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Sunflower Cake as a Natural Composite: Composition and Plastic Properties

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Nowadays, the end-of-life of plastic products and the decrease of fossil energy are great environmental problems. Moreover, with the increase of food and nonfood transformations of renewable resources, the quantities of agro-industrial byproducts and wastes increase hugely. These facts allow the development of plastic substitutes made from agro-resources. Many researches show the feasibility of molding biopolymers extracted from plants like a common polymeric matrix. Other natural macromolecules are used like fillers into polyolefins, for example. However, limited works present results about the transformation of a natural blend of biopolymers into a plastic material. The aim of this study is the determination of the composition of sunflower cake (SFC) and also the characterization of its components. These were identified by chemical and biochemical analysis often used in agricultural or food chemistry. Most of the extraction and purification processes modify the macrostructure of several biopolymers (e.g., denaturation of proteins, cleavage or creation of weak bonds, etc.). So, the composition of different parts of the sunflower seed (husk, kernel, and also protein isolate) was determined, and the plasticlike properties of their components were studied with thermogravimetric analysis, differential scanning calorimetry, and a dynamic mechanical thermal analysis apparatus. Finally, this indirect way of characterization showed that SFC can be considered a natural composite. In SFC, several components like lignocellulosic fibers [40%/dry matter (DM)], which essentially come from the husk of sunflower seed, can act as fillers. However, other biopolymers like globulins (~30% of the 30% of sunflower seed proteins/DM of SFC) can be shaped as a thermoplastic-like material because this kind of protein has a temperature of glass transition and a temperature of denaturation that seems to be similar to a melting temperature. These proteins have also viscoelastic properties. Moreover, SFC has similar rheological properties and other physicochemical properties compatible with shaping or molding behaviors of plastic-processing machinery.

KEYWORDS: Sunflower cake; chemical composition; sunflower protein; TGA; DSC; viscoelastic properties; biopolymers; water uptake; natural biocomposite

INTRODUCTION

Since the middle of the 20th century, the rapid development of the plastics industry has led to the extensive use of plastics and, consequently, numerous environmental problems (pollution, sorting, recycling, and greenhouse effects). These difficulties linked to the manufacturing and to the end-of-life of common plastics have given rise to the development of green biodegradable plastics and/or plastics made from renewable raw materials such as those derived from agroresources. Several studies show the feasibility of shaping biocomposites (*1*−*5*), bioplastics (*6*−*9*), and agromaterials (*10, 11*). Many of them use only one or two extracted and purified biopolymers that have been subjected to extensive chemical, biochemical, and physicochemical analyses. Comparatively few studies have been devoted to the plastic properties of whole agro-industrial byproducts with regard to their transformation into agromaterials (*10, 12, 13*).

Sunflower cake (SFC) is currently used in animal feed, but it has lower nutritional value for cattle feed than other oilseed crop cakes (canola, rapeseed, and soybean) (*14, 15*). Nevertheless, on the basis of the estimated future production of sunflower oil for industrial uses (biolubricants, biosolvents, and biofuel), the production of SFC will increase, and it will be necessary to find other means of valorisation. Ayhllon-Mexueiro et al., Orliac et al., and Rouilly et al. show the film-forming ability of sunflower protein isolate (SFPI) by casting (*16*), by thermo-

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molding (*17*) or injection molding (*18*), and by extrusion (*19*), respectively. The feasibility of shaping pieces from only SFC by injection molding has been demonstrated by Rouilly et al. (*20*).

The chemical composition of sunflower seeds, defatted flour, or oil cake is generally provided when these ingredients are used for animal feed. The aim of our work was to study the chemical/biochemical composition of industrial SFC and its physicochemical properties to complete earlier studies about thermal and rheological properties of sunflower proteins (*18, 21, 22*) that were carried out to demonstrate the plastic properties of this agro-industrial byproduct. Plastic properties depend on the structure of polymers (e.g., molecular weight, polymerization degree, branching degree, degree of crystallinity, etc.). As extraction and/or purification processes could modify the macro- and/or microstructure of biomacromolecules, the characterization of their plasticlike properties is not so easy. Then, an indirect method was carried out by studying several fractions of sunflower seed. After determining and comparing the compositions of SFC, sunflower husks (SFH), sunflower defatted kernel flour (SFKF), and SFPI, as well as the protein composition of SFC, their physicochemical properties, their water adsorption isotherms, and their thermal and viscoelastic properties were characterized. The sum of results will allow us to conclude that SFC has a plasticlike behavior, and it makes it possible to attribute different kinds of sunflower biopolymers to the matrix or to the filler fraction of this natural composite.

MATERIALS AND METHODS

Materials. Industrial SFCs, SFC1, SFC2, and SFC3, were prepared at the SAIPOL crude sunflower oil refinery (Sète, France) from the 1995, 2002, and 2003 sunflower seed harvests, respectively. They were supplied by Toulousaine de Céréales (Baziège, France). SFC pellets were ground using a hammer mill.

Sunflower seeds, which were harvested in 2003 by the agricultural marketing cooperative, were manually husked. SFH and sunflower kernels were then obtained. Those kernels were ground with a mortar, their oil was extracted with a Soxhlet extractor with cyclohexane (>97%, Fluka, France), and residual oil was extracted from kernel flour in the same way. SFKF was dried under air flow at ambient temperature.

SFPI was obtained by alkaline extraction (in aqueous NaOH solution at pH 12.0 and 50 °C for 20 min) from ground SFC (solid/liquid ratio, 1/20). After centrifugation, the soluble proteins were precipitated at their isoelectric point by the addition of sulfuric acid at pH 5.0. A second centrifugation then allowed their separation from the aqueous phase. The third stage consisted of drying SFPI at 50 °C (*17, 23*).

Methods. *Determination of SFC Composition.* Dry matter, ash, and water-soluble contents were determined by gravimetric methods. The dry matter content of cake, husk, defatted kernel flour, and protein isolate from sunflower was determined by weight difference before and after drying in a ventilated oven at 103 °C for 12 h. The ash content was determined according to the standard, NF V 03-922: 1 g of matter was placed in a furnace at 550 °C for 5 h. The water-soluble content was determined by introducing 1 g of matter into 100 mL of distilled water. This mixture was boiled for 1 h and then filtered and dried in an oven (103 °C, 12 h). The water-soluble matter is the difference between the mass of the dried matters of initial material and the mass of dried residue.

Hemicelluloses, cellulose, and lignin contents were obtained by the acid detergent fiber−neutral detergent fiber method, adjusted by Van Soest and Wine (*24*−*26*). Residual lipids were extracted with a Soxhlet extractor with cyclohexane (>97%, Fluka, France) and then dried and weighed according to the standard, NF ISO 0734-1. The protein content was calculated from the nitrogen total content (NTK) determined by a Kjeldahl assay (procedure detailed in NF V 18-100). The NTK was multiplied by 6.25, the coefficient for sunflower seed flour and cake.

Globulin, albumin, glutelin, and prolamin contents were obtained by selective solubilizations according to Osborne and Campbell's classification (*27*) and Kjeldahl assays. Globulins, albumins, glutelins, and prolamins were extracted with 1 M NaCl, NaOH at pH 11.0, distilled water, and aqueous ethanol at 70% (stirring for 30 min at room temperature), respectively.

Sodium Dodecyl Sulfate−Polyacrylamide Gel Electrophoresis (SDS-PAGE). Sunflower extractible proteins were studied by SDS-PAGE electrophoresis. They were extracted in phosphate buffer at pH 6.9, with a solid/liquid ratio of 1/20 (w/v) at 50 °C. After 2 h of extraction, the mix was centrifuged, and a Kjeldahl assay was made on the supernatant to calculate the yield of sunflower protein extraction in phosphate buffer with or without 2% SDS (SDS for electrophoresis approximately 99%, Sigma Aldrich, France). SDS-PAGE contained 12% polyacrylamide. The range of studied proteins was therefore 6.5 and 205 kDa that was the same molecular mass range of the SigmaMarkers Wide Range M4038 (Sigma Aldrich, France).

Phenolic compounds were obtained by UV spectroscopic assay of chlorogenic acid with Folin−Ciocalteu reagent. Chlorogenic acid was the main phenolic acid of the sunflower seed and, therefore, of SFC (59.6%/total phenolic acids) (*28, 29*). Phenolic compounds were first extracted from sunflower matter with an acetone/water mixture (v/v 60/40) used as a solvent. This extraction took place under stirring at ambient temperature for 2 h. The extract was collected after centrifugation. It was necessary to repeat this extraction five times to obtain the impoverishment of phenolic components from SFC solid matter. All extracts were mixed and concentrated by distillation under vacuum. This concentrated extract was diluted in distilled water for the chlorogenic acid UV assay at a 760 nm wavelength with Folin−Ciocalteu reagent.

Characterizations of SFC Components. Physical and Chemical Characterizations. The bulk densities of SFC, SFKF, and SFH were measured using a Densitap ETD-20 (Granuloshop, France). A 250 mL glass cylinder was filled, and the sample mass was plotted (W). This full glass cylinder was fixed onto a Densitap ETD-20 that beats the sample 1500 times at 250 strokes per minute. When the sunflower powder was compacted, the volume was plotted (V_f), and the bulk density was calculated as follows:

$$d_b = W/V_f \quad (1)$$

The particle size distribution of sunflower materials was obtained with standardized sieves ranging from 63 to 1600 μm (ASTM). The sieves were piled onto the stirring base (Tamisor). Two hundred grams of sunflower powder was placed in the 1600 μm sieve, and the sieve column was stirred for 10 min.

The swelling rate (τ) was determined by introducing 20 g (W_{SF}) of SFC equilibrated at ambient room temperature into a glass cylinder. Aqueous NaOH (controlled pH, ambient temperature) was gradually added until the first supernatant drops appeared. The absorbed liquid volume (V_a) was plotted, and the swelling rate was calculated as follows:

$$\tau = V_a/W_{SF} \quad (2)$$

Microscopic observations were carried out by a Nikon SMZ 1500 binocular microscope equipped with a Nikon DMX 1200 digital camera.

Adsorption Isotherms. Vapor sorption was carried out using dynamic vapor sorption (SMS, United Kingdom). Before the test, samples were dehydrated for 3 days under vacuum at 60 °C with P_2O_5 as a desiccant. The dynamic vapor sorption optimized the 10 mg sample dehydration for 120 min at 60 °C and 0% relative humidity before plotting the sample weight at 25 °C and 0% relative humidity. The apparatus plotted eight sample weights at 25 °C and from 0.0 to 92.0% relative humidity with a step program. The relative humidity step changed when $(dm)/(dt) \leq 5.10^{-4}$ g min^{-1} for at least 5 min or when the relative humidity step reached 10 h.

Thermal Stability. Thermogravimetric analysis (TGA) and thermal differential analysis (TDA) were carried out with TGA/TDA Setaram 92-16.18 (France) under air flow. The assay conditions were as follows: isotherm at 20 °C for 2 min and heating from 20 to 600 °C at 10 °C min^{-1}. Ten milligrams of equilibrated samples was introduced into the apparatus, and the measurements were plotted during the heating.

Thermal Properties. The differential scanning calorimetric (DSC) study was carried out using a Pyris 1 power compensation calorimeter

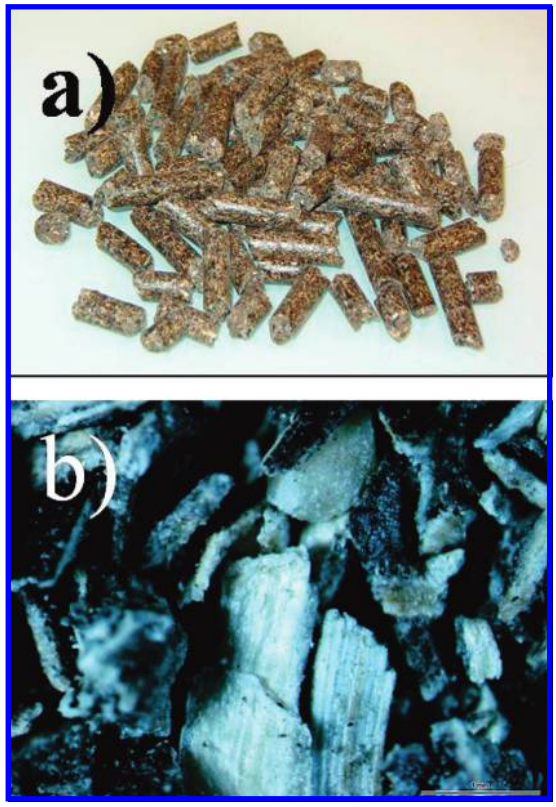

Figure 1. SFC pictures: (**a**) SFC pellets and (**b**) crude ground SFC (optical microscopy 30×).

(Perkin-Elmer) equipped with an Intracooler cooling system as described by Rouilly (*21, 22*)

Viscoelastic Properties. Dynamic mechanical thermal analysis (DMTA) was carried out using a Dynamic Mechanical Analysis Triton. Sunflower powder samples were first dehydrated at 60 °C under vacuum with P_2O_5. The powder was then introduced into a special metallic pocket (30 mm × 7 mm × 1.3 mm) that is inert with respect to material relaxations. A single cantilever method was used. The displacement of one of the both clamp was 50 μm at 1 Hz, and the range of temperature was from 0 to 250 °C with a gradient of 3 °C min^{-1}.

Rheological Properties. A Rheomex single screw extruder (Haake Polylab System, Karlsruhe, Germany) equipped with a capillary die (L/D = 10; D = 3 mm) was used for rheological measurement as described by Rouilly et al. (*20*). The temperature of the die was 120 °C. The screw speed was between 30 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 online acquisition of the system characteristic units (output, temperature, and pressure).

To realize the measurement under SFC powder, its moisture content had to be adjusted at 30% by amounting water. After mixing, a rest time was necessary to reach a good equilibrium.

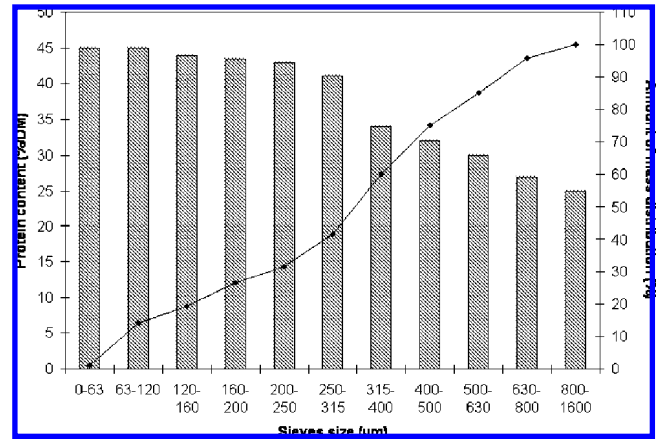

Figure 2. Mass distribution of ground SFC and the protein content of each fraction.

RESULTS AND DISCUSSION

Sunflower Material Composition. *SFC Composition.* Industrial strawy SFCs were obtained using a common industrial oil extraction process from whole sunflower. This raw material consists of husk particles and defatted kernel agglomerates as shown in **Figure 1**.

The composition of the three SFC batches is described in **Table 1**. The SFC composition is considerably stable even if intrinsic and extrinsic factors (genetic, climate, soil, and extraction process) may induce some little variations in the composition. The main part of the SFC is made of cell wall components such as lignocellulosic fibers (around 40%/dry matter). The second major part is represented by protein fractions (around 30%/DM). The other 30% is made up of many other components that contribute to the matrix or to the fillers, many of which are water-soluble. **Figure 2** shows that the smallest particles are mostly made of proteins: Below 315 μm, fine particles contain more than 40% proteins; beyond this size, a significant decrease of protein content can be seen. Optical microscopic observations make it possible to count both fractions of the seed (**Table 2**); they confirm the kernel origin for the majority of sunflower proteins.

The mass distribution of husk and kernel in sunflower seed is approximately 23.5 and 76.5%, respectively. However, the kernel is defatted in SFC: It loses 66.6% of its weight. Therefore, the mass distribution of husk and defatted kernel in SFC is approximately 50% for both.

SFH and SFKF Compositions. The compositions of SFH and SFKF are shown in **Table 3**. With regard to its composition, SFC can be considered as the amount of SFH and SFKF with the same mass contribution. **Table 3** shows that 88% of the SFC fibers come from the husk and that 90% of its proteins

Table 1. SFC Composition

	methods	SFC1	SFC2	SFC3
moisture content at equilibrium (%/total dry matter)	NF V 03-903	9.9	11.0	10.3
components (%/dry matter)				
proteins	NF V 18-100	35.0	29.4	31.5
cellulose	ADF-NDF (Van Soest and Wine)	18.3	24.2	25.1
lignins		9.1	8.1	8.0
hemicelluloses		10.9	15.4	12.5
lipids	NF ISO 0734-1	1.5	1.3	3.2
chlorogenic acid	UV spectroscopy (Folin−Ciocalteu reagent)	2.7	2.9	
phenolic acids	estimated	4.5	4.9	
water-soluble components	boiled water	24.9	22.4	21.2
ash	NF V 03-922	7.2	7.0	7.1

Table 2. Distribution of Husk and Defatted Kernel Particles in Each Fraction of Ground SFC[a]

fraction size (μm)	63−120	120−160	160−200	200−250	250−315	315−400	400−500	500−630	630−800	800−1600
husks (%)	35	33	42	47	52	57	62	64	72	86
undefined (%)	17	13	16	16	15	14	13	14	11	6
defatted kernel (%)	48	54	42	37	33	29	25	22	17	9

[a] Below 63 μm, the particles are too small to be counted.

Table 3. SFH and SFK Composition and the Comparison of the Proportion from the Seed in the Case of SFC

components (%/DM)	methods	SFH	SFK	SFH + SFK	SFC3	SFPI (*17*)
proteins	NF V 18-100	2.4	28.2	30.6	31.5	90.0
cellulose	ADF-NDF (Van Soest and Wine)	21.3	2.6	23.9	25.1	0
lignins		10.8	0.9	11.7	8.0	1.7
hemicelluloses		8.1	2.2	10.3	12.5	0
lipids	NF ISO 0734-1	2.4	0.0	2.4	3.2	0.6
water-soluble components	boiled water	4.3	16.8	21.0	21.2	
ash	NF V 03-922	1.4	4.4	5.8	7.1	2.4

come from the kernel. This last result confirms the optical microscopic observations and mass distribution as compared with its protein content described above. The other 30% of SFC are mainly water-soluble components as well as some cell wall polysaccharides from the kernel and residual lipids and ash.

SFC is the sunflower seed without its own oil. Its composition is divided into equal parts of SFH and SFKF. Its main components are lignocellulosic fibers (40%/DM) and proteins (30%/DM). Lignocellulosic fibers mainly come from the seed husk and proteins come from the kernel. A large part of the other 30% is water-soluble components. By analogy with the use of lignocellulosic fibers into a common polymeric matrix, this mainly components of SFH can be considered as the greatest part of filler into SFC.

SFPI Composition. As described by Orliac, SFPI contains 90% proteins, 4.8% phenolic acids, 2.4% ash, 1.7% lignin, and 0.6% lipids, and its moisture content is approximately 6% (*17*). Cellulose and hemicelluloses are eliminated, but a few lignins and lipids are extracted during the protein extraction. Phenolic acids can bind with proteins, giving SFPI its typical green-brown color.

SFC Protein Composition. First, the protein composition of SFC was determined by the selective extraction of proteins as described by Osborne and Campbell. **Table 4** presents this protein distribution. There are few results available on the protein composition of SFC in the literature. Most of the results are given for sunflower dehusked cake meal or defatted meal, rather than for industrial strawy SFC. Gueyasuddin showed that sunflower meal proteins contain 56.2% globulins, 17.0% glutelins, 22.0% albumins, 1.3% prolamins, and less than 4.0% insoluble proteins (*14*). For Sammour et al., this protein distribution is as follows: 39.0% globulins, 17.1% glutelins, 38.3% albumins, and 5.5% prolamins (*30*). The protein distribution of the used industrial strawy SFC is very different. One of the reasons might be the origin of the product: Sunflower meal comes from the defatted kernel alone, whereas SFC comes from a mixture of equal parts of SFH and defatted kernel. Moreover, the sunflower meal and SFC are obtained by laboratory and industrial oil extraction processes, respectively. In the case of the used SFC, thermal and mechanical treatments may have modified several properties as well as the structure of proteins. This hypothesis could explain the very low content of recoverable albumins (<1%) and the high insoluble protein content (>35%) (*14, 30, 31*). **Table 5** shows the amino acid composition of SFC. For a total of 18 amino acids, the proportion of hydroxyproline is significant (3.8%). This amino acid is specific to plant cell wall proteins such as extensine, and this parietal protein is classified with albumins, proving the presence of a high proportion of albumins in SFC proteins that cannot be solubilized by distilled water at room temperature.

Table 4. Protein Distribution According to the Classification of Osborne and Campbell[a]

protein class (%/total proteins)	solvents	SFC1	SFC2	SFC3
globulins	1 M NaCl	28.9	29.2	34.4
glutelins	NaOH, pH 11.0	17.3	25.3	23.2
albumins	distilled water, pH 6.5	0.7	0.2	0.2
prolamins	aqueous ethanol, 70%	2.1	3.2	3.0
insoluble proteins		51.0	42.1	39.2

[a] Stirred for 2 h at room temperature.

Table 5. Amino Acid Composition of SFC Proteins

	Asp-Asn	Glu-Gln	Ser	His	Gly	Thr	Ala	Arg
SFC	91	163	54	20	107	42	71	61
globulins	90	203	58	18	118	33	58	73
albumins	119	92	46	18	46	37	101	83

	Tyr	Cys	Val	Met	Phe	Ile	Leu	Lys	Pro	Hyp
SFC	20	25	57	13	42	45	67	26	55	38
globulins	18	20	38	15	38	33	55	28	68	40
albumins	18	0	46	9	37	46	55	46	100	100

Nonselective Extraction of SFC Proteins. In a second phase, the effect of pH on the efficiency of nonselective protein extraction was studied. A phosphate buffer at pH 6.9 and a borax buffer at pH 9.0, with or without 2.0% SDS (for electrophoresis, Sigma Aldrich, France) were tested. The protein extraction yield is lower at pH 6.9 than at pH 9.0 (**Table 6**), but the balance is better with phosphate buffer at pH 6.9. This buffer makes it possible to avoid the gelation of extracted proteins, which is not the case with a buffer at pH range from 7.0 to 11.0 (*32, 33*). Phosphate buffer with 2% SDS extracts all soluble proteins (**Tables 4** and **6**). It also makes it possible to double the protein extraction yield in comparison with the phosphate buffer. In SFC, the protein network could be maintained by weak bonds such as hydrogen or hydrophobic bonds.

SDS-PAGE Electrophoresis Nonselective Extracted Proteins from SFC with Phosphate Buffer at pH 6.9. Twelve percent SDS-PAGE gel allows the separation of the majority of the sunflower protein subunits and of the little sunflower proteins such as albumins or oil body membrane protein (*34*). With this 12% SDS-PAGE gel, the native helianthinin 15 S $\{([\alpha\beta]_6)_n\}$ and 11 S $([\alpha\beta]_6)$ forms with molecular masses of 600 and 300−350 kDa, respectively, cannot be analyzed (*35*−*37*). This electrophoresis is able to separate proteins with molecular masses of between 6.5 and 205 kDa. We could thus analyze proteins ranging from 7 S globulin ($[\alpha\beta]_3$, M_w = 190 kDa) to

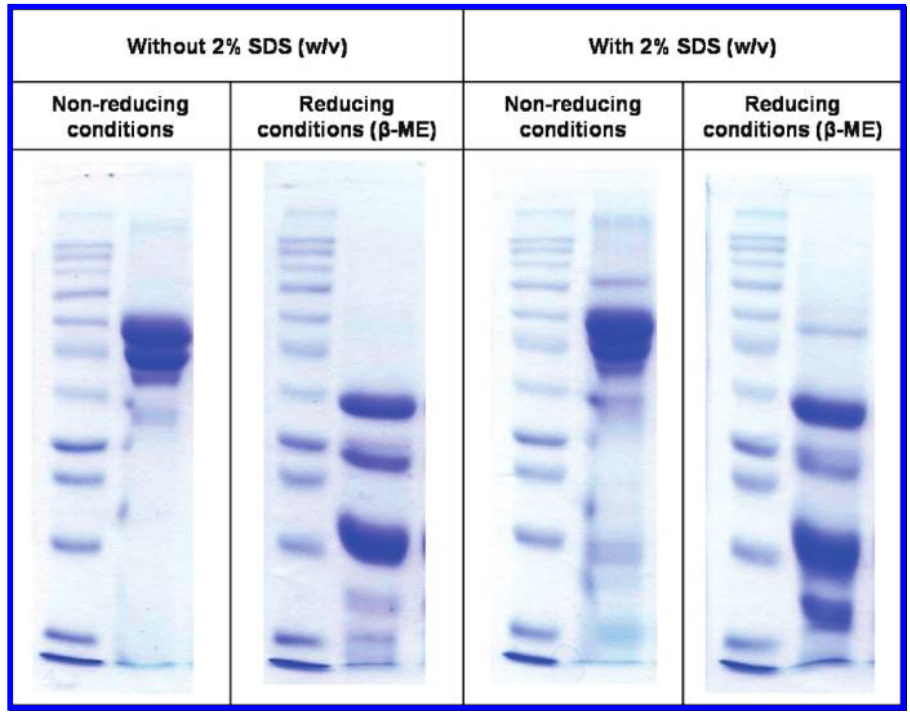

Figure 3. SDS-PAGE electrophoresis gels of SFC protein extracts (phosphate buffer, pH 6.9). To the left of the gels, M4038 Sigma wide range protein markers from 6.5 to 205 kDa (from the bottom to the top: 6.5, 14.2, 20, 24, 29, 36, 45, 55, 66, 84, 97, 116, and 205 kDa).

α- or β-polypeptides or other small proteins. **Figure 3** shows different classes of proteins. The two gels obtained under nonreducing conditions show some bands around 80 and 115 kDa, but these proteins cannot be identified from the literature. Probably, they are protein agglomerates formed during the industrial oil extraction process. With 2% SDS in the extraction buffer and under nonreducing conditions, the band at 115 kDa is more visible because big protein agglomerates would be more dissociated by the 2% SDS in the phosphate buffer. However, most of the proteins have a molecular mass of around 62, 60, 54, 52, 48, 46, 40, and 39 kDa. They should come from of the dissociation of 15 and 11 S sunflower globulin, and the 57 kDa band results from the dissociation of the 7 S sunflower globulin. These polypeptides are 2−3 S dimmers ([αβ]) (*19, 20*). Without SDS in the extraction buffer SDS-PAGE gel, other bands can be seen as follows: 40 and 45 kDa and 35 and 32 kDa may be α- and β-polypeptides, respectively (*37, 38*). With SDS in the extraction buffer, these same bands are observed more intensely as well as new bands around 15−17 and 10 kDa that may be albumins (*39*).

For both protein extracts, electrophoresis under reducing conditions confirms that the majority of extracted proteins could be attributed to the globulin fraction as well as to the albumin fraction in the presence of SDS in the extraction buffer. This result explains the very low proportion of extracted albumin (**Table 4**): The industrial oil extraction process could allow the agglomeration of albumins in a network maintained by weak bonds (*40*).

The most common proteins are globulins and albumins, even if these albumins became insoluble as a result of the industrial

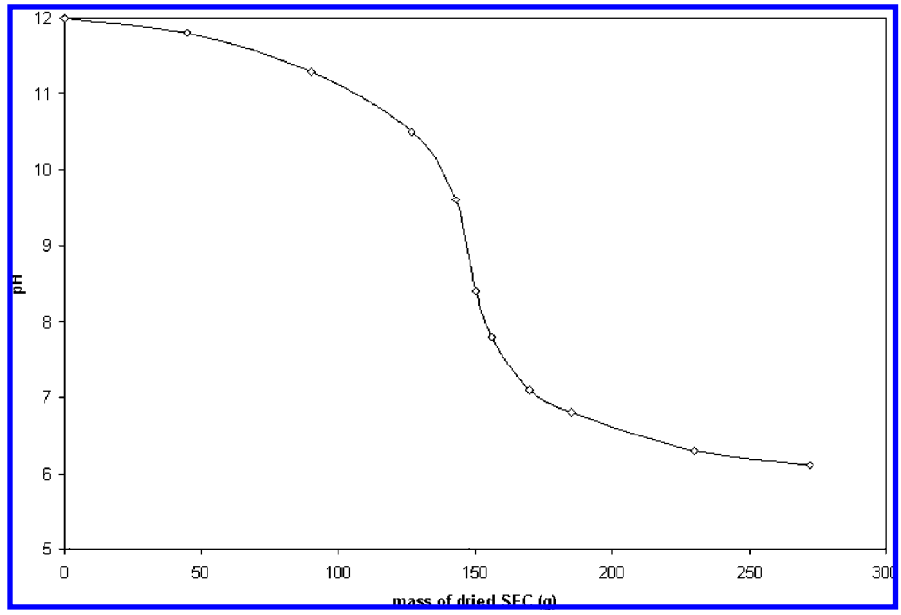

Figure 4. pH of SFC.

Table 6. Protein Extraction Yield from SFC3

solvent	phosphate buffer (pH 6.9)	phosphate buffer (pH 6.9) + 2% SDS	borax buffer (pH 9.0)	borax buffer (pH 9.0) + 2% SDS
extraction yield (%)	27.9 ± 1.46	58.8 ± 0.00	16.6 ± 0.06	27.0 ± 0.32
part of total protein in the centrifugation pellet (%)	74.6 ± 9.09	41.1 ± 8.08	31.7 ± 3.17	11.9 ± 0.24
balance (%)	~100	99.9	48.3	38.9

Table 7. Effect of the pH on the Swelling Rrate of SFC, τ

	distilled water	aqueous NaOH		
pH	6.5	10.5	12.0	13.5
swelling rate, τ	1.57	1.76	1.90	2.04

Table 8. Adsorption Isotherm Characteristics for SFC, SFH, SFKF, and SFPI

	SFC	SFH	SFKF	SFPI
m_m (mg/g DM)	50.3	56.6	48.7	52.7
C	5.937	5.372	6.436	7.021
K	0.869	0.814	0.900	0.874

Table 9. Average Temperature and Enthalpy Reported at the Sample Mass, Dry Matter, Dry Protein, and Dry Globulin of the Endothermic Peak Observed on DSC Scans of SFCs in Pressure-Resistant Pans, According to Their Moisture Content

	%/DM			enthalpy			
	MC (%)	protein content	globulin content	peak temperature (°C)	J/g$_{sample}$	J/g$_{DM}$	J/g$_{protein}$	J/g$_{globulin}$
SFC1	8.7	35.0	10.1	152	2.6	2.8	8.0	27.8
SFC2	8.5	29.4	8.6	153	3.1	3.4	11.5	39.3
SFC3	8.6	31.5	10.8	154	3.2	3.5	11.1	32.3

oil extraction process. Other analysis like AFFFF-MALLS should confirm this hypothesis. Moreover, it could give some interesting polymer characteristics like weight-average and number-average molecular weight (respectively, absolute value of M_w and M_n), index of polydispersity [$I_p = (M_w)/(M_n)$], radius of gyration (R_g), etc.

Characterization of SFC Components. *Physicochemical Properties of SFC.* At equilibrium, ground SFC has a moisture content of 10.1 ± 1.1%. More than 50% of SFC has a diameter of less than 315 μm, and these particles contain more than 40% of proteins (**Figure 2**). Moreover, more than 30% of ground SFC are larger than 250 μm. This particle size and this content are compatible with the molding behavior of a common composite.

The bulk density of SFC is 0.609 ± 0.003 g cm^{-3}. It is similar to a filled polymer like polyolefins: The bulk density of unfilled polypropylene is around 0.9 g cm^{-3}; fillers are often used to relieve the weight of the polymer.

Table 7 shows the variation of the swelling rate τ of SFC with respect to the pH. The swelling rate of SFC increases with a coefficient of 1.30 from pH 6.5 to 13.5. This is because cellulosic fibers swell in alkaline media (*41*) and/or because the ionization of proteins increases their hydration at alkaline pH. As for partially crystalline polymers, the swelling rate of SFC is limited. The solvent (water for SFC) increases the space between macromolecules: It can act as a lubricant; thus, the mobility of polymeric chains increases. **Figure 4** shows that the SFC pH reaches a stable value around pH 6.0 because many proteins have their isoelectric point below 7.0 and also because the quantity of phenolic acids is significant (around 4.5−5.0, **Table 1**).

Water Uptake Isotherm. **Figure 5** shows water uptake isotherms at 25 °C for SFC, SFH, SFKF, and SFPI. They have a sigmoid shape. These isotherms follow the GAB model. The equation used to describe the mass of water adsorbed by 1 g of dry matter is

$$m = \frac{m_m C K a_w}{(1 - K a_w)[1 + (C - 1) K a_w]} \quad (3)$$

where m_m is the mass of the monomolecular layer of water, C is the Guggenheim constant that represents the condensation heat of water vapor at a given temperature, K is an energy constant representative of the multimolecular layer of water according to the free water, and a_w is the water activity [a_w = relative humidity (%)/100]. There are few differences between each curve except in the zone of high relative humidity (a_w > 0.7) where greater differences can be seen for water uptake of SFC, SFH, SFKF, and SFPI. **Table 8** gives the values of m_m, C, and K for the different sunflower materials. The monomolecular water layer forms more easily for SFKF at a_w < 0.2 [$m_{m(SFKF)} < m_{m(SFPI)} < m_{m(SFC)} < m_{m(SFH)}$]. For relative humidity between 20 and 70%, water uptake is easier for SFPI ($C_{SFPI} > C_{SFKF} > C_{SFC} > C_{SFH}$). For a_w > 0.7, water uptake is easier for SFKF ($K_{SFKF} > K_{SFPI} > K_{SFC} > K_{SFH}$). The lower water affinity of husk is due to its high lignocellulosic fiber content: It acts as a water barrier for the kernel. The high hydrophilic behavior of SFKF is mainly due to its water-soluble compounds and also to its proteins, as in the case of SFPI. SFC has an intermediate water affinity between that of SFKF and SFH.

For all of these sunflower materials, water acts as a lubricant with their biopolymers when they adsorb 15% with respect to their dry matter: The point of inflection of isotherms presents ideal conditions for the glass transition to appear. Water could be considered as the natural plasticizer of SFC and especially for its proteins. So, SFC proteins (30%/DM of SFC) seem to participate in the matrix fraction of the natural composite.

Thermal Stability. TGAs show that the loss of matter begins around 50 °C for all samples, but the kinetics of thermal decomposition is different for SFC, SFH, SFKF, and SFPI (**Figure 6a**). These raw materials first lose around 10% of their own weight between 50 and 150 °C, in agreement with the dehydration of sunflower materials (**Figure 6b**). Their components are considerably stable until 190−220 °C because the loss of matter is not significant. However, between 100 and 220 °C, reactions such as Maillard's reaction or the condensation between phenolic acids and proteins may occur (*29*). As of 225 °C, the loss of matter is significant, and the phenomena are exothermic (**Figures 6a** and **7**) for all sunflower materials. At 300 °C, SFKF and SFPI lose around 30% of their initial weight. SFC and SFH lose 35 and 40% of their own weight, respectively. The loss of mass between 225 and 325 °C may agree with the thermal degradation of some water-soluble compounds, hemicelluloses, and cellulose. Around 400 °C, the loss of mass is greater for SFH: It may represent the thermal degradation of lignin (*42*). Between 300 and 550 °C, SFHs are degraded more quickly than sunflower materials with higher protein contents.

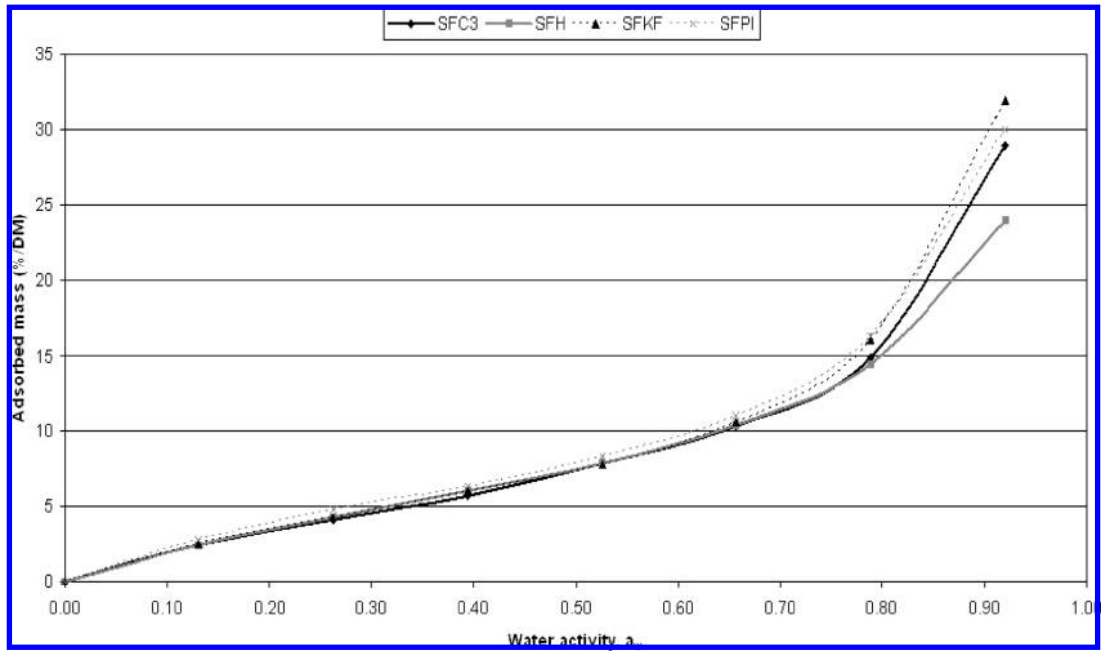

Figure 5. Comparison of adsorption isotherms of SFC, husk, defatted kernel flour, and protein isolate.

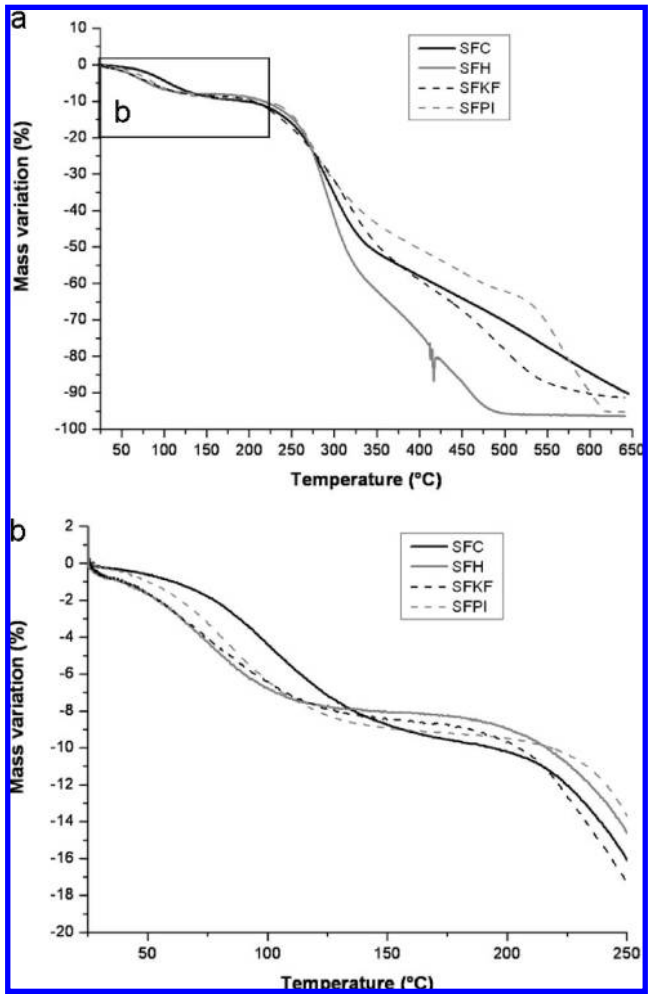

Figure 6. TGA of SFC, SFH, SFKF, and SFPI.

A large part of sunflower proteins increases the thermal stability of SFC in comparison with a polysaccharide/lignocellulosic fiber material.

The thermal stability of proteins seems higher than for other components. In fact, they probably undergo many reactions

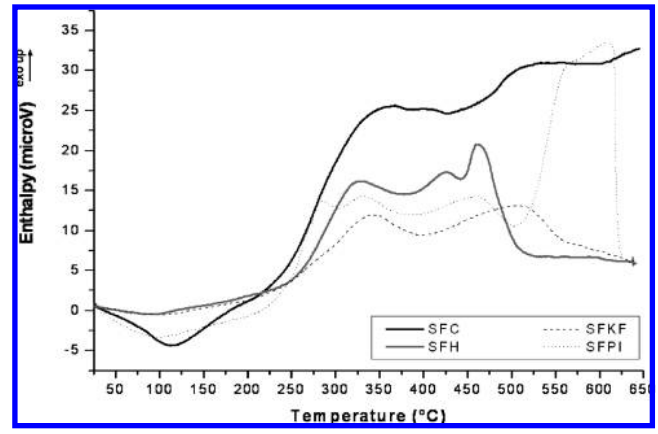

Figure 7. TDA of SFC, SFH, SFKF, and SFPI.

before their thermal decomposition, such as Maillard's reaction or cross-linking or condensations with phenolic components, etc., because proteins have many functional groups. The thermal stability of SFC (190−220 °C) is lower than the most of polymers, but it is very close to the thermal stability of polymethyl-methacrylate (PMMA, 180−280 °C).

DSC Study. DSC analyses on SFPI and SFC have been carried out (*21, 22*). Those studies show that several relaxations exist for protein material and they depend on the moisture content of sunflower material. The DSC study of SFPI presents two phenomena that depend on the moisture content of this matter. First, for moisture content between 6 and 17%, a little endothermic peak can be seen as follows: It is described as a relaxation of biopolymers of SFPI (*21*). This relaxation of sunflower proteins only occurs when water hydrates the polar function of biopolymers and maintains their organization. The relaxation temperature is around 60 °C, but its enthalpy is a function of the moisture content of SFPI. The second phenomenon is a secondary order transition described by Rouilly et al. as the glass transition of SFPIs (*21*): The glass transition temperature T_g of SFPI depends on the moisture content of this matter (from 180.8 to 5.3 °C for moisture contents from 0.0 to 26.1%). That result confirms that sunflower proteins are thermoplastic-like and also that water is a good plasticizer for

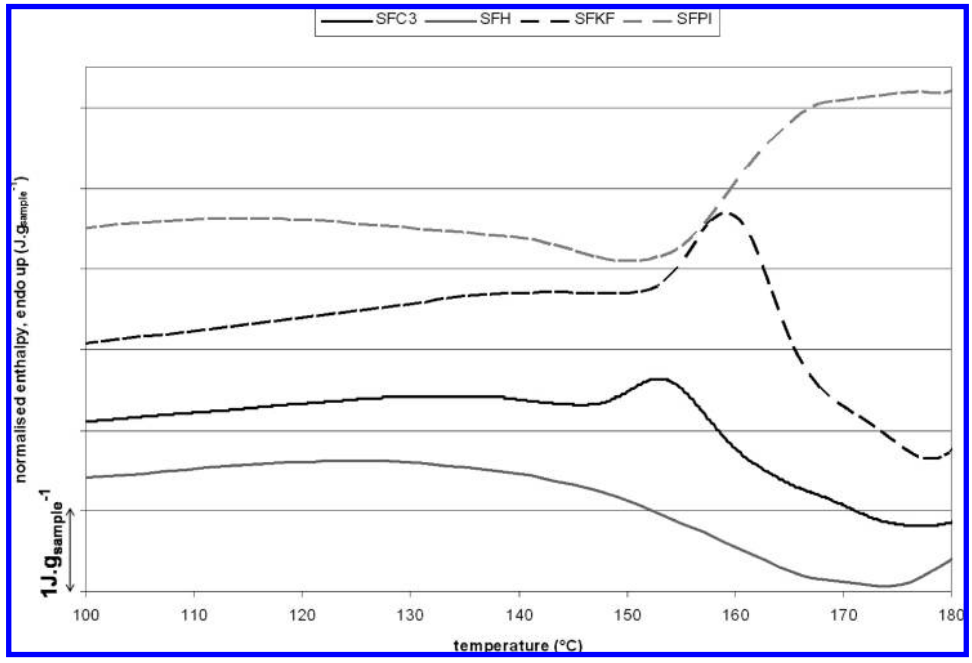

Figure 8. DSC curves in pressure-resistant pans of different sunflower matters.

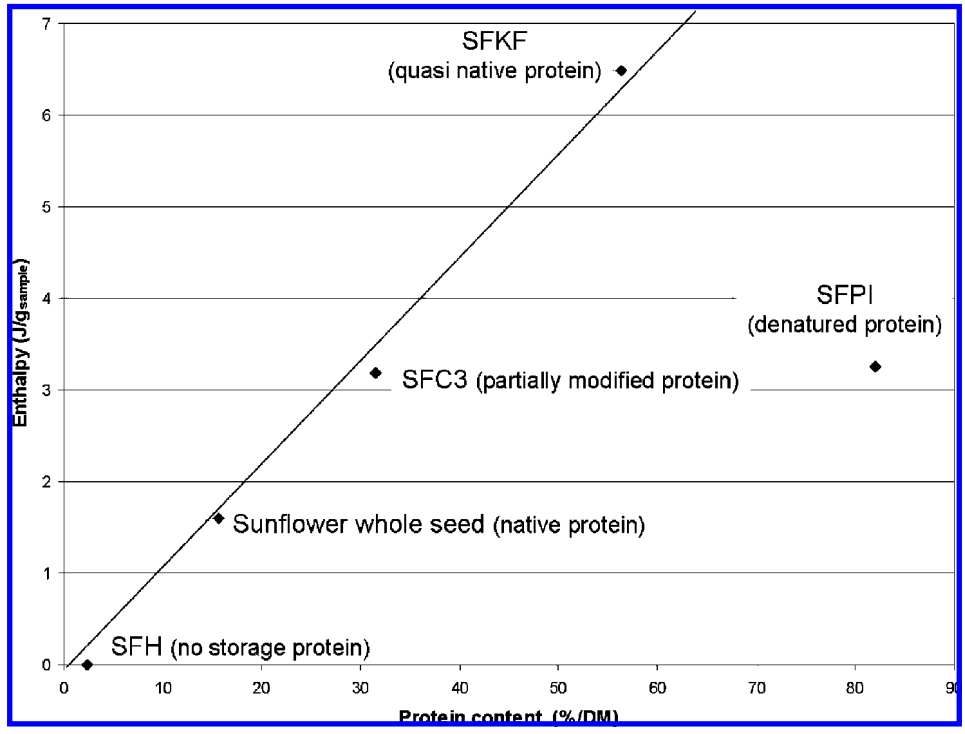

Figure 9. Enthalpy of primary level transition as a function of protein content: whole sunflower seed (*43*).

these biopolymers. At equilibrium (9−11% MC), SFPI presents a relaxation at around 63−65 °C (enthalpy 1.85−2.50 J g^{-1}) and a glass transition at around 78−68 °C.

Rouilly et al. also studied the SFC and described another transition of the primary order as an irreversible denaturation of sunflower globulin (*22*). The temperature and the enthalpy of this endothermic phenomenon depend on the moisture content of SFC: For moisture contents from 0 to 30.0%, peak temperatures range from 190 to 120 °C and enthalpy from 2.6 to 3.3 J g^{-1}.

This present study compares DSC curves of SFC, SFH, SFKF, and SFPI (**Figure 8**). We focused on the last endothermic peak. **Table 9** shows that peak temperature is a function of moisture content. The enthalpy is more proportional to the total protein content than to the globulin content. A similar DSC study carried out on SFPI extracted in an alkaline environment shows that the endothermic peak disappears (*22*). **Figure 8** shows DSC curves for SFC, SFH, SFKF, and SFPI. Only the curves of SFC and SFKF are very similar regarding to a DSC curve of a partially crystalline thermoplastic. Nevertheless, the enthalpy decreases with the protein content (**Table 3**) as well as with the transformation to which the proteins are subjected (**Figure 9**). The industrial oil extraction process modifies protein networks, leading to an increase of insoluble protein content and a slight decrease in the enthalpy of the endothermic peak. When sunflower proteins are totally denatured by an alkaline

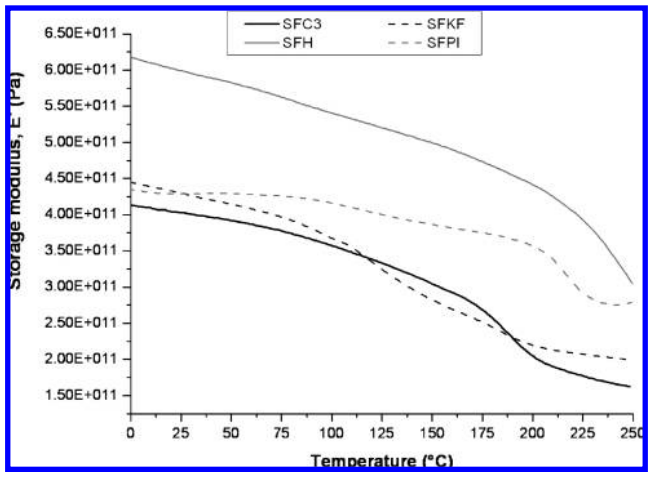

Figure 10. Comparison of storage moduli of SFC, husk, defatted kernel flour, and protein isolate.

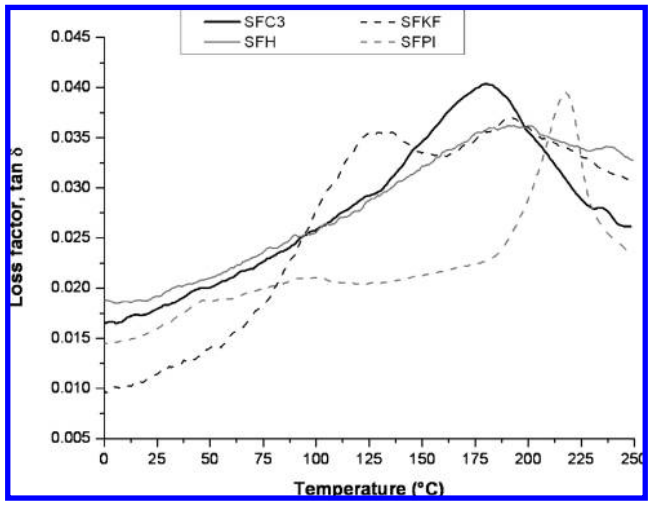

Figure 11. Comparison of loss factor of SFC, husk, defatted kernel flour, and protein isolate.

environment or high temperatures (>160 °C at equilibrium), the endothermic peak is very low with respect to the protein content. In this case, SEM observations show that the proteins coagulate after melting (*22*). This primary order transition is the irreversible protein denaturation and the fusion of sunflower proteins from a polymeric material point of view. We can then refer to the denaturation temperature (T_d) or melting point temperature (T_m) of SFC proteins. The DSC curves of SFC and SFKF show that the presence of a T_g for undenatured sunflower proteins and their irreversible fusion could allow us to consider them as a quasi thermoset polymer.

This DSC study confirms that the main part of sunflower proteins could act as a partially crystalline thermoplastic at temperatures lower than T_d/T_m or more probably as a thermoset-like matrix in SFC for temperatures above T_d/T_m. So, the temperature of process of transformation of SFC into material should be well-controlled due to the denaturation/fusion of proteins/matrix of the natural composite.

Viscoelastic Properties. Preliminary tests show that the storage modulus (E') of sunflower materials is independent of the frequency of the mechanical load and that these materials are rigid. For the loss modulus (E'') and the loss factor ($\tan \delta = E''/E'$), the top of the peak decreases when the frequency increases, but the temperature of this peak does not change; sunflower materials are pseudoplastic. The specificity of the dynamic mechanical analysis on powders and the many kinds of biopolymers in SFC make it difficult to interpret DMTA curves. The comparison of DMTA curves for SFC, SFH, SFKF, and SFPI requires some explanations. SFH are more rigid than SFC because their lignocellulosic fibers content is higher: Lignocellulosic husk fibers act as a mechanical barrier for the kernel. The storage moduli of SFC and SFKF are rather similar: Lignocellulosic fibers do not seem to increase the rigidity of SFC in comparison with SFKF (**Figure 10**). At low temperature storage, the modulus of SFPI is very close to the loss moduli of SFKF and SFC, but it is greater at over 75 °C. Proteins extracted in an alkaline environment could cross-link themselves between 80 and 200 °C, increasing the rigidity of SFPI. A loss factor peak reveals a thermal transition of a polymer: It becomes rubberlike from its glassy state; a peak is often indicative of a glass transition. In **Figure 11**, loss factor peaks are not well-defined like they are for common polymeric materials because sunflower materials contain many different biopolymers. Their glass transition can occur at very close temperatures. The slight increase of slope for SFC storage moduli (**Figure 10**) and the slight shoulder on the SFC loss factor curve at around 130 °C (**Figure 11**) could represent the glass transition of cell wall polysaccharides such as pectins and/or hemicelluloses. This hypothesis is confirmed by a significant

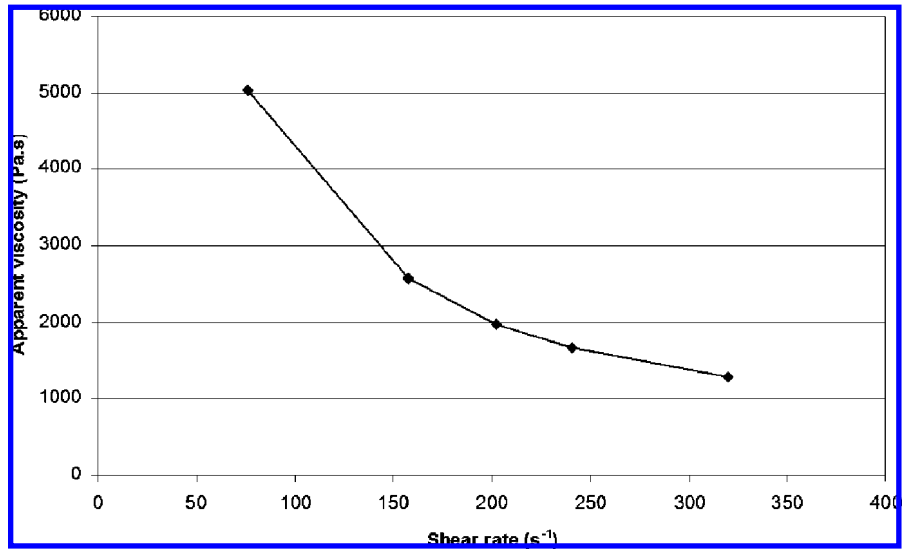

Figure 12. Rheological curve of SFC (moisture content, 30%; capillary die temperature, 120 °C).

increase of the SFKF slope of the storage modulus and a considerable loss factor peak for SFKF at the same temperature: SFKF contains more than 40% of pectin in relation to total dry matter (**Figures 10** and **11**). Moreover, Jorda showed that for a moisture content of 1−5%, the glass transition temperature of sugar beet pulp pectins is between 125 and 140 °C (*44*). Even if sunflower materials are dehydrated before DMTA, 1−4% of water could remain linked to sunflower biopolymers before starting the assay. Between 180 and 200 °C, several glass transitions seem to be superposed. First, the glass transition of lignocellulosic fibers could occur around 180−185 °C because the main large peak is observed at these temperatures for the SFH sample. Above 185 °C, it could be the glass transition of sunflower proteins. The T_g of proteins seems to depend on the level of transformation: The tan δ peak for SFKF is around 180 °C, a shoulder is obsevred around 190 °C for SFC, and the well-defined tan δ peak for SFPI is around 220 °C. Those T_g values are important because sunflower materials are dried and also because the temperature change rate is low (3 °C min^{-1}). However, at over 200−220 °C, other loss factor peaks may correspond to thermal degradation phenomena.

In conclusion, the DMTA study shows that SFC is a pseudoplastic matter. Lignocellulosic fibers are more elastic than proteins. That confirms the property of reinforcement of lignocellulosic fibers (fillers). The oil extraction process allows a very good blend of the different fraction of sunflower seed because a single peak is observed for SFC. Moreover, the DMTA curve of SFC is similar to DMTA curve of elastomer, but its temperature of glass transition is lower. With respect to the temperature, SFC could have a viscoelastic behavior between a thermoset and an elastomer behavior. DMTA and DSC studies show that SFC proteins have some relaxations such as common polymers: glass transition and denaturation of proteins similar to the melting point of proteins. Their temperatures are around 68−78 and 150−160 °C, respectively, for equilibrated SFC (9−11% moisture content). It is therefore essential to control the moisture content of SFC to transform it into a melting phase at temperatures below 200 °C.

Rheological Properties. The temperature of measurement (120 °C) is closed to the temperature of denaturation/fusion of SFC proteins for a SFC moisture content of 30% (*22*). **Figure 12** shows a pseudoplastic behavior of melting SFC: It is a non-Newtonian liquid as common plastic. During the measurement, a slight extrudate swelling is observed as for rubberlike materials. Moreover, SFC (30% MC) follows the Ostwald/de Waele power law

$$\eta = K \times \dot{\gamma}^{m-1} \quad (4)$$

as many melt plastics. The consistency value (K) and the pseudoplasticity index are calculated as $K = 318640$ Pa s and $m = 0.04$. These values show that under these measurement conditions, hydrated ground SFC has a state very close to a solid ($m \sim 0$). So, even if SFC has indisputable plastic properties, it would be necessary to improve its rheological behavior in future works to mold it easier by plastic-processing machinery.

In conclusion, this work shows that SFC is similar to a natural composite. The main part of the polymeric matrix consists of proteins (globulins and albumins), and the fillers are mainly represented by lignocellulosic fibers. The protein matrix of SFC has pseudoplastic and viscoelastic properties, as well as thermal properties similar to a common polymer. SFC seems to have a plastic behavior closer to filled thermoset polymer than reinforced elastomer or thermoplastic polymers. Both kinds of components (thermoset-like, elastomer-like, and thermoplastic-like) should coexist in the matrix of this natural composite, but the main part is thermoset-like biopolymers (proteins).

To develop the used of whole agroresources as raw material to make plasticlike products, it will necessary to determine the chemical composition and the physicochemical properties of these components. On this focus, this study initiates a systematic way of work to transform agroresources into agromaterials by plasticization, chemical modification, or thermomechanical process.

LITERATURE CITED

(1) Coffin, D. R.; Fishman, M. L.; Ly, T. V. Thermomechanical properties of blends of pectin and poly(vinyl alcohol). *J. Appl. Polym. Sci.* **1996**, *61*, 71–79.

(2) Mohanty, A. K.; Misra, M.; Hinrichsen, G. Biofibres, biodegradable polymers ans biocomposites: An overview. *Macromol. Mater. Eng.* **2000**, *276/277*, 1–24.

(3) Fung, C.-P.; Hwang, J.-R.; Hsu, C.-C. The effect of injection-molding process parameters on the tensile properties of short glass fiber-reinforced PBT. *Polym.-Plast. Technol. Eng.* **2003**, *42*, 45–63.

(4) Chabba, S.; Netravali, A. N. "Green" composites. Part 2: Characterization of flax yarn and glutaraldehyde/poly(vinyl alcohol) modified soy protein concentrate composites. *J. Mater. Sci.* **2005**, *40*, 6275–6282.

(5) Chivrac, F.; Kadlecova, Z.; Pollet, E.; Avérous, L. Aromatic copolyester-based nano-biocomposites: elaboration, structural characterization and properties. *J. Polym. Environ.* **2006**, *14*, 393–401.

(6) Bastioli, C. Properties and applications of Mater-Bi starch-based materials. *Polym. Degrad. Stab.* **1997**, *59*, 263–272.

(7) Bear, M.-M.; Renard, E.; Randriamahefa, S.; Langlois, V.; Guerin, Ph. Preparation of a bacterial polyester with carboxy groups in side chains. *C. R. Acad. Sci. Paris, Chimie/Chemistry,* **2001**, *4*, 289−293.

(8) Stevens, E. S. Part 1: Plastics. Part 2: Bioplastics. In *Green Plastics: An Introduction to the New Sciences of Biodegradable Plastics*; Princeton University Press: Princeton, NJ, 2002.

(9) Vaz, C. M.; de Graaf, L. A.; Mulder, W. J. Chapter 14: Adhesives, coating and bioplastics from protein sources. In *Biopolymers*; Steinbüchel, A., Fahnestock, S. R., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2003; Vol. 8.

(10) Peyrat, E.; Rigal, L.; Pluquet, V.; Gaset, A. Vegetable material from cereal plants and process for making the same. EP0989228, 2000.

(11) Rouilly, A.; Rigal, L. Agro-materials: A bibliographic review. *J. Macromol. Sci., Part C: Polym. Rev.* **2002**, *42*, 441–479.

(12) Leyris, J.; Silvestre, F.; Gaset, A.; Rigal, L. Method for making shaped objects from a vegetable raw material by pressing. EP0987089, 2000.

(13) Rigal, L.; Leyris, J.; Silvestre, F.; Doumeng, C. Method for making shaped objects from a vegetable raw material by injection-moulding. EP0988948, 2000.

(14) Gueyasuddin, S.; Cater, C. M.; Mattil, K. F. Preparation of a colorless sunflower protein isolate. *Food Technol.* **1970**, *24*, 242–243.

(15) Bach Knudsen, K. E. Carbohydrate and lignin contents of plant materials used in animal feeding. *Anim. Feed Sci. Technol.* **1997**, *67*, 319–338.

(16) Ayhllon-Mexueiro, F.; Vaca-Garcia, C.; Silvestre, F. Biodegradable films from isolate of sunflower (*Helianthus annuus*) proteins. *J. Agric. Food Chem.* **2000**, *48*, 3032–3036.

(17) Orliac, O.; Rouilly, A.; Silvestre, F.; Rigal, L. Effects of additives on the mechanical properties, hydrophobicity and water uptake of thermo-moulded films produced from sunflower protein isolate. *Polymer* **2002**, *43*, 5417–5425.

(18) Orliac, O.; Silvestre, F.; Rouilly, A.; Rigal, L. Rheological studies, production and characterization of injected-molded plastics from

sunflower protein isolate. *Ind. Eng. Chem. Resour.* **2003**, *42*, 1674–1680.
(19) Rouilly, A.; Mériaux, A.; Geneau, C.; Silvestre, F.; Rigal, L. Film extrusion of sunflower protein isolate. *Polym. Eng. Sci.* **2006**, *46*, 1635–1640.
(20) Rouilly, A.; Orliac, O.; Silvestre, F.; Riagal, L. New injection-moldable composite material from sunflower oil cake. *Bioresour. Technol.* **2006**, *97*, 553–561.
(21) Rouilly, A.; Orliac, O.; Silvestre, F.; Rigal, L. DSC study on the thermal properties of sunflower proteins according to their water content. *Polymer* **2001**, *42*, 10111–10117.
(22) Rouilly, A.; Orliac, O.; Silvestre, F.; Rigal, L. Thermal denaturation of sunflower globulins in low moisture conditions. *Thermochim. Acta* **2003**, *398*, 195–201.
(23) Silvestre, F.; Rigal, L.; Leyris, L.; Gaset, A. Aqueous adhesive based on a vegetable protein extract and its preparation. EP0997513, 2000.
(24) Van Soest, P. J. Use of detergents in the analysis of fibrous feeds II A rapid method for the determination of fiber and lignin. *J. Assoc. Off. Anal. Chem.* **1963**, *46*, 829–835.
(25) Van Soest, P. J. W. R. The determination of lignin and cellulose in acid detergent fiber with permanganate. *J. Assoc. Off. Anal. Chem.* **1968**, *51*, 780–787.
(26) Van Soest, P.; Wine, R. Use of detergents in the analysis of fibrous feeds. IV. Determination of plant cell-wall constituents. *J. Assoc. Off. Anal. Chem.* **1967**, *50*, 50–56.
(27) Osborne, T. B.; Campbell, G. F. The proteins of sunflower seed. *J. Am. Oil Chem. Soc.* **1897**, *19*, 487–494.
(28) Brumett, B. J.; Burns, E. E. Pigment and chlromogen characteristics of sunflower seed *Helianthus annuus*. *J. Food Sci.* **1972**, *37*, 1–3.
(29) Saeed, M.; Cheryan, M. Chlorogenic acid interactions with sunflower proteins. *J. Agric. Food Chem.* **1989**, *37*, 1270–1274.
(30) Sammour, R. H.; El-Shourbagy, M. N.; Abo-Shady, A. M.; Abasary, A. M. Characterization of sunflower seed proteins by electrophoresis techniques. *Arab Gulf J. Sci. Res.* **1995**, *13*, 591–604.
(31) Schwwenke, K. D.; Pähtz, W.; Linow, K.-J.; Raab, B.; Schultz, M. On seed proteins. Part 11. Purification, chemicalcomposition, and some physico-chemical properties of the 11S globulin (Helianthinin) in sunflower seed. *Die Nahrung.* **1979**, *23* (3), 241–254.
(32) Sanchez, A. C.; Burgos, J. Thermal gelation of trypsin hydrolysates from sunflower proteins: Effect of pH, protein concentration and hydrolysis degree. *J. Agric. Food Chem.* **1996**, *44*, 3773–3777.
(33) Sanchez, A. C.; Burgos, J. Thermal gelation of sunflower globulin hydrolystes: Rheological and calorimetric studies. *J. Agric. Food Chem.* **1997**, *45*, 2407–2412.
(34) Raymond, J.; Inquello, W.; Azanza, J. L. The seed proteins of sunflower: Comparative studies of cultivars. *Phytochemistry* **1991**, *30*, 2849–2856.
(35) Sabir, M. A.; Sosulski, F. W.; MacKenzie, S. L. Gel chromatography of sunflower proteins. *J. Agric. Food Chem.* **1973**, *21*, 988–993.
(36) Schwwenke, K. D.; Hinze, W.; Schultz, M.; Linow, K.-J.; Prahl, L., Beklke J.; Reichelt, R.; Braudo, E. E.; Sologub, L. P. Helianthinin—The main storage protein in sunflower seeds *Helianthus annuus* L.). *Abh. DDR* **1978**, *4N*, 45–62.
(37) Molina, M. I.; Petruccelli, S.; Añon, M. C. Effect of pH and ionic strength modifications on thermal denaturation of the 11 S globulin of sunflower (*Helianthus annuus*). *J. Agric. Food Chem.* **2004**, *52*, 6023–6029.
(38) Dalgalarondo, M.; Raymond, J.; Azanza, J.-L. Sunflower seed proteins: characterization and subunit composition of the globulin fraction. *J. Agric. Food Chem.* **1984**, *35*, 1618–1628.
(39) Kortt, A. A.; Caldwell, J. B. Low molecular weight albumins from sunflower seed: Identification of a methionin-rich albumin. *Phytochemistry* **1990**, *29*, 2805–2810.
(40) Shahidi, F.; Nazck, M. An overview of the phenolic s of canola and rapeseed: Chemical, sensory and nutritional significance. *J. Am. Oil Chem. Soc.* **1992**, *69*, 917–924.
(41) Isogai, A.; Onabe, F.; Usuda, M. Swelling behaviour of cellulose by chemical and mechanical treatments. *Sen-I Gakkaishi.* **1992**, *48*, 487–492.
(42) Hatakeyama, T.; Hatakeyama, H. In *Thermal Properties of Green Polymers and Biocomposites*; Kluwer Academic Publishers: Dordrecht, 2004.
(43) Evon, P. Direct extraction of oil from sunflower seeds by twin-screw extruder according to an aqueous extraction process: Feasibility study and influence of operating conditions. *Ind. Crops Prod.* **2007**, *26*, 351–359.
(44) Jorda J. Etude du procédé d'extraction alcaline et de purification de pectines de pulpe de betterave: étude des propriétés chimiques et physico-chimiques. Institut National Polytechnique, Toulouse, 2003.

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