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Mechanical behaviour of corn flour and starch–zein based materials in the glassy state: A matrix–particle interpretation

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Abstract

Starch–zein systems were characterised by their dynamic mechanical behavior. Although the main relaxation temperatures were located in the same range of temperature for the various zein contents, significant differences were observed for the tan δ peak amplitude. They were related to the morphology of the system, i.e., dispersed zein aggregates in starch matrix or dispersed amorphous starch in zein matrix, the phase inversion domain, determined by image analysis, being in the (17–34%) phase concentration interval. When testing processed corn flour under different thermomechanical conditions, at a moisture content of 12.0% (wb), higher values of tan δ peak were found when starch transformation was increased. For the same trend, values of E' modulus in the rubbery state continuously decreased which was attributed to the reduction of remaining starch granules within the flour.

The application of models of composites materials points out the matrix–particles behaviour of processed corn flour and starch–zein blends, whatever the particles composition. The quality of adhesion between starch and zein is inferred for the mechanical properties of their blends.

Keywords: Corn flour; Glass transition; Biopolymers blends; Matrix–particles materials; Viscoelastic behaviour; Dynamic mechanical analysis

1. Introduction

Cereals products, made from corn for instance, are obtained by thermal and mechanical processes, like extrusion, which induces strong modifications, involved in the creation of an interesting texture of the final products. Flours are constituted of different biopolymers, consisting mainly of starch and proteins, which undergo structural changes during processing. Structural modifications of starch under such conditions have been widely studied at the molecular, crystallites and granular scales (Barron, Bouchet, Della Valle, Gallant, & Planchot, 2001; Colonna & Mercier, 1989; Gomez & Aguilera, 1984; Wang & Zheng, 1995). In the case of extrusion, the combined effects of temperature and mechanical energy induce the melting of crystallites and the fragmentation of starch granules. The flow behaviour of a partially molten starch was observed to be similar to the one of a molten starch suspension dispersing semi-crystalline starch fragments (Barron, Della Valle, Colonna, & Vergnes, 2002). These results show that starch granules and fragments, can be considered like particles, to understand the behaviour of partially transformed starch materials. Protein denaturation was mainly studied in term of the loss of solubilisation properties and chemical changes (Attenburrow, Davies, Goodband, & Ingman, 1992; Fisher, 2004; Stanley, 1989) or disruption of the entities containing storage proteins, like protein bodies (Batterman-Azcona & Hamaker, 1998; Batterman-Azcona, Lawton, & Hamaker, 1999). Viscoelastic properties of extruded materials have been studied to determine the role of water and understand processing but starch–protein interactions have not been addressed (see for instance, Brent, Mulvaney, Cohen, & Bartsch, 1997a, 1997b). They rarely address the phase or particle level of structural

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organisation of cereal biopolymer blends as commonly achieved for synthetic polymers blends.

Phenomenological models of polymeric materials have been developed to predict the mechanical properties at large deformations, and viscoelastic behaviour of composites, i.e., polymer matrix filled with particles. The basic model involves particle–matrix adhesion effect and suggests that for a tensile test, the rupture stress of the composite, σ_C, can be obtained from the volumic fraction of particles, V_P, and the knowledge of the matrix behaviour, i.e., rupture stress, σ_{matrix} (Nicolais & Nicodemo, 1974)

$$\sigma_C = \sigma_{matrix}(1 - a \cdot V_P^b), \quad (1)$$

where a is a constant, related to the stress concentration and the adhesion, b to the particle geometry. In the case of spherical particles without adhesion, $a = 1.21$ and $b = 2/3$.

Viscoelastic behaviour is affected by the presence of particles, as well. When there is no interaction between matrix and particles, the dynamic thermomechanical behaviour of the composite is also modified, although its glass transition temperature T_g is unchanged. A decrease of the $\tan\delta$ peak amplitude of the composite, $\tan\delta_C$, is commonly observed and related to the volumic fraction of particles, V_P, and the mechanical relaxation of the matrix, defined by $\tan\delta_M$, according to the relation, proposed by Nielsen (1969)

$$\tan\delta_C = \tan\delta_M \cdot (1 - V_P). \quad (2)$$

In a recent study, we have pointed out the importance of the morphology of processed starch–zein blends on the mechanical properties: the microscopic observations of processed corn flour showed a biphasic morphology, with a continuous phase of amorphous starch, and a dispersed phase of proteins (Chanvrier, Colonna, Della Valle, & Lourdin, 2005). The aim of this current study is to determine whether mechanical and thermomechanical properties of biopolymer blends products can be described by models of a polymer matrix filled with particles. To achieve this, starch–zein blends and corn flour materials with different starch transformation levels were prepared under various thermomechanical conditions in order to study the influence of their morphology on their thermomechanical behaviour. An attempt was made to apply models of composite materials to these blends.

2. Material and methods

2.1. Materials

Corn starch was purchased from Roquette (F-62 Lestrem, France). The initial moisture content was 13.5% (wb). Zein powder was purchased from Fluka BioChemika (Germany). It is a mixture of two alcohol–soluble polypeptides with a molecular mass of 25,000 and 29,000 Da. Loss due to drying and ash were less than 4% and 1%, respectively. Corn flour was a gift from M.C. Technologies (F-63 Ennezat, France). Protein content (6.6%, db) was determined by the Kjeldahl method and starch content (83%, db), according to the method described by Mc Cleary, Gibson, and Mugford (1997).

Corn gluten meal, Glutalys®, is a commercial gluten from Roquette Frères (F-62 Lestrem, France), dried by hot air. It is composed of 70.3% proteins, 16.3% starch, 5.7% lipids, and 3.9% fibres.

2.2. Sample preparation

2.2.1. Pre-shearing treatment

To control accurately the treatment intensity, and particularly the level of transformation corn flour was processed in the Rheoplast®, a proven means of simulating extrusion as described in detail by Barron, Buleon, Colonna, and Della Valle (2000).

About 15 g of corn flour (moisture content MC 26%, wb) were processed in one batch and sheared in the barrel with a piston speed of 100 rpm for 15 s, leading to an apparent shear rate of 40 s^{-1}. Barrel temperature was adjusted through two heating elements at 90–100, 115–125, 120–130, and 135–145 °C for four treatments. Sample temperature, measured before the die, was 100, 128, 140, and 160 °C, respectively. Rod samples were obtained after flow through capillary die (L/D = 16). These samples are termed CF100, CF128, CF140, and CF160.

2.2.2. Extrusion

The extrusion has been used as a thermomechanical process close to common industrial transformation. Extrusion on a laboratory-scale was used to prepare starch–zein blends with a zein content lower than 20% (w/w), which led to an amorphous starch according to the extrusion conditions detailed in Chanvrier et al. (2005). Corn flour and starch were extruded at two temperatures, 120 and 110 °C, respectively, to obtain two levels of starch transformation measured by DSC.

2.2.3. Thermomoulding

2.2.3.1. Blends of native with extruded corn flour. The objective of this preparation was to obtain samples representative to partially transformed flours. By this method, the ratio transformed/non-transformed part is perfectly controlled. Extruded corn flour (ECF), for which starch was totally transformed, was reduced to a powder by cryogrinding. Then it was blended with native corn flour (NCF) using a laboratory kneading machine. The quality of miscing was controlled visually. After equilibrium under KC1 saturated solution, the moisture content of different blends ECF/NCF was 16% (wb) which lead to a glass transition temperature of 55 °C Powder blends were then thermomoulded at 60 °C. The conditions allowed solid materials to be obtained without modifying the native corn flour for different compositions. The blends compositions, ECF/NCF studied are: 90/10, 80/20, 70/30, 60/40, and 50/50.

2.2.3.2. Starch–zein blends. Thermomoulding was used to produce starch–zein blends with a wide range of zein content (0–100%, w/w), according to the procedure described previously (Chanvrier et al., 2005).

These samples are noted SZ X/Y where X and Y correspond to the concentration (in weight) of starch and zein, respectively. A glossary is available at the end of the paper.

2.3. Water determination

The Karl Fisher method was used to measure the moisture content of the samples after storage at controlled relative humidity. Water was extracted from the samples at 150 °C for 30 min under a dry nitrogen flow. The water content in the gas was further measured.

2.4. Starch transformation level

2.4.1. Gelatinisation endotherm

Differential scanning calorimetry was used to determine residual gelatinisation enthalpy. DSC experiments were performed with a DSC 121 (Setaram, France). Sample (20 mg) and deionised water (100 mg) were weighed directly in the pan and sealed hermetically. Pans were heated from 5 to 160 °C at a rate of 3 °C min^{-1}. Native and residual gelatinisation enthalpy, ΔH (J g^{-1}), were calculated by integration of the endothermic peak. The level of residual starch in the flour corresponds to the ratio ($\Delta H_{residualCF}/\Delta H_{nativeCF}$). X_{starch}, where $\Delta H_{residualCF}$ is the measured residual gelatinisation enthalpy of the transformed flour, $\Delta H_{nativeCF}$ is the gelatinisation enthalpy of the native flour and X_{starch} is the concentration of starch in the flour (0.83).

2.4.2. Crystallinity

X-ray diffraction measurements were performed with Inel X-ray equipment (France), at 40 kV and 30 mA. CuKα_1 radiation ($\lambda = 0.15045$) was selected using a quartz monochromator. A curved position-sensitive detector (Inel CPS 120) was used to monitor diffraction intensities over a 2 h exposure period. After hydration on saturated $BaCl_2$ solution at 25 °C (relative humidity: 90%, corresponding to a moisture content of 20%, wb) for 1 week, corn flour samples (40 mg) were sealed between sticking tapes to prevent any moisture loss during measurement. The crystallinity ratio and the amount of A-type structure were determined by applying a multilinear regression procedure based on that used by Gernat, Radosta, Damaschun, and Schierbaum (1990). This method assumes that experimental normalised diagrams are a linear combination of three elementary patterns: amorphous, A-, and B-types. A-type spherulites were taken as the crystalline references, as corn starch is known to display. A-type crystalline structure, and extruded potato starch as the amorphous reference. Diffraction diagrams were all normalised at the same total scattering value, with 2θ ranging from 3° to 30°.

2.5. Mechanical properties

Results obtained by a three-point bending test of materials were taken in the preceding work (Chanvrier et al., 2005).

2.6. Samples morphology

The method of microstructure observation by confocal scanning light microscopy (CSLM) is described in the previous work (Chanvrier et al., 2005). From these results the morphology of materials was quantified by image analysis.

A Matlab program (Mathworks, Sevres 92-France) was designed to obtain binary images from the CSLM images (160×160 μm^2) which are in grey levels, ranging from 0 to 255. The binarisation threshold, defined from the histograms of the grey levels, was given a grey level value of 50 for each image. Each finite particle in an image was labelled. From the labelled images, the number of particles (NP) and the mean surface of each particles (MSP) were determined. The surfacic ratio SRZ is the ratio between the zein surface and the total surface of an image. The variation of the binarisation threshold (±10) induced surface (absolute or relative) uncertainty of the particles of about 8%. NP and MSP could finally be plotted as a function of the surfacic ratio of zein.

2.7. State changes by calorimetry and dynamic mechanical analysis (DMA)

The variation of glass transition temperature T_g of components with water content, was measured by DSC. Amorphous samples were stored at constant relative humidity until equilibrium, before filling in pressure-tight cells (about 70 mg of matter per cell). After a first scan from 5 to 150 °C to delete any thermal event due to ageing phenomena occurring during the storage, samples were rapidly cooled to 5 °C (60 °C/min). Measurements were performed during a second scan at 3 °C/min from 5 to 150 °C. Graphic determination of glass transition temperature was carried out according to the procedure recommended by Wünderlich (1992), with $T_g^{1/2}$, corresponding to a half the change in heat capacity during transition.

Mechanical relaxation measurements were performed on a Dynamic Mechanical Analyser (DMTA MK IV, Rheometric Scientific, USA). Samples were coated with a silicone-based hydrophobic grease to limit dehydration during experiments at high temperatures, after having checked that it had no effect on thermomechanical properties. Extruded or moulded materials (strips, $22 \times 10 \times 1$ mm^3) were measured in the dual cantilever mode with a vibration frequency of 0.2 Hz, a strain of 0.05% and a heating rate of 3 °C/min. Rod samples (obtained by Rheoplast®) were measured in the tensile mode, in the same conditions as for strips but with a prestress 15% higher than the dynamic force. The temperature of the glass–rubbery relaxation T_α, associated with the

calorimetric glass transition of the material, was determined at the maximum of $\tan\delta = E''/E'$.

3. Results and discussion

3.1. Starch–zein blends

3.1.1. Phase morphology of the blends

The distribution of the protein in the model blends has been observed by CSLM for several zein contents and two mains types of morphology were described (Chanvrier et al., 2005). Continuous/dispersed phases morphologies were observed when one of the biopolymers is in majority, two co-continuous phases were observed for the intermediate concentration domain (Fig. 1). The size of dispersed domains is probably dependant to the powder granularity used for thermomoulding. This hypothesis could be confirmed, by similar studies from different granularities.

The strong contrast obtained on CSLM images made it possible to implement an image analysis in the purpose of delimiting the domain of phases co-continuity. The mean particles size (MPS) and number of particles (NP) are shown as function of the surfacic ratio of zein (SRZ) on Fig. 2. A large drop of NP values was obtained below 0.19, a value beyond which NP could be well fitted by a linear function of SRZ ($r^2 > 0.9$). Conversely, MPS was linearly fitted until SRZ = 0.38 ($r^2 > 0.9$), a value beyond which MPS values were more scattered. These results suggest that zein aggregates tend to connect for SRZ > 0.19 and a continuous phase of zein, in which amorphous starch domains are embedded, is obtained for SRZ > 0.38. In the interval defined by these threshold values, two continuous phases may coexist.

Assuming that the system is uniform and isotropic, as required by the stereologic relationships (Underwood, 1970), the mass ratio of zein could be approximated from SRZ and the density of the components of the blends ($\rho_{zein} = 1.24$ and $\rho_{starch} = 1.47$ g/cm^3). Consequently, the interval of zein content 17–34% (w/w) can be considered to present a co-continuous phases morphology.

3.1.2. Glass transition temperature of both phases with equilibrium relative humidity

To analyse the calorimetric behaviour of immiscible blend, the glass transition temperature (T_g) of separate components, i.e., amorphous starch and zein, have been measured by DSC for samples conditioned in different relative humidity (Fig. 3). The water content of components has been accurately determined. Starch contains a greater water content than zein, for all ERH. For example, at the equilibrium relative humidities (ERH) of 59%, amorphous starch contains 12.0% water, and zein contains 7.1%. T_g measured in this study and their dependence with water content are in agreement with values previously published on starch (Bizot et al., 1997) and zein (Lawton, 1992; Madeka & Kokini, 1996). The representation of T_g with ERH chosen for this study, provide different information to the T_g dependence on water content. Indeed, despite different water contents at the same ERH amorphous starch and zein have similar T_g values and T_g variation is mainly dependent to relative humidity. The calorimetric behaviour has also been measured for starch–zein blends. The water content at equilibrium relative humidity of 59% is 12.0%

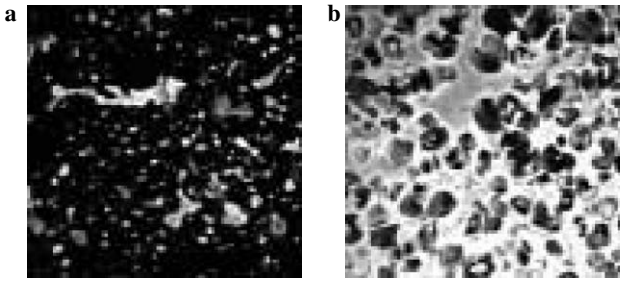

Fig. 1. CSLM observations of zein in thermomoulded starch–zein blends, (a) SZ 95/5, (b) SZ 50/50 (159.7 × 159.7 μm^2).

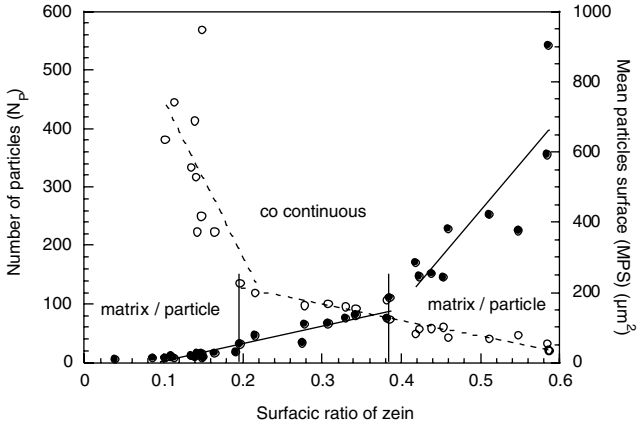

Fig. 2. Particles number (○) and mean particles surface (●) of zein vs. surfacic ratio of zein.

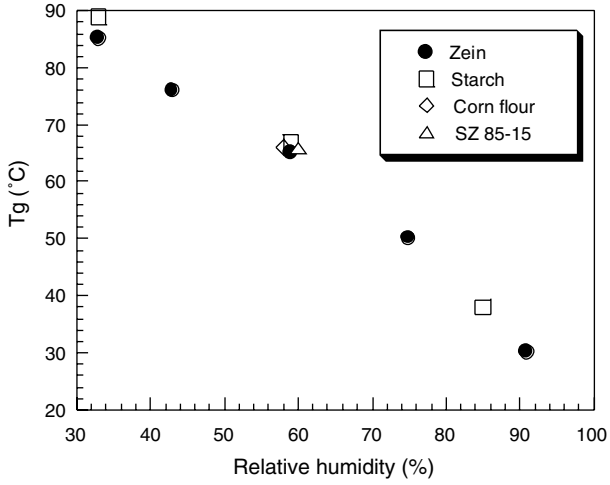

Fig. 3. Glass transition temperatures of starch and zein vs. relative humidity.

for SZ 85/15, 10.5% for SZ 70/30, 9.5% for SZ 50/50, 7.1% for SZ 15/85. Over the whole composition domain, from pure starch to pure zein, a heat capacity change is detected in the temperature domain situated between 65 and 70 °C. The value found at 68 °C for SZ 85/15 at 59% ERH is reported on the Fig. 3. From T_g results obtained on pure starch and zein it can be easily deduced that the heat capacity change measured on the blends corresponds to the superimposition of the glass transition of each component. From these observation the glass transition of corn flour at 68 °C can be interpreted also as a superimposition of the T_g of the two major components.

3.1.3. Mechanical properties

Results of stress at break (σ) obtained previously (Chanvrier et al., 2005), are presented as a function of zein content (w/w) (Fig. 4). Materials studied were thermomoulded and extruded starch–zein system, starch/corn gluten meal blends, thermomoulded and extruded flour. For all these samples, and independently to the material processing, the stress at break decreased when the protein content increased until approximately 20% w/w. A similar trend is obtained for the variations of strain at break. Both, results show that protein particles weakened the starch matrix.

The rupture stress of starch–zein blends has been calculated with Eq. (1), where (σ_m) is the stress at break measured on starch and (V_P) the zein volume fraction calculated from density values indicated before. The calculated values (dotted curves) from the composite model with no adhesion are in agreement with experimental data for the domain of zein concentration corresponding to the matrix (starch)/particle (zein) morphology (left part of the figure). On the other hand, there is a deviation between experimental and calculated values for the matrix (zein)/particle (starch) morphology (right part of the graph). Although the three point bend geometry also encompasses traction, the use of the model is not rigorous, because it has been developed for pure traction data. However, these results suggest a very weak or even no adhesion between the starchy matrix and zein aggregates. Indeed, a perfect adhesion between the two phases would result in a value of stress at break clearly larger than the one obtained here. The mechanical property of the mixture would not be far from the average of pure components, predicted by a simple mixture rule as proposed by Torquato (2000).

3.1.4. Thermomechanical behaviour of the blends

Fig. 5a displays the variation of the storage modulus E' vs. temperature for starch–zein blends from 0% to 100% zein. E' values at room temperature were between 1 and 2 GPa, without any significant variation with zein content with regard to the accuracy of the technique. The $\tan\delta$ vs. temperature curves for starch–zein blends are presented in Fig. 5b. Corn starch, SZ 85/15 and SZ 70/30 present a

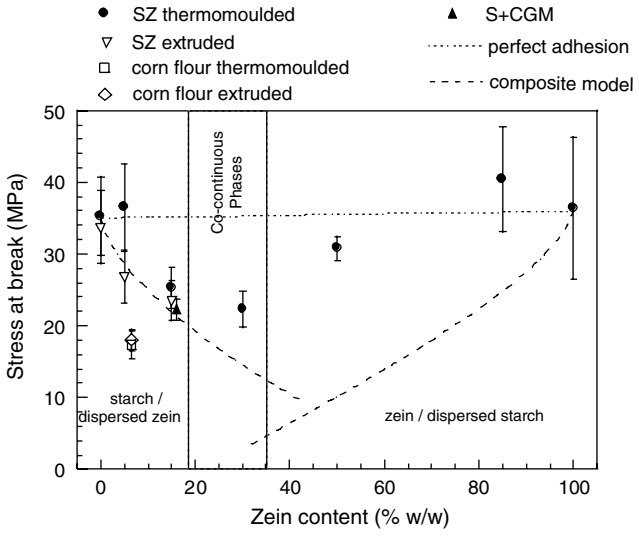

Fig. 4. Stress at break for moulded (filled symbols) and extruded (open) starch–zein blends, processed corn flour, S/CGM blend. Long dot: stress calculated by the model of Nicolais and Nicomedo (1974). Short dot: average of mechanical properties of pure components.

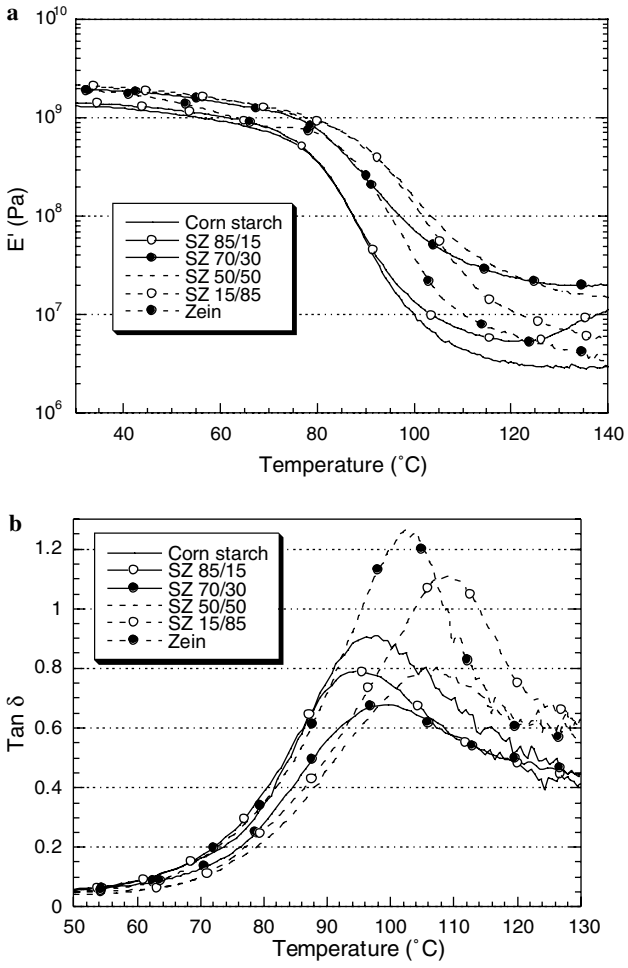

Fig. 5. Dynamic mechanical behaviour of starch–zein blends at 0.2 Hz, 0.05% strain. Water content at equilibrium relative humidity of 59% is 12.0% for starch, 12.0% for SZ 85/15, 10.5% for SZ 70/30, 9.5% for SZ 50/50, 7.1% for SZ 15/85, and 7.1% for zein.

main relaxation with a maximum of the tan δ peak between 96 and 98 °C. Higher values of T_α, between 102 and 108 °C, are obtained for zein, SZ 15/85 and SZ 50/50. For all blends, the main relaxation peak is in the range of temperature of the pure components main relaxation. Large differences are observed in the tan δ peak amplitude. Highest values of tan δ peak amplitude are reached for pure components, whereas lowest ones are obtained for the blends, with a minimum for SZ 70/30.

Consequently, and despite the unavoidable moisture loss at high temperatures significant differences of the storage modulus E' values are observed beyond the E' drop associated with the glass-rubber transition. The E' drop characterizing the continuous phase, starch or zein, decreases when the concentration of the dispersed phase, zein or starch, respectively, increased. At $T_\alpha + 30$ °C, chosen arbitrarily as temperature reference, for systems with zein as major component, E' values vary from 6.2 MPa for pure zein to 11.2 MPa for SZ 15/85 and 25.8 MPa for SZ 50/50. All these samples have a continuous zein phase. Conversely, $E'(T_\alpha + 30$ °C) values vary significantly from 3.3 MPa for pure amorphous corn starch to 5.4 MPa for SZ 85/15 and 24.0 MPa for SZ 70/30. As a conclusion, E' characterizing the rubbery states (i.e., above glass transition temperature) takes values larger for blends with a morphology of co-continuous phases in comparison to blends with a matrix/particle morphology.

3.2. Corn flour materials

On the basis of the results obtained for starch–zein blends, processed corn flour is studied in the same way, including the starch transformation level depending on the process intensity.

3.2.1. Starch transformation level

Materials obtained from corn flour processed in the Rheoplast® at a specific mechanical energy of about 200 J g^{-1}, are homogeneous and solid. The level of non-transformed starch in each sample was estimated by the measurement of the residual gelatinisation enthalpy and compared to those of native corn flour (Table 1). Only those processed at 100 and 128 °C (CF 100 and CF 128) contained residual native starch, whereas when processed at 140 and 160 °C (CF 140 and CF 160), starch is completely amorphous. This result is consistent with the melting temperature of corn starch at this initial moisture content (26%, wb), for which the melting point is located between 120 and 130 °C (Colonna & Buléon, 1994). Fig. 6 presents the X-ray diffraction patterns obtained for the four processed corn flour. Native corn flour shows four mean peaks at 2θ values of 15° and 23°, and between 15 and 20 characteristic of the A-type crystallinity. These peaks decrease considerably for CF 100 and CF 128 and nearly disappear for CF 140 and CF 160. Concomitantly to A-type disappearance, peaks at $2\theta = 13.3°$ and 19.7°, typical of V-type crystallinity, increase with the temperature of treatment. This result reflects the formation of amylose–lipid complexes commonly formed after thermomechanical treatment of flours (Colonna & Buléon, 1994). The calculated fraction of A-type crystallinity is reported in Table 1. It provides an evaluation of the non-amorphous starch content, by taking into account the native starch granules and the dispersed fragmented starch granules, as described by Barron et al. (2001).

3.2.2. Thermomechanical behaviour and transformation level

Storage modulus E' (Pa) and tan δ curves vs. temperature are presented in Fig. 7 for corn flours processed at various temperatures. All samples present a tan δ peak characterising the main relaxation around $T_\alpha = 94$ °C (±2 °C) for a moisture content of 12% (wb). This observation does not corroborate previous result obtained by Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, and Lillford (1992) on the increase of T_g with increase of starch crystallinity. The samples are glassy at room temperature and the value of their storage modulus is between 2 and 3 GPa,

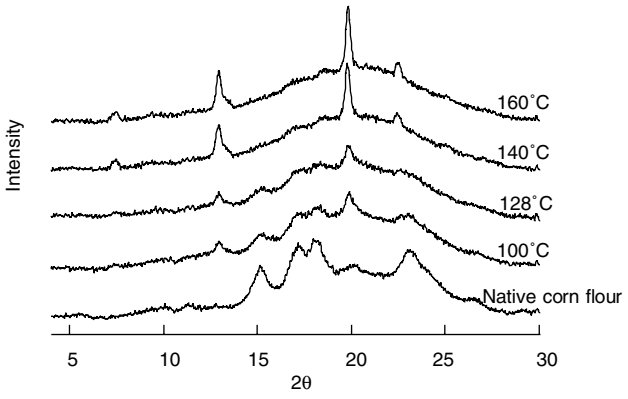

Fig. 6. X-ray diffraction patterns for corn flour treated by Rheoplast® at different temperatures.

Table 1
Characteristics of corn flour after transformation under different processing: residual gelatinisation enthalpy and crystallinity

Processing	Coded names	Temperature (°C)	ΔH (J g^{-1})	Degree of residual starch granules (%, DSC)	A-type crystallinity of samples (%)
	–	Native	13–14	–	48
	CF100	100	2.12	13.5	16
Rheoplast®	CF128	128	0.46	2.9	8.5
	CF140	140	0.0	0.0	7.3
	CF160	160	0.0	0.0	6.9

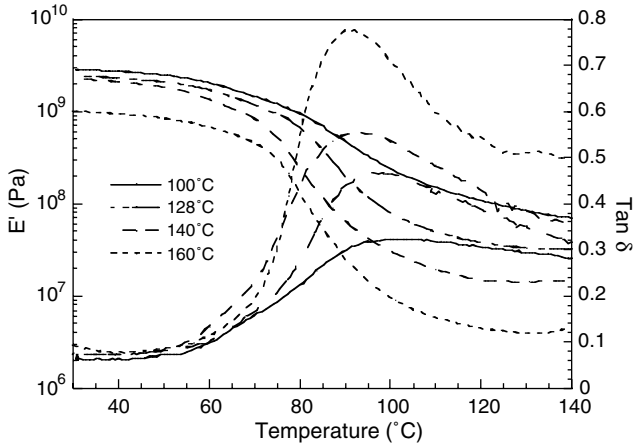

Fig. 7. Dynamic mechanical behaviour of corn flour treated by Rheoplast (moisture content 12%), treatment temperatures: 100, 128, 140, and 160 °C at 0.2 Hz, 0.05% strain.

except for CF 160 which has a slightly expanded structure. The trend of the storage modulus at 25 °C of CF 100, CF 128 and CF 140 is a decrease when the temperatures of treatment increase, i.e., the increase of transformation intensity. For $T > T_\alpha$, the values of E' values drop and rank in the order of increasing processing temperature, in a ratio larger than 10 between corn flour transformed at 100 and 160 °C. Although, moisture loss cannot be completely avoided by grease coating and affect the accuracy of the measurement, the variations of the E' values are large enough to reflect a significant variation due to the difference of transformation level, from 86.5% to 100% as evaluated by DSC. Concomitantly, the amplitude of $\tan\delta$ peaks increased from 0.3 to 0.8 when corn flour transformation increased.

3.2.3. Thermomechanical behaviour of blends of native and processed corn flour

Because of their different composition, the blends of extruded corn flour with native corn flour (ECF/NCF) are representative of processed flour with different transformation level. The variation of storage modulus E' vs. temperature obtained by DMA for five compositions, 90/10, 80/20, 70/30, 60/40, and 50/50, for 14% moisture content (wb), are represented in Fig. 8a. Tan δ peaks are located between 62 and 68 °C for all compositions (Fig. 8b). The differences of temperature of the $\tan\delta$ peak (T_α) can be explained by the uncertainty of the moisture content (±0.5%), which leads to a variation of about 5 °C in the glass transition temperature. In the glassy state, at room temperature, E' values are not significantly different, between 0.8 and 1 GPa. In the rubbery state, at temperature larger than T_α, significant differences can be observed. The lowest values of modulus E' are observed for ECF/NCF 90/10 compared to the largest one obtained for ECF/NCF 50/50. The amplitude of $\tan\delta$ peak decreases with the increase of the level of native flour fraction. These trends are similar to those observed for the variations of

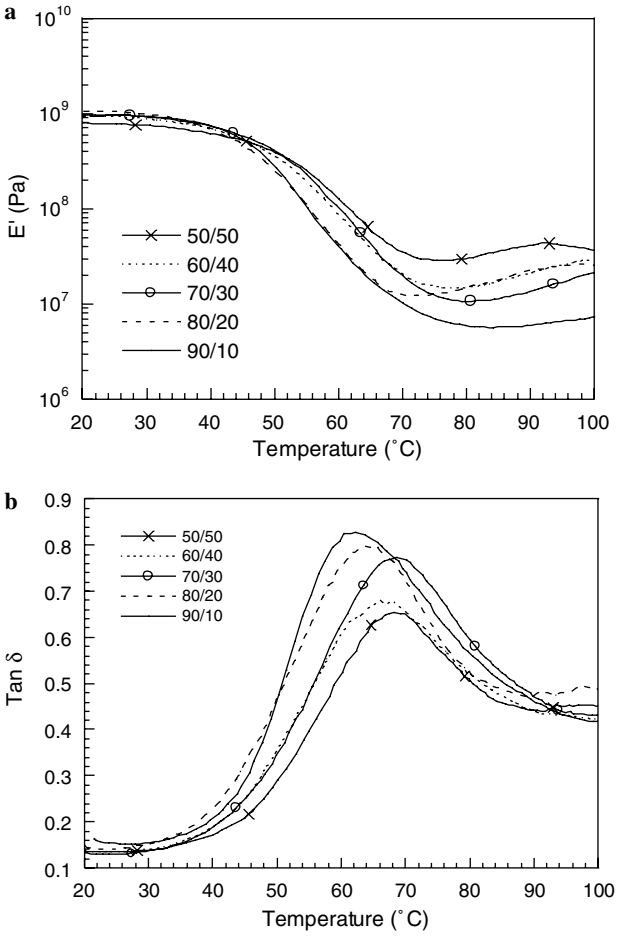

Fig. 8. Dynamic mechanical behaviour of extruded corn flour (ECF)/native corn flour (NCF) moulded blends (moisture content 14%), at 0.2 Hz, 0.05% strain.

$\tan\delta$ peak and modulus $E'(T > T_\alpha)$ of corn flour processed by Rheoplast®, according to the starch transformation levels.

4. General discussion

4.1. Morphology–mechanical properties relationships

4.1.1. Starch–zein system

The T_g of starch–zein blends remains localised in the domain 65–70 °C for all starch–zein ratio and a small variation of T_g due to strong matrix–particle interactions could not be observed. Concerning the mechanical properties of the material, the incompatible particles which constitute zein aggregates were shown to have a weakening effect (Fig. 4). From a model established for composite materials (Nicolais & Nicodemo, 1974), this behaviour is interpreted by a lack of adhesion between zein and starch which hinders the stress transfer from the matrix to the particles. During deformation the starchy matrix has to withstand the stress, which thus increases in the continuous phase when the particle content increases. This interpretation is supported by the results from the

thermomechanical analysis. Variations of the amplitude of tan δ peak of the main relaxation were plotted vs. zein content in starch–zein blends (Fig. 9). The amplitude is decreased by the addition of zein in amorphous starch continuous phase, and also by the addition of amorphous starch in zein continuous phase. Such a decrease of the amplitude of tan δ peak, when the particle content is increased, has been observed in matrices of synthetic polymer filled with glass beads or crystalline cellulose (Alberola & Bergeret, 1994; Dufresne & Cavaillé, 1998; Dufresne, Kellerhals, & Witholt, 1999). Although the existence of an interphase with specific properties, because of specific matrix–particles interactions, may be invoked, the main cause of this event is the decrease of matrix quantity, i.e., a decrease of amount of material with a glass transition in the temperature domain of observation. In such systems, the T_g of particles is very different from the T_g of the matrix. Starch–zein blends are quite different from the systems studied by these authors, as the glass transition of the two components, and consequently the main relaxation, occurs at the same temperature for both components (see Fig. 3). Consequently, the amount of matter which induces the main relaxation does not change with the starch–zein blends ratio. An average of the tan δ peak amplitude of the pure components would be expected, but, surprisingly, a linear decrease of the amplitude with the ratio of particles is observed (Fig. 9). The calculation of tan δ peak amplitude with volumic fraction of particles V_P, by Eq. (2), according to Nielsen model (1969), presents the same trend as experimental data (Fig. 9, dotted line). The system seems to behave as a continuous matrix filled with voids. The decrease of the tan δ peak amplitude is close to the one predicted by the model, and is certainly induced by a lack of adhesion between starch and zein. Similar observations can be made when zein is the continuous phase and the particles are starch (for zein >34%).

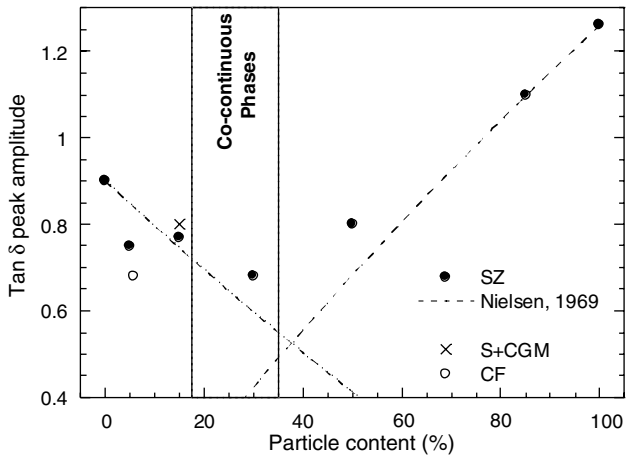

Fig. 9. Tan δ peak amplitude obtained for starch–zein blends, processed corn flour and S/CGM blend conditioned at 59% relative humidity. Dotted line: amplitude calculated by the model of Nielsen (1969).

4.2. Corn flour products

On the basis of the results obtained for starch–zein blends, the lack of adhesion between the starchy matrix and proteins is the main cause of the fragility of the products. Nevertheless, the stress at break of processed corn flour (18 MPa) is much lower than the one of the starch–zein model blend (27 MPa), for a similar amount of proteins (6.6%, db) (Fig. 4). In a similar way, the tan δ amplitude measured on flour is lower than the one obtained with the corresponding, blend (Fig. 9). Such deviation can be interpreted by considering the effect of the total content of particles contained in corn flour which are likely to be incompatible with the matrix. In the corn flour, starch represents 83% (db) and it might be argued that the amount of starchy matrix is close to this value. Referring to the corn flour composition (Watson, 1987), the last 17% are composed of proteins (6.6%), cellulose and others polysaccharides (3–4%), insoluble fraction (fibres, 1%) and soluble fibres (0.5%). The non-protein elements, incompatible with starch (about 5%, db), like insoluble fibres or cellulose, can be also considered as particles within the starchy matrix, which induces defaults, leading to an enhanced fragility of the material. Therefore, by taking into account all the particles in corn flour, which constitute the dispersed phase, the amount of particles within the processed corn flour is clearly higher than 6%, and rather close to 12%, which leads to experimental values of rupture stress and tan δ of corn flour, closer to the predicted ones.

This is confirmed by the fact that, when corn gluten meal (CGM), composed of these elements (proteins and fibres), is added in starch at 15%, the decrease of the mechanical properties of starch–corn gluten meal blend (S/CGM) are well predicted by the model (Fig. 4). Furthermore, the value of the amplitude of tan δ peak is the same as the one obtained for SZ 85/15, close to the value predicted by the composite model (Fig. 9). This result confirms that the variations of the amplitude of tan δ peak are mainly governed by the particles fraction, which have a lack of adhesion with the matrix, rather than the biochemical nature of the particles.

4.3. Generalisation of particles effect: The starch transformation level

In addition to non-starchy components, the particles in processed corn flour can also contain native or fragmented starch granules. As shown before, residual starch granules or native flour influence the tan δ peak amplitude in the same way as zein particles (Figs. 7 and 8). Table 2 reports different kinds of particles in the studied samples, with an estimation of their concentration in weight. Materials constituted by a zein matrix dispersing starch particles are also taken into account. By plotting the relative tan δ peak amplitude as a function of total particles weight content, the trend observed in Fig. 9 is extended and the overall "particle effect" is presented (Fig. 10). The relative tan δ

Table 2
Evaluation of type and concentration of particles contained in materials studied

(%) sample type	Particles					
	Starch granules or fragments	Amorphous starch domains	Protein aggregates (zein)	Fibres and insoluble components	Native flour particles	Total
Amorphous starch	–	–	–	–	–	0
Starch partially transformed	10	–	–	–	–	10
AZ blends with starch matrix	–		5			5
	–	–	10	–	–	10
			15			15
AZ blends with zein matrix	–	15	–	–	–	15
	–	50	–	–	–	50
Amorphous starch + corn gluten meal	–	–	6	9	–	15
Flour completely transformed	–	–	6	6		12
Flour partially transformed	2.9 (Rheoplast®)	–	6	6	–	14.9
	13.5 (Rheoplast®)	–	6	6	–	25.5
	14.8 (extrusion)	–	6	6	–	26.8
Native/extruded flour blends	–	–	–	–	10	10
	–	–	–	–	20	20
	–	–	–	–	30	30
	–	–	–	–	40	40

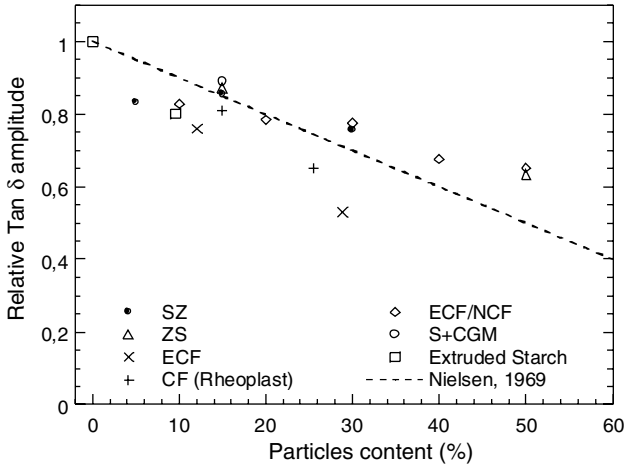

Fig. 10. Tan δ peak amplitude vs. particles content for different samples CF, corn flour; SZ, dispersed zein in continuous starch; ZS, dispersed starch in continuous zein; ECF/NCF, extruded/native corn flour.

peak amplitude is defined by the value measured on the sample divided by the value obtained for the matrix without particle (starch or zein). For partially transformed corn flour, particles are protein aggregates, native remnant structures of corn flour particles (as previously described by Chanvrier et al., 2005), incompatible elements (fibres, cellulose), and native starch granules. The overall trend of experimental results is in agreement with values calculated with Nielsen model (dotted line): the amplitude of tan δ decreases quasi linearly with particle content. The deviation from the model could be explained by an underestimation of the particle amount. The presence of ghost granules, more or less swollen, or different intermediate transformation levels of starch in the processed corn flour are not taken into account as particles. Such starch fragments, which have lost their crystalline structure, might behave like particles within the fully molten amorphous matrix, but their incompatibility with this matrix is questionable. This hypothesis could be checked by microscopic methods, in order to assess the amount of ghost granules. The existence of amylose–lipid complexes, revealed by V-type crystallinity, may also have a particle behaviour. Indeed their presence in extruded plasticised starches has been shown to significantly increase the G′ when tested in dynamic oscillatory shear rheometry at $T > T_g$ (Della Valle, Buleon, Carreau, Lavoie, & Vergnes, 1998). In other words, crystalline amylose–lipid complexes embedded in the amorphous matrix, may also be considered as particles. Finally, differences between experimental and calculated stress values can also be related to the shape and the size of particles, considered as spherical in the models. In the processed corn flour, CSLM observations revealed irregular protein aggregates, with various shape and size (Chanvrier et al., 2005). Compared with the spherical assumption, these irregularities increase the area of weak adhesion between the phases, related to, and could contribute to weaken the material. A better knowledge of the particles shape and interfacial surface, possibly determined by image analysis, could better elucidate the contribution of the matrix–particles interface. Such investigations would require microscopic methods to observe and quantify the whole particles of the processed corn flour, in complement to the previous characterisation of protein aggregates. For all systems, the ''particle effect'' on E' modulus is always more marked in the rubbery state than the vitreous state It seems to be due to a particle reinforcing effect above T_g. Such phenomena could be evidenced on similar materials with higher water content leading to a T_g below ambient temperature.

5. Conclusions

This study focused on the processed corn flour, for which the morphology, composed of proteins aggregates and residual starch granules dispersed in a major phase of amorphous starch, depends on thermomechanical treatment. Zein particles were shown to influence the mechanical properties, following a model used for matrix–particles materials, with no or weak adhesion between the components. Residual starch granules in processed corn flour were shown to exert a similar "particle" effect on the thermomechanical properties of corn flour. The relative good fit with the model of Nielsen (1969) confirms that the particle content has much more influence than the particle composition.

If these results underline the lack of adhesion between starch and zein, further studies, as mechanical properties testing, should be implemented to investigate the adhesion between residual starch granules and amorphous starchy matrix. Finally, every particle within the processed corn flour constitutes heterogeneity and is potentially responsible for the fragile behaviour of transformed corn flours. The debonding of these particles during a mechanical solicitation could be confirmed by a coupling between mechanical testing and in situ observations. This study also brings complementary information that can be used to ascertain the structural basis of the crispy properties of low hydrated cereals products.

Besides the investigation of thermomechanical properties of biopolymer blends, DMA has shown to be highly sensitive and informative tool to study the morphology of such materials.

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Glossary

CGM: Corn gluten meal
CF: Corn flour
ECF: Extruded corn flour
NCF: Native corn flour
SZ: Starch zein
MSP: Mean surface of particules
NP: Number of particules
Vp: Volumic fraction of particules