higher (Table 1). The “texturization” of proteins was much improved with a disulphide treatment allowing a better flow in the mould. And the easier the flow, the better the compaction of this agromaterial in the mould and the higher the mechanical resistance.

Conclusions

The by-product of common industrial extraction of oil from sunflower seeds presents interesting properties for its transformation by injection moulding. When this sunflower cake is extruded in a first step, its flow is improved only if the condition of extrusion is rather soft. Indeed the protein denaturation has to be partial, otherwise the ESFC becomes too sticky and the feeding of the plasticization screw of the extruder or injection press is no longer possible. A satisfactory flow with low moisture content is obtained by mixing ESFC with a plasticizer or even with disulphide. Mechanical properties are also improved with extrusion treatment and disulphide reduction, and they are even linked to rheology. We can forecast a further decrease in the moisture content of ESFC in order to realize injected-moulded pieces of good quality: compounds of ESFC seem to be a interesting way of work.

References

Avérous, L., Fringant, C., and Moro, L. 2001. Starch-based biodegradable materials suitable for thermoforming packaging. Starch/Stärke. 53:368-371.

Baganz, K., Lang H., and Meissner, G. 1999. Industrial use of oilseed meal: a reasonable injection moulding compound. Fett/Lipid. 101:306-307.

Borcherding, A., and Luck, T. 1998. Application of plant proteins as thermoplastics. *In*: Proteins from European Crops. Springer, Berlin, Germany. p. 313-318.

Di Gioia, L. 1998. Obtention et étude de biomatériaux à base de protéines de maïs. Ph.D. Thesis, Ecole National Supérieure Agronomique de Montpellier, Montpellier, France.

Doane, W. M., Swanson C. L., and Fanta, G. F. 1992. Emerging polymeric materials based on starch. Ch. 13 in Emerging technologies for materials and chemicals from biomass. ACS Symposium series 476, USA. . p. 197-230.

Morel, M.H., Bonicel, J., Micard, V., and Guilbert, S. 2000. Protein insolubilization and thiol oxidation in sulfite-treated wheat gluten films during aging at various temperatures and relative humidities. J. Agric. Food Chem. 48:186-192.

Rouilly, A. 2002. Nouveaux agro-matériaux composites à matrice protéique ou polysaccharidique: étude du fractionnement, de la transformation et de la mise en forme par extrusion et par injection-moulage de la pulpe de betterave et du tourteau de tournesol. Ph.D. Thesis. Institut National Polytechnique de Toulouse, Toulouse, France.

Rouilly, A., Orliac, O., Silvestre, F., and Rigal, L. 2003. Thermal denaturation of sunflower globulins in low moisture conditions. Thermochimica Acta. 398:195-201.

Sala, R., and Tomka, I. 1993. Water uptake in partially frozen and plasticized starch. J. M. V. Blanshard and P. J. Lillford (eds). The Glassy State in Foods, Nottingham University Press. p. 483-489.