Effect of morphology on the elastoplastic behaviour of pea based starch-protein composites

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Imen JEBALIA, Jean-Eudes MAIGRET, Anne-Laure REGUERRE, Sofiane GUESSASMA, Denis LOURDIN, Guy DELLA VALLE, Magdalena KRISTIAWAN

INRA, UR 1268 Biopolymers Interactions and Assemblies (BIA), 44316 Nantes, France

Abstract:

The texture of starchy extruded food, considered as solid foam, is defined by its structure and mechanical properties of constitutive material. This material is envisioned as dense composite of starch and proteins. In addition to the composition, its mechanical properties depend on the morphology created during extrusion. In this context, the aim of our study is to determine the relationship between morphological features and mechanical properties of starch-legume protein composites using experimental and FEM simulation approach. In this purpose, dense pea composites having various starch-protein morphologies were obtained by a twin-screw extruder. The morphology of the composites displayed protein aggregates dispersed in an amorphous starch matrix, revealed by microscopy. This microstructure can be described by some parameters, such as median width of protein aggregates, their total perimeter and area, from which a protein-starch interface index was derived. These morphological features depended on formulation and specific mechanical energy SME (100-1100 kJ/kg). FEM simulation of three-point bending test indicated that the elastic-plastic constitutive model following Voce scheme represented adequately macroscopic mechanical behaviour of pea composites. The impact of morphological features, in particular starch-protein interface index, on mechanical properties was explained by the poor interfacial adhesion between pea starch and pea proteins.

Keywords: bending test, starch-protein interface, protein aggregates, FEM, microstructure

1 Introduction

Low moisture extrusion is often used to produce cereal-based expanded foods. The supplementation with pulse legumes (pea, lentils, beans…) may contribute to the health benefits of these foods thanks to the complementary amino acid profiles of legumes and cereals [1]. In food science, mechanical approach can be used to characterise the textural parameters (hardness, crispness…), instead of sensory analysis. The texture of expanded foods considered as solid foams is governed by their structure at different scales: their density, their cellular structure and the mechanical properties of the intrinsic material that can be envisioned as a dense starch-protein composite considering the large contrast on mechanical properties between phases [2]. In addition to the composition, its mechanical properties

depend on the morphology created during extrusion. Indeed, high input of thermo-mechanical energy leads to structural modification of the biopolymers, including starch melting and depolymerisation, and protein aggregation [3]. These structural modifications that depend on the formulation and extrusion variables, govern the morphology of composites. The precise knowledge of constitutive laws of the intrinsic material is primordial to predict the texture of solid foams. The aim of this work is to determine the relationship between the morphological features and mechanical properties of legume composites. To do this, the morphology of pea flour and blends of pea starch and pea protein isolate extruded composites were analysed and the parameters of constitutive model (i.e. elastic-plasticity) was predicted using Finite Element Modelling (FEM).

2 Material and methods

2.1 Composite processing and morphology

Dense composites were obtained as ribbons by extrusion of pea flour and starch-protein (SP) blends, having starch content of 33–63% (dry basis), using a laboratory scale co-rotating twin-screw extruder (Thermo Scientific™ Process 11, Germany). The die temperature was regulated at temperature lower than 100°C to avoid composite expansion. In order to obtain composites with a wide range of starch-protein morphologies and mechanical properties, the extrusion parameters were varied in the following intervals: moisture content MC (25-35%, wet basis), screw rotation speed (120-700 rpm) and the temperature of the last barrel of the extruder (T_m-20°C, T_m, T_m+20°C), where T_m is the melting temperature of the raw material. Specific mechanical energy (SME, J/g) was calculated as follows:

$$SME = \frac{C.N}{Q} \quad (1)$$

where C is the measured torque (N.m), N the screw speed (rad/s), and Q the mass flow rate (g/s).
Immediately after extrusion, the composites were dried at 40°C for 24 h in order to avoid starch retrogradation. Then, they were stored in conditioning chamber at stable relative humidity of 59% at 20°C for two weeks, to obtain a uniform moisture distribution in the material (MC 12+0.5%, wet basis) before the mechanical testing. The name of selected samples for mechanical analysis and the corresponding chemical composition and extrusion variables (*SME, MC*) were reported in Table 1.

Table 1. Composition and extrusion variables (*SME, MC*) of pea composites selected for mechanical analysis

Name	Starch (% db)	Protein (% db)	SME (kJ/kg)	Moisture content (% wb)
F1	46	24	141	35
F2	46	24	1149	25
B1	63	32	992	25
C1	47	46	354	25
C2	47	46	1067	25
D1	31	61	1077	25

The organisation of starch and proteins of composites was investigated using Confocal Laser Scanning Microscopy (CLSM). Image analysis was performed using Matlab software to determine the median particle width (D_{50}, µm), total area (A, mm^2) and total perimeter (P, mm) of protein aggregates. The starch-protein interface index (I_i, dimensionless) was computed as follow:

$$I_i = \frac{P}{\sqrt{A}} \tag{2}$$

2.2 Mechanical testing of the composites

The mechanical properties of specimen ribbons (t_h x 100 x 10 mm^3) were determined by a three-point bending test mounted on a dynamometer (Adamel Lhomargy, France). The thickness (t_h) of specimens was measured with a Vernier caliper. The crosshead speed was 100 mm/min. The tests were performed until specimens broke. The force F (N) and the crosshead displacement d (mm) were recorded during the test and converted to engineering bending stress σ (Pa) and strain ε (%), respectively as follows:

$$\sigma = \frac{3FL}{2ht_h^2} \tag{3}$$

$$\varepsilon = \frac{6dt_h}{L^2} \tag{4}$$

where L is the support span (0.04 m) , h is the specimen width (0.01 m). The measurements of mechanical properties were performed with ten repetitions, leading to a relative error of 20%.

2.3 FEM simulation

The Structural Mechanics module of COMSOL® Multiphysics v. 5.3 was used to the FEM simulation of three-point bending test. Parallepipedic geometry having the same dimensions as the specimens used for experimental bending test was built and meshed. Meshing was performed using 3D tetrahedral elements. Each element is described by four nodes, and each node has three degrees of freedom (u, v, w) corresponding to displacements in the main X, Y and Z directions. The nodes of the central upper line are constrained to displacement in the other directions than vertical one ($U_X = U_Y = 0$). Nodes of lateral bottom lines are constrained against vertical displacement ($U_Z = 0$) and are free to translate in the other directions. In order to avoid rotation of the specimen, the lateral displacement of lateral nodes was coupled by antiperiodic conditions ($U_{source} = -U_{destination}$).

A simple elastic-plastic constitutive model was used for the material. The elastic behaviour of isotropic material (as our composites) is described with Young's modulus (E_Y) and Poisson's coefficient (0.34, [4]). The plastic (irreversible) deformation was described using Voce model [5], developed for isotropic hardening material:

$$\sigma_{ys} = \sigma_{ys0} + \sigma_{sat}\,(1 - e^{-\beta\varepsilon_{pe}}) \tag{5}$$

where σ_{ys0} is the yield stress, σ_{sat} is the saturation flow stress, β is the saturation exponent and ε_{pe} is the plasticity strain.

A non-linear static analysis was performed in the following steps to predict elastic-plastic parameters (E_Y, σ_{ys0}, σ_{sat}, β). First, a set of parameters values was suggested using sweep analysis. Second, the FEM response for reaction force– displacement curve was converted to bending stress –strain curve using equations (3) and (4), and the last curve was compared to the experimental one. Third, the

parameters were adjusted to make the best match between the numerical and experimental responses. Since the pea flour composite behaviour displayed only an elastic behaviour, the plasticity analysis was not performed.

3 Results and discussion

A large interval of SME values was obtained (100-1100 kJ/kg) (Table 1) by the variation of extrusion variables, indicating that a wide range of biopolymer changes may be expected. Figure 1 presents an example of the organisation of starch and proteins of pea composite (sample B1).

The CLSM images revealed that the morphology of all composites displayed protein aggregates dispersed in a continuous matrix of amorphous starch. The size and shape of protein aggregates was not uniform between different composites. The morphological features such as median size (D_{50}) and interface index (I_i) of protein aggregates depend strongly on the processing variables (SME) (results not shown) and formulation. Pea flour composites had a higher I_i (1.8-3.1) and lower D_{50} (8-18 µm) than blend composites (I_i =0.72-1.6 and D_{50} = 19-51 µm). Some voids was observed at the interface of starch and protein domains. These voids can result from the lack of adhesion between biopolymers. The poor interfacial adhesion was also observed for starch-zein blend composites [6, 7].

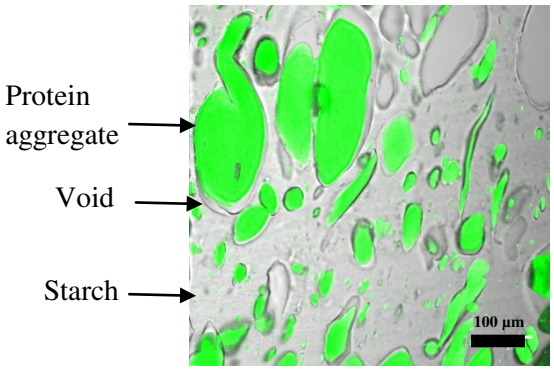

Figure 1. Example of CLSM image obtained for pea composite (sample B1). The proteins were stained green with fuchsin acid. Unstained amorphous starch was in grey. The white space at the interface of starch and protein aggregates indicated the void.

Figure 2 displays the engineering bending stress- bending strain curves obtained during three-point bending tests of pea composites with different formulations. Mechanical testing revealed that pea flour composite exhibited brittle behaviour with rupture in the elastic domain. However, the bending stress– bending strain response of SP blends composites exhibited a deviation from elastic behaviour following a plastic deformation, where the rupture occurred at this stage. The breaking bending stress and bending strain of SP blends composites were higher than those of pea flour and they decreased with increasing pea protein content. The weakened effect of proteins was also observed in the case of maize starch-zein composites [8]. The high fibre content of pea flour (26% db) compared to SP blends (3%) may partly explain their brittle behaviour [9].

According to figure 2, a good agreement (error 13%) between the experimental results and FEM simulation was obtained for the most of pea composites. This result shows that the elastic-plastic model, based on Voce plasticity model for isotropic hardening material is adequate to describe the macroscopic mechanical behaviour of pea composites. The predicted values of Young's Modulus (1.2-2.36 GPa) were

in the same order as the observed flexural modulus (1–2.38 GPa). The discrepancy for the composite B1, that appears beyond the yield stress can be attributed to the effect of morphology. The organisation of starch and protein domain and the interface was not taken into account in the FEM geometry.

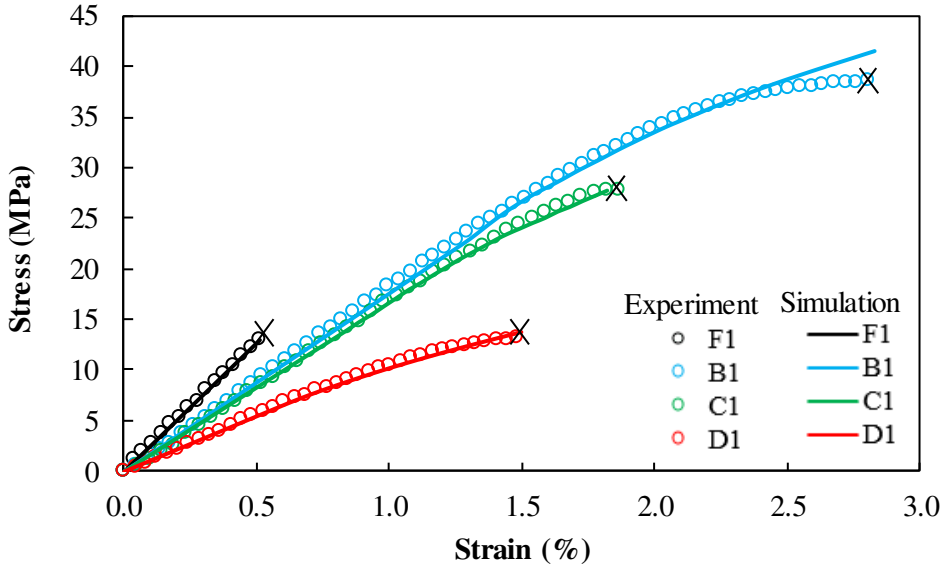

Figure 2. Engineering bending stress - bending strain curves of pea composites deformed during 3-point bending test: experiment versus FEM simulation using elastic-plastic model. Measurement conditions: temperature 20°C, moisture content MC 12 ± 0.5% wb. X indicates the measured breaking bending stress and bending strain.

To understand the effect of morphology on global mechanical behaviour of composites, the elastic-plastic model parameters, computed using FEM, were related to morphological features, in particular the starch-protein interface index I_i (Fig. 3).

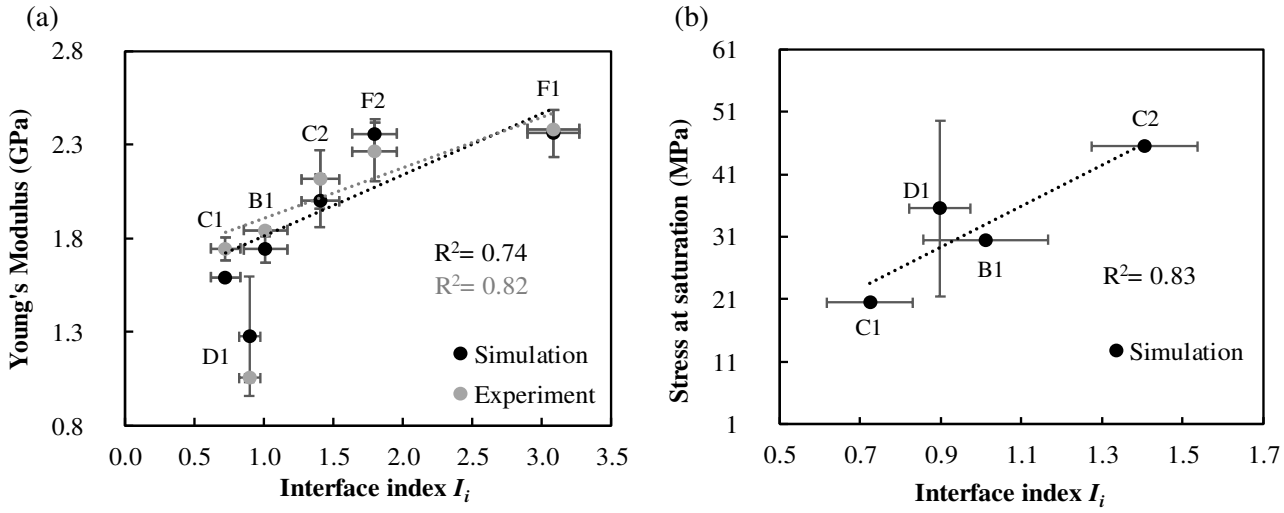

Figure 3. Impact of starch-protein interface index on (a) Young's modulus and (b) predicted stress at saturation (Equation 5).

Young's modulus was positively correlated to the interface index (Fig.3 a). This result indicates that the higher interfacial adhesion between starch and proteins led to a stiffer material. However, by increasing the deformation, the interface index negatively affected the composite breaking bending stress (results not shown), which indicates the increase of interfacial debonding under higher strain. The debonding is more pronounced when the interfacial adhesion is poor (presence of voids, Figure 1). Indeed, the strength of composites strongly depends on the stress transfer between the particles and matrix [10]. The plasticity parameters, i.e. stress at saturation (20-45 MPa) were correlated well with the morphological features, i.e. interface index I_i (Fig. 3b). Therefore, in-depth study, using experimental and FEM approaches at microstructure scale is required to understand precisely the impact of the morphology and interface properties on local mechanical behaviour of composites.

4 Conclusion

The extruded pea flour and starch-protein blends presented composite morphology with continuous starch matrix containing dispersed protein aggregates. The organisation of protein aggregates varied according to the formulation and *SME* level. Mechanical tests revealed brittle behaviour of pea flour with rupture in the elastic stage. Whereas, the rupture of starch-protein SP blends occurred in the plastic stage. The increasing of protein content led to more brittle behaviour. The FEM simulation of three-point bending test revealed that the elastic-plastic model, based on Voce plasticity model was adequate to describe global mechanical behaviour of pea composites. The FEM modelling in the macroscopic scale allowed us to predict the elasticity and plasticity parameters that depended on morphological features, mainly the interfacial index of starch and proteins. To better understand morphology dependence of local mechanical behaviour of composites, FEM modelling will be performed at the microscopic scale by taking into account the starch and protein organisation and the imperfect interface (voids). Then, the obtained constitutive laws for starch-protein composites will be integrated into multi-scale numerical models to predict the mechanical properties of legume based solid foams.

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