Development and Characterization of Extruded Biodegradable Foams based on Zein and Pearl Millet Flour

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ABSTRACT

The aim was to establish a preliminary processing window for extrusion foaming of blends of zein and pearl millet flour and to estimate the properties of the extrudates. The weight ratios of zein:pearl millet flour were 75:25, 72:28 or 70:30 and foamed extrudates with a circular geometry were produced with bulk densities between about 350 and slightly higher than 500 kg/m^3. Compounds with a higher zein content tended to give a more foamed structure. The stiffness (modulus) in compression of the foams was in the range 25-50 MPa with higher values at a higher bulk density. At a given density, the specimens with a higher zein content appeared to give a stiffer structure.

INTRODUCTION

Plastic foam-based materials are extensively used in different application such as insulations and for protection in packaging. These foams combine adequate mechanical properties with a low density which makes them useful in a number of situations. A typical example would be expanded polystyrene (PS) which is light and exhibits a good water resistance, which certainly is beneficial with regard to protection of goods. However, conventional polymers of this kind are normally based on fossil resources, i. e. not on renewable materials, and are in many cases not biodegradable. In many cases, products of this kind are only used once and then discarded off[1]. Hence, both from the resource point of view as well as from the disposal aspect, there is a need to replace, at least to some extent synthetic polymers based on fossil resources with renewable and biodegradable alternatives that possess adequate mechanical and functional properties, cf also Ma et al.[2].

As a consequence, the interest in the potential of different biopolymers as raw materials for sustainable (and biodegradable) thermoplastic materials has steadily increased over the last years. Typical examples here are starch and cereal proteins which are abundant in nature, in principle cheap and can exhibit appealing material properties. Starch is biodegradable in soil and water and is a good candidate for replacing synthetic polymers in selected applications[3]. An important characteristic of starch is, as is well known, that it can be transformed into a thermoplastic state[4,5]. The cereal proteins of interest in this context are usually the prolamins. The prolamin zein is the storage protein of corn, it is alcohol-soluble, can acquire a thermoplastic state and can be obtained from by-products from the brewing and biofuel industries, cf Core[6].

Zein is relatively hydrophobic due to its high content of non-polar amino acids[7]. A higher hydrophobicity is certainly of value in several packaging applications. There are different forms of zein, α-, β-, γ- and δ-zein[8], and α-zein is the most abundant corn prolamin and amounts to about 70 % of the total[9]. Pearl millet is draught-tolerant cereal crop which is of interest for the production of bioplastics. It could also play an important role in the production of ethanol and other bioindustrial products, especially in dry areas where other crops are not as easily grown. Pearl millet is grown in western and southern India and in the western region of Africa, including Nigeria. It contains fibrous material, ash and starch in amounts of 1.4-7.3, 1.6-3.6 and 63.1-78.5 %, respectively, as well as protein and oil in the amounts 8.5-19.5 and 1.5-6.8 %, respectively, relative to the dry material[10].

The aim is here to establish a preliminary processing window for extrusion foaming of blends of zein and pearl millet flour and to estimate the properties of the extrudates. This was performed just in order to assess the feasibility of foaming such blends and note trends, not to optimize the process or the foam properties. The blends contain initially some amount of the water which is transformed into steam when exiting the extrusion die thus providing the foaming of the structure. The foaming was further enhanced by an addition of ammonium bicarbonate. The nature of the foaming process is clearly complex. Harmann and Harper[11] attributed the final porosity of the foam to a number of interacting factors, such as the distribution of the water in the melt, the viscosity of the melt and the normal forces acting in the die region. It may be remarked that pearl millet has not been used extensively for production of foams in combination with zein.

EXPERIMENTAL

Materials

Zein was obtained from Sigma-Aldrich (Schnelldorf, Germany). Prior to melt preparation, the zein was defatted in n-hexane as decribed by Oom et al.[12] The protein content 95%.

The pearl millet (*Pennisetum glaucum* [L.] R.Br.) was carefully washed in water several times in order to remove any contaminants. The grains were subsequently dried on a Formica table at 25 ^{o}C for about 72 hours to a moisture content of about 12 weight-%. The dried material was then milled using a Mills Retsch ZM-1 Retsch, Germany.

Poly(ethylene glycol) (PEG) was used as a plasticizer for the zein/millet blend. The PEG-grade used was 400 from Prolabo and 20 g of the polymer per 100 g of the blend was added.

All materials were blended in a kitchen mixer, Braun Combimax 750, equipped with a rotating knife. The materials were blended for 4 minutes at room temperature.

Methods

Several pre-trials were performed in order to find a suitable component formulation for the extrusion foaming experiments. These indicated that suitable millet contents were 25, 28 or 30 weight-% of pearl millet, the rest being zein. The compounds also contained 4.6 g water, 20 g PEG and 3.0 g ammonium bicarbonate (NH_4HCO_3) per 100 g of the zein/millet blend. The extrusion was performed using a Brabender compact extruder, Brabender OHG, Duisburg Germany. The screw speed was varied between 20 and 150 rpm and the temperature profile along the barrel (from hopper to die) was 65, 105, 95 and 80 ^{o}C (the last being the die temperature). A circular die was chosen for the experiments with the diameter 1.5 or 2 mm (a larger diameter produced less perfect foam). The specimens and extrusion conditions are given in Table 1 below.

Table 1. Extrusion conditions

Specimen	Die diam-eter (mm)	Compo-sition*	Screw speed (rpm)	Moisture content (weight-%)
1	1.5	75:25	120	11.8
2	1.5	75:25	150	11.8
3	2.0	75:25	60	11.8
4	2.0	75:25	100	11.8
5	1.5	72:28	100	12.0
6	1.5	72:28	150	12.0
7	2.0	72:28	20	12.0
8	2.0	72:28	40	12.0
9	1.5	70:30	50	12.1
10	1.5	70:30	100	12.1
11	2.0	70.30	80	12.1

*Given as zein:pearl millet flour (by weight)

Fig. 1 shows the foaming of the extrudate as it exits the die of the extruder.

Figure 1. Extrusion foaming of the zein/pearl milletflour blend.

The moisture content of the specimens were determined gravimetrically after exposure to heat as described in AOAC[13]. The measurements were carried out in triplicates and given as an average value.

The bulk density of the foamed cylinders were evaluated from the geometry of the specimens and their weight, cf Qing-Bo et al.[14]. An average value of ten measurements for each specimen was reported.

The expansion ratio was evaluated as the ratio between the cross-sectional area of the foamed specimen and that of the circular die of the extruder. Each reported result was an average of 15 measurements.

A Göttfert Rheograph 2002 (Germany) capillary viscometer was used in order to measure the shear viscosity as a function of the shear rate for the blends at 90 ^{o}C. The capillary used had a length of 20 mm and a diameter of 2 mm. the viscosity was evaluated at shear rates between approximately 200 and 800 s^{-1}. At lower shear rates, the measurements tended to be unstable. No Rabinowitsch or Bagley corrections were applied to the results.

Small cubes of 3x3x3 mm^3 were cut out from the samples. The sample cubes were air-fixed with formalin and glutaraldehyde in $CaCO_3$ over night. Thereafter the sample cubes were air-fixed a second time with 1 % OsO_4 for 5h, followed by dehydration in a graded ethanol series 50, 70, 90, 100 volume-%. The cubes were then embedded in Technovit 7100. For the LM examination, thin sections (1.0 μm) were cut with a glass knife using an ultramicrotome, stained with Lugol´s iodine solution and light green for visualising the pearl millet phase and the protein phase, respectively. The thin sections were examined with the Nikon Microphot FXA microscope (Japan) using the 10x objective (N.A.=0.45). Images were taken with an Altra 20 camera.

Specimens with a height at least equal to the diameter were compressed in an Instron 5542 single-column universal materials testing machine (Instron, Norwood, MA, USA). All the samples were conditioned at 23^{o} C and 50% relative humidity (RH) for at least 48 h before testing. The tests were replicated at least four times. The testing speed was set to 2.1 mm/min. The results were given as the Young's modulus, the compressive strength and the compressive strain at failure. The compressive strength is here taken as the maximum nominal stress value recorded during the compression test.

RESULTS AND DISCUSSION

Fig. 2 shows the shear viscosity as a function of the shear rate for the different blends at a temperature of 90 ^{o}C. The viscosity apparently increased slightly with increasing shear ate, but not dramatically. There were no appreciable differences between the different materials in this respect, which is to be expected considering their similarity in composition. The blend with the lowest zein content exhibited a somewhat lower viscosity than the others. A possible reason for this is that the pearl millet flour had a particulate nature (see below) and thus acted as filler particles. A higher filler content normally results in an increased viscosity. The magnitude of the viscosity was in the range 200-300 Pas in the investigated shear rate region, which is lower than the viscosity of thermoplastic starch used for film blowing at the chosen processing temperature[5].

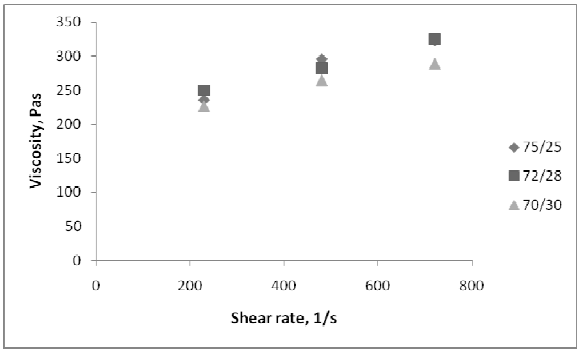

Figure 2. The viscosity of the blends as a function of the shear rate at 90 ^{o}C. The weight relation between the components (zein/pearl millet flour) is given in the legend.

With the compositions chosen and with the stated extruder setting, it was possible to foam the zein/millet blends. The expansion ratio was typically in the range 2-3.2 for the used processing conditions and formulations. As a result of the extrusion the moisture content in the blends decreased from ca 12 weight-% to 6.3-7.1 weight-%, depending on the specimen. Only a limited series of experiments could be performed due to the limited amounts of material available, but some trends can be noted, and a processing window was apparently at hand for this thermoplastic biopolymer blend.

Fig. 3 shows light micrographs of specimens 4 and 11 as well as of a reference sample (not foamed). As expected the protein zein forms the continuous matrix and the pearl millet can be seen as discrete particles. In general, these particles were somewhat smaller in the foamed material than in the reference indicating a slight disintegration of the extrusion process. The effect is however not very pronounced. In the foamed material there are a significant amount of small pores due to the foaming (of the size around 5μm) in the protein phase, whereas the protein phase in the reference sample is smooth and even without pores.

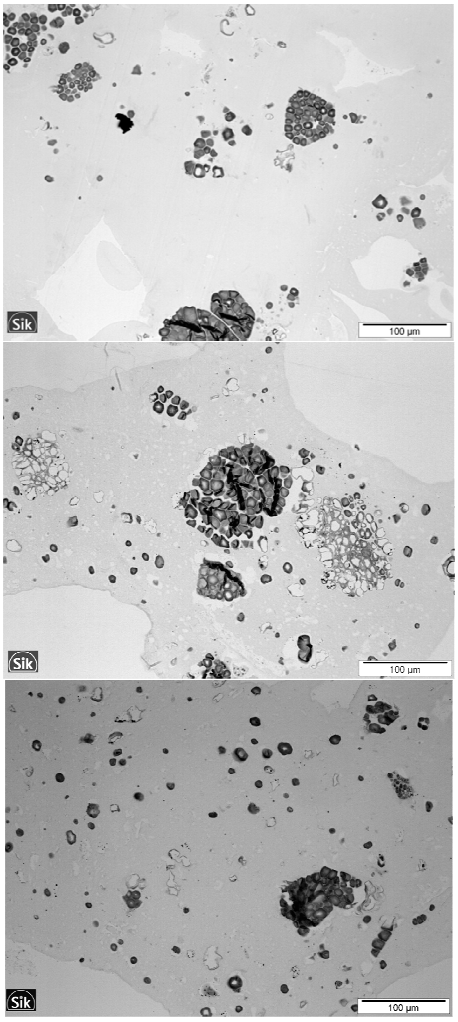

Figure 3. Light micrographs of a reference sample (not foamed, top), specimen 7 (middle) and specimen 9 (below). The protein constitutes the matrix with embedded pearl millet particles.

Fig. 4 shows photographs of cross-sections of the reference (not foamed) and of some of the foamed circular extrudates. The porous structure of the extrudates is obvious and there is a distribution of pore sizes with large as well as small pores. The pore size distribution can thus not be regarded as very homogeneous.

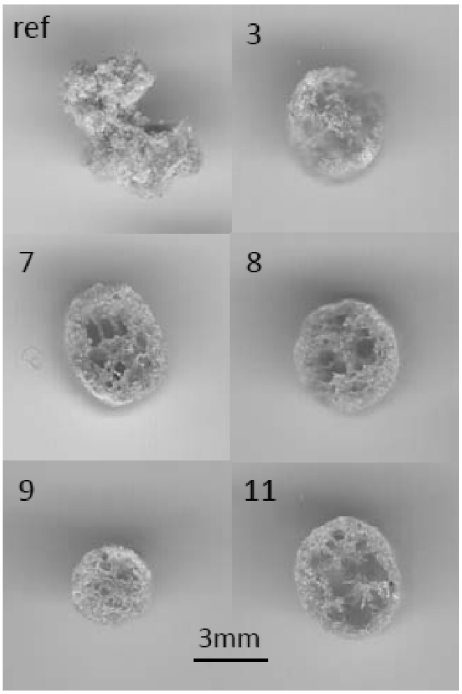

Figure 4. Cross-sections of the reference material (not foamed) and some of the foamed extrudates. The numbers refer to the specimens given in Table 1.

In the following, some properties of the foams are reported. It should be clearly understood that these data only indicate the range of properties that could be attained. Variations in the foam structure along the extradite length were noted, partly as a result of the limited amount of available material resulting in rather short extrusion trials. As a result, the experimental scatter is admittedly rather high. The differences between the three different blends are not very significant, which is to be expected since they were quite close in composition.

Figs 5 and 6 show the elastic (Young's) modulus in compression and the ultimate compressive strain, respectively, as a function of the foam density.

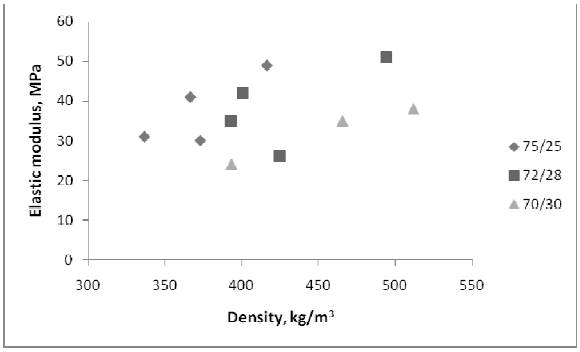

Figure 5. The compressive elastic (Young's) modulus of the foamed specimens as a function of their density. The weight relation between the components (zein/pearl millet flour) is given in the legend.

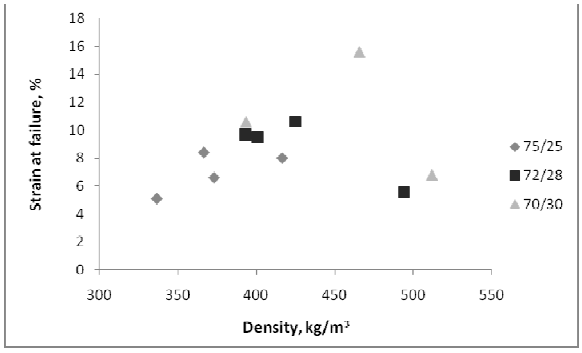

Figure 6. The strain at failure of the foamed specimens as a function of their density. The weight relation between the components (zein/pearl millet flour) is given in the legend.

There is a trend that the zein/millet blend 75:25 gave a more foamed structure, i. e. a lower density, than the other mixtures. The elastic modulus was in general between about 25 and 50 MPa with indications of a higher stiffness towards higher densities (which may not be unexpected). Due to the relatively large experimental scatter, it is not possible make any definite statements, but at a given density, the blend 75:25 appeared to produce a somewhat stiffer structure. Also the compressive strain at failure appeared to increase with increasing foam density as a result of a more coherent structure. The ultimate strain was in most cases in the range 5-10 %. As evident from Table 2, the stress at failure was, with some exceptions, 0.5 to 0.9 MPa. The experimental scatter was as pointed out relatively high and the experimental data only indicate an attainable range.

CONCLUSIONS

As pointed out in the Introduction, the aim of this preliminary study was to clarify if the blend of these two biomaterials could be used for producing a foamed structure with extusion. Suitable processing conditions were identified and foams with densities in the range 350-500 kg/m^3 could be made. There was no attempt to optimize the blend composition or the mechanical properties of the foams. It is certainly likely that improvements of the foamed structure and its properties can be attained by tuning the processing conditions and the composition of the blends (including the water content).

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REFERENCES

1. Pushpadass, H.A., Babu, G.S, Weber, R.W and Hanna, M.A. (2008), "Extrusion of starch-based loose-fill packaging foams: effects of temperature, moisture and talc on physical properties", *Packaging Technol. Sci.,* **21**, 171-183.

2. Ma, X., Chang, R. P., Yu, J. and Stumborg, M. (2009), "Properties of biodegradable citric acid–modified granular starch/thermoplastic pea starch composites", *Carbohydrate Polymers,* **75**, 1–8.

3. Park, H. M., Lee, W. K., Park, C. Y., Cho, W. J. and Ha, C. S. (2003), "Environmentally friendly polymer hybrids", *J. Mater. Sci.,* **38**, 909–915.

4. Shogren, R., Fanta G. and Doane, W. (1993), "Development of starch-based plastics – a reexamination of selected polymer systems in historical perspective", *Starch/Stärke,* **45**, 276-280.

5. Thunwall, M., Kuthanová, V., Boldizar, A. and Rigdahl, M. (2008), "Film blowing of thermoplastic starch", *Carbohydrate Polymers,* **71**, 583-590.

6. Core, J. (2002), "Corn coproduct cuts ethanol production costs", *Agricultural Res.,* **50** (April), 20-21.

7. Tihminlioglu, F., Atik, I. D. and Özen, B. (2011), "Effect of corn-zein coating on the mechanical properties of polypropylene packaging films", *J. Appl. Polym. Sci.,* **119**, 235-241.

8. Kim, C. S., Woo, Y., Clore, A. M., Burnett, R. J., Carneiro, N. P. and Larkins, B. A. (2002), "Zein protein interactions, rather than the asymmetric distribution of zein mRNAs on endoplasmic reticulum membranes, influence protein body formation in maize endosperm", *The Plant Cell,* **14***,* 655-672.

9. Gillgren, T. (2010), "Material properties of starch and cereal protein films and foams", Ph. D. thesis, Chalmers University of Technology, Gothenburg, Sweden.

10. Lorenz, K. (1983), "Tannins and phytate content in proso millet (*Panicum miliaceum*)", *Cereal Chem.,* **60**, 424-426.

11. Harmann, D. V. and Harper, J. M. (1973), "Effect of extruder geometry on torque and flow", *Amer. Soc. Agricultural Eng.,* **16**, 1175-1178.

12. Oom, A., Petersson, A., Taylor, J. and Stading, M. (2008), "Rheological properties of kafirin and zein prolamins", *J. Cereal Sci.*, **47** (1), 109-116.

13. AOAC (1984), "Official methods of analysis", 14th ed., Association of Official Analytical Chemists, Washington DC, USA.

14. Qing–Bo, D., Ainsworth, P., Tuker, G and Marson, H. (2005), "The effect of extrusion conditions on the physicochemical properties and sensory characteristics of rice–based expanded snacks", *J. Food Eng.,* **66**, 284 -289.