

Special Issue: Bio-based Packaging

Guest Editors: José M. Lagarón, Amparo López-Rubio, and María José Fabra
Institute of Agrochemistry and Food Technology of the Spanish Council for Scientific Research

EDITORIAL

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Development of bioplastics based on agricultural side-stream products: Film extrusion of *Crambe abyssinica*/wheat gluten blends for packaging purposes

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ABSTRACT: The purpose of this work was to add economic value to crambe meal, the protein-rich byproduct from the industrial extraction of *Crambe abyssinica* seed oil, by using it as a potential feedstock for oilseed meal-based plastics. The feasibility to produce continuous, flexible plastic films of glycerol-plasticized crambe meal blended with wheat gluten (WG) to improve extrudate properties and urea as a protein denaturant using extrusion was investigated. The effect of process parameters and blend composition were studied with regard to the extrusion performance and the film properties. Tensile properties and oxygen permeability were determined, and the film morphology was analyzed with scanning electron microscopy. A die temperature between 125 and 130°C resulted in films with the most homogeneous surfaces and highest tensile strength and extensibility. The use of compression molding after extrusion improved the surface quality and film strength and lowered the oxygen permeability. A decrease in the plasticizer content (from 30 to 20 wt %) improved the extrudability and showed the highest tensile strength, whereas the extensibility was essentially unaffected. The importance of the presence of WG was shown by the fact that strength and extensibility decreased when the crambe content was increased from 60 to 80 wt %. It was shown that crambe-based biopolymer blends could be extruded as continuous flexible plastic films that exhibited promising mechanical and oxygen barrier properties. The operational window was, however, found to be narrow. The results provide a first basis to further develop the process and the blend toward industrial applications, for example, as packaging materials. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42442.

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INTRODUCTION

Packaging is the largest application sector for plastic materials in Europe (www.plasticsconverters.eu). Besides providing an appealing appearance, packaging has the important function to protect its content and to guarantee product safety during the whole life cycle. Especially with regards to food packaging, the barrier properties to oxygen and water are often important for fulfilling this demand. Moreover, the interaction between material and product and the mechanical properties are important aspects for packaging materials used in food applications. Today, these functions are provided by oil-based polymers, either used as monomaterials or in multilayer laminates.^{1,2} However, with a finite fossil-fuel resource and increasing envi-

ronmental concerns, the attention is increasing toward the development of biobased plastics. Among the various groups of resources, protein-based materials are promising candidates for packaging film applications, as they are abundant with good mechanical and oxygen barrier properties.³

The focus of this work was to develop and characterize bioplastics made from a combination of two protein-rich materials: defatted meal of *Crambe abyssinica* oil seeds and wheat gluten (WG). The purpose of adding WG to crambe was to improve the properties of the extruded material, extrusion being a common technique of producing sheets and films for potential applications, for example, in packaging. Ideally, 100% crambe (with a minimum amount of plasticizer) would be desirable;

Additional Supporting Information may be found in the online version of this article.

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however, currently, its properties do not allow for this. Both crambe and WG are byproducts/coproducts from the oil, fuel, and/or starch industry. The defatted crambe meal that is left after oil seed extraction is rich in protein and crude fibers; however, it is unfortunately unsuitable as human or animal feedstock because of the presence of high levels of nonedible components.⁴ Alternative uses for crambe meal are thus currently explored. The details of *Crambe abyssinica*, based on Refs. [5–10], are given in the Supporting Information.

Johansson¹¹ showed that it is generally possible to compression mold crambe using 15 wt % glycerol as a plasticizer and a processing temperature of 100°C. However, tensile testing of compression-molded films indicated a brittle material. Oxygen permeability values could not be measured, indicating large transmission rates.¹¹ Later studies showed that a pressing temperature of 130°C lowered, significantly, the water absorption and also increased the tensile strength possibly due to a larger extent of protein crosslinking.^{4,12}

The findings by Henne¹² were in accordance with the study of Newson *et al.*,⁴ who investigated the changes that occur in plasticized crambe (10–30 wt % glycerol) when compression molded at different temperatures, ranging from 100 to 170°C. The optimum processing temperature was found to be 130–140°C, corresponding to the most developed protein network with the best tensile properties. Above 140°C, thermal degradation was observed. However, a clear relationship between protein solubility and tensile properties could not be established, which was attributed to the contribution of the large fiber fraction in the crambe meal.

WG has been studied significantly more than crambe, and its properties are therefore not discussed here. For reviews on WG, see Refs. [13–15].

The most widely used plasticizer for biobased materials, like proteins, is glycerol. It is a nontoxic, colorless and odorless viscous liquid that is commonly used as humectant, preservative, or sweetener in the pharmaceutical and food industry. Large amounts of glycerol are produced as a byproduct from the biodiesel industry, which drives the interest in giving it additional value in new applications.

Urea is known to be an effective protein denaturant. It promotes the unfolding of proteins by screening intermolecular hydrogen bonds and by minimizing the hydrophobic effect.¹⁶ In the case of soybean films, it has also been observed that urea has a beneficial effect on the aging properties.¹⁷ Türe *et al.*,³ using a single-screw extruder, succeeded in improving the extrudability in the presence of 10–20 wt % urea, allowing die temperatures up to 130°C, leading to very low oxygen permeabilities.

In this study, we decided to build our investigation on findings and suggestions from the study by Henne¹² on a miniextruder. As a result of that study, a recipe was recommended for further explorations containing 60/40 (crambe/WG), 30 wt % glycerol, and 15% urea, extruded at 105°C. The first step in the current study was thus to investigate if this formulation could be used to up-scale the extrusion and produce films using a corotating,

twin-screw extruder, equipped with a flat sheet die. Process parameters, such as barrel and die temperatures and screw speed, were carefully selected. It was investigated if the material could be pre-extruded as strands and then pelletized to facilitate the feeding of the material into the extruder and to simulate a more continuous, master batch-like extrusion process. The pellets were further extruded to films to explore which pellets would perform best and whether the film quality decreased using pre-extruded, pelletized material in comparison with the previously extruded films from nonpelletized material. In addition, for industrial applications, the potential of volumetric feeding of pelletized material was established.

We also evaluated a postextrusion process on the extruded films (compression molding) to improve the cohesion and homogeneity of the films with regards to improving the mechanical properties and oxygen barrier. This process simulates the effect of implementing an additional pressure/heat treatment directly after the extruder die.

Another aim of this study was to investigate the effect of increasing the crambe content and decreasing the glycerol and urea content on the film quality and on the required process parameters. The reason behind the latter two changes in composition was to facilitate the dough preparation and feeding of the material into the extruder.

EXPERIMENTAL

Materials

Crambe meal (residual from oil extraction of cultivar *Galactica* seeds) was supplied by Plant Research International, Wageningen, Netherlands. WG powder was kindly supplied by Lantmännen Reppe AB, Sweden. According to the supplier, the WG powder contains 77.7% (w/w) gluten, 8.1% (w/w) starch, and 1.34% (w/w) fat. Glycerol of 99.5% purity was obtained from Karlshamn Tefac AB, Sweden. Urea (purity \geq 99.5%, MW: 60.06 g/mol) was purchased from Sigma Aldrich, Germany.

Extrusion Equipment

Film extrusion was performed on a twin-screw extruder (Type LTE20–48; Labtech Engineering, Thailand). Two corotating screws with a length to diameter ratio of 48 : 1 were used. The screw configuration is presented in the Supporting Information.

The extruder barrel is divided into 11 different heating zones (named 1–11), from the hopper to the die. A flat sheet die (45 mm \times 0.7 mm) was used for the extrusion of the films. At the die, all extrudates were picked up by a conveyor belt (Air Cooling Conveyor Unit type LAC-2.6; Labtech Engineering), operated at a speed of 2.0 m/min and cooled by air ventilation (fans) as the film moves along the belt. Pelletization was performed on a scientific Laboratory Pelletizer (Type LZ-120; Labtech Engineering). For volumetric feeding, an automatic feeding unit (Model M250), equipped with a hopper featuring a single screw, was used.

Material Formulations

The formulations of the crambe meal powder (CR), WG powder, glycerol (GLY), and urea (UR), which were used for experiments on the extruder, are summarized in Table I.

Table I. Composition of Blends A–E

Material	Scope	Ratio: liquid/solid	Amount used in total mixture (g)				Amount used in total mixture (wt %)			
			CR	WG	GLY	UR	CR	WG	GLY	UR
A	Standard	0.34	357	238	255	150	35.7	23.8	25.5	15.0
B	Less urea	0.34	357	238	235	92	38.7	25.8	25.5	10.0
C	Less glycerol	0.25	357	238	186.5	150	38.3	25.6	20.0	16.1
D	70CR_30WG	0.34	416.5	178.5	255	150	41.65	17.85	25.5	15.0
E	80CR_20WG	0.34	476	119	255	150	47.6	11.9	25.5	15.0

The main part of the work was based on Formulation A, which was initially developed by Henne.¹² Glycerol was used at a concentration of 30 wt % of the CR_WG_GLY content, which resulted in a total glycerol content of 25.5 wt %. Crambe and WG, which contribute together with 59.5 wt % to the total composition, are mixed in a ratio of 60/40 (w/w). The total liquid to solid ratio was 0.34. Urea was considered as a solid, even though it was dissolved in glycerol.

In Formulation B, the urea content was decreased to 10 wt % of the total formulation. At the same time, the amount of glycerol was reduced to keep the liquid to solid ratio constant at 0.34 and to enable a comparison with Formulation A. This is based on the assumption that glycerol (liquid) affects all components (urea, crambe, and WG).

In Formulation C, the glycerol content was decreased to 20 wt %, whereas the amount of all other components was maintained as in Formulation A. This resulted in a liquid to solid ratio of 0.25. Using the same amount of urea as in Formulation A resulted in a slightly higher overall urea content (16 wt %). It was assumed that urea, in turn, did not affect glycerol, only crambe and WG, which makes it comparable with Formulation A.

In Formulations D and E, the ratio of crambe to WG was altered, whereas the total amount of crambe and WG (595 g/59.5 wt %) was maintained. It was here of importance to reveal that higher contents of crambe yielded materials that could be extruded. The crambe fraction was increased to 70 and 80 wt %,

whereas the WG fraction was decreased to 30 and 20 wt %, respectively. Glycerol and urea concentrations were maintained as in Formulation A.

Dough Preparation

Milling of Crambe. From delivery until processing, crambe meal was stored in a freezer at -18°C to prevent the material from aging. As a first processing step, the crambe meal was sieved to remove large fiber fractions, using a round, fine-meshed stainless steel kitchen sieve. To decrease the particle size and to homogenize the material, the sieved crambe meal was then pulverized with the help of a rotary ball mill (Pascal Engineering, England), as suggested in Ref. [12]. The mill house had a volume of 7 L and contained 215 ceramic balls with a diameter of 25 mm. Then, 250 g of crambe meal was processed at a time. The jar revolution of the mill was 53 rpm, and the milling proceeded for 24 h. Before further processing, the ball-milled CR and the WG powder were conditioned for at least 48 h at room temperature and $23\% \pm 0.25\%$ relative humidity (RH; Figure 1).

Mixing. For the preparation of Materials A–E, urea was dissolved in glycerol prior to mixing it with crambe and WG. The urea powder was ground to fine particles using a mortar and pestle. Glycerol was heated to 65°C in an oil bath, and the urea powder was successively added. The mixture was stirred with a magnetic stirrer at 65°C until the urea powder was completely dissolved in the glycerol. Crambe CR and WG powder were blended in a kitchen machine (Cloer 660, Germany) at “Speed



Figure 1. Crambe meal before (left) and after ball milling for 24 h (middle) and the fraction excluded by sieving (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2" for 5 min. The glycerol–urea mixture was slowly added while stirring the mixture at "Speed 3." Mixing was continued for ~ 2 min until a homogeneous dough was obtained. A total of 500 g of mixture was prepared in each batch.

Extrusion

Development of the Extrusion Process and Process Parameter Investigation. In the early stage of this study, focus was drawn to the determination of possible process parameters for the film extrusion of standard material A using the Labtech extruder. The initial temperature profile (subsequently called low T-profile) was chosen based on the study of Türe *et al.*,³ maintaining the target temperatures for Zones 1–10 along the extruder barrel (from hopper to die) at 75–75–75–80–80–80–80–85–85–85°C to prevent WG crosslinking in the barrel. At this barrel temperature profile, the extrusion performance was studied for different die temperatures, which were 105°C–(105°C), 110°C–(110°C), 125°C–(115°C), 130°C–(120°C), and 140°C–(125°C). The values in the brackets correspond to the respective temperatures in Zone 11, anterior to the die, which was adjusted to reach the target melt temperature in the die. The screw speed was varied between 30 and 200 rpm, and the die pressure was recorded. In addition, the temperature profile (subsequently called high T-profile) 85–85–85–100–100–100–110–110–120–120–120°C (Zones 1–11) with die temperatures of 125°C and 130°C was examined. The dough was fed manually through the hopper using a wooden pusher to support the material flow toward the screws. Generally, all samples were stored in polyethylene bags until further processing.

Development of the Extrusion Process and Film Extrusion after Pelletization. The pellets were produced from Material A by first extruding the material as continuous strands, using the Labtech extruder equipped with a two-strand die. The extruder barrel was set to the low T-profile, and the screws were operated at a constant speed of 60 rpm. Different die temperatures were studied, including 130°C–(125°C), 125°C–(115°C), 105°C–(100°C), and 85°C–(85°C). After the conveyor belt, the strands were fed into the pelletizer, operated with a cutting speed of 7 m/min. Each batch of pellets was further extruded to films, applying the low T-profile inside the barrel and a die temperature of 125°C–(115°C). The screw speed was kept constant at 30 rpm. The pellets were fed manually through the hopper.

Development of the Extrusion Process and Volumetric Feeding. Automatic feeding was simulated for the extrusion of Material A pellets, previously produced at a die temperature of 85°C (subsequently referred to as the A_85 pellets). The feeder was connected to the extruder, and the feeding mode of the hopper was set to volumetric feeding. The extruder screw speed was varied from 30 up to 220 rpm, whereas the feeding volume and the hopper screw speed were adjusted manually, until sufficient material entered the screws to produce a continuous film at the die. As a final setup for the process, the feeding volume was 35 kg/h, the hopper screw speed was 16 rpm, and the extruder screw speed was 120 rpm. The extruder barrel temperature was set to the low-temperature profile, and a die temperature of 125°C–(115°C) was applied.

Material Composition. For the extrusion of Materials B–E (Table II), the Labtech extruder was operated at the low

Table II. Mechanical Properties of Films from Materials with Different Crambe Content Extruded at a 125°C Die Temperature

Material	Modulus (MPa)	Maximum stress (MPa)	Strain at maximum stress (%)
A (CR_60:WG_40)	5.6 ± 1.8	0.5 ± 0.1	14 ± 2
D (CR_70:WG_30)	4.9 ± 0.6	0.3 ± 0.1	9 ± 2
E (CR_80:WG_20)	5.1 ± 0.3	0.3 ± 0.02	7 ± 1

T-profile with an initial die temperature of 125°C–(115°C) and 30 rpm screw speed. The material was not pelletized prior to film extrusion. The dough was fed manually through the hopper using a wooden pusher to support the material flow toward the screws.

Postextrusion Process and Compression Molding

As a postextrusion process, films from Material A, previously extruded at 125°C (subsequently called A_125 films), were compression molded, using a Polystat 200T Hot Press (Servitec Machine GmbH, Germany). Two different experimental setups were investigated. For the first setup, two extrudates were cut to pieces of 4.4 cm × 7.0 cm and 2.6 cm × 7.0 cm, respectively (due to the frame being wider than the extrudates), and placed next to each other in a rectangular aluminum frame (7 cm × 7 cm × 0.5 mm). The frame was sandwiched between two aluminum plates, with a PET film in between as a release film, and then placed into the preheated press. Molding pressures of 20.4 and 40.8 MPa were used based on the sample area. At each molding pressure, the films were pressed with press temperatures of 110, 120, and 130°C for 10 and 20 min. As a reference to the pre-extruded samples, films were pressed from freshly prepared nonextruded material. Then, 7.2 g of fresh material (equal to the weight of the extruded samples) was centered in the aluminum frame and pressed using the same parameters as above. For the second setup, the extrudates (4.4 cm × 4.4 cm) were pressed as described above but without the frame. The pressure gauge was set to produce a pressure of 12.9, 19.4, and 25.8 MPa based on the original film area before pressing. For each molding pressure, the films were pressed for 5 min, applying 110, 120, or 130°C press temperature.

Characterization

Tensile Testing. Dumbbell-shaped specimens were punched out from the samples with the help of an Elastocon EP04 cutter press (Elastocon, Sweden), equipped with an ISO37 Type 3 cutter die. The total length of the specimens was 64 mm, whereas the length and width of the narrow section were 16 mm and 4 mm, respectively. The specimens of the extrudates were taken from the center of the film and oriented in the machine direction (MD). For compression-molded samples, the specimens were punched out in random orientations. All specimens were conditioned for at least 48 h at 23°C ± 1°C and 50% ± 1% RH. The mean thickness of the samples was measured at five points using a thickness tester type 21 from Lorenzen and Wettre, Sweden. The mechanical properties were analyzed using a Zwick Z010 tensile tester (Zwick GmbH, Germany), with a 200 N load cell, controlled by testXpert 7.1. The measurements were

conducted according to ASTM D-882-02 at $23^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and $50\% \pm 1\%$ RH. The crosshead speed was 10 mm/min, and the initial grip-to-grip separation was 40 mm. Strain was measured as the increase in grip-to-grip separation relative to the initial grip-to-grip separation. Stress was measured as the force divided by the initial narrow cross section, and Young's modulus was calculated as the initial slope of the stress-strain curve. For each extruded and compression-molded sample, 10 replicates were analyzed. The mean value and a confidence interval of 95% confidence level were calculated.

Oxygen Permeability. The oxygen transmission rate was determined according to ASTM D-3985-95 at 50% RH and 23°C , using a Mocon Ox-Tran Twin apparatus (Mocon, USA). Each sample was sandwiched between two self-adhering aluminum foils, exposing 5 cm^2 to oxygen. The specimens were mounted in isolated diffusion cells and initially purged with nitrogen gas to measure the oxygen background leakage of the instrument. Subsequently, one side of the specimen was exposed to flowing oxygen (99.95%) at atmospheric pressure. The oxygen permeability was calculated by normalization of the oxygen transmission rate with respect to the sample thickness and the atmospheric oxygen pressure.

Scanning Electron Microscopy. The surface and cross section (obtained by breaking the specimen) morphology of the extruded and the compression-molded samples were analyzed with a field emission scanning electron microscope (SEM; Hitachi S-4800, Japan), operated at 2 kV, and a tabletop SEM (Hitachi TM3000). Prior to imaging, the samples were coated for 30 s with a conductive palladium-platinum layer, using a Agar High-Resolution Sputter Coater (Cressington 208RH). The sputter current was set to 80 mV.

Density Measurements and Moisture Content. The density was measured using the Archimedes principle, where the sample was weighed in air and in *n*-hexane. The moisture content was obtained according to ASTM D-664-9466. The samples were preconditioned for 96 h at $23^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and $50\% \pm 1\%$ RH. After drying at 105°C for 24 h and cooling in a desiccator containing silica gel for 1 h at room temperature, the final weight was determined.

RESULTS AND DISCUSSION

Development of the Extrusion Process, Process Setup, and Parameter Investigation

The dough that was obtained after mixing the individual components of Material A was dark brown and very tough (Supporting Information Figure S2). As it had rested for a couple of minutes, the color changed to dark brown and it became even tougher, which was suggested to be due to increasing protein crosslinking. Because of the high viscosity, it was very difficult to feed material into the extruder. Instead of being drawn-in by the screws, material was stuck in the lower part of the hopper, where it crosslinked even more, due to the combination of shear-induced heating and the elevated temperature inside the barrel. To enable material supply into the barrel, it became necessary to press the material into the screws with the help of a wooden pusher.

In general, the film extrusion of Material A was performed successfully. However, continuous films with smooth surfaces could only be obtained within a narrow processing window.

For all investigated recipes and extrusion conditions, especially the die pressure, which at constant screw speed was regulated by the feeding rate, was identified as the most important property to control to get satisfactory film formation. Continuous homogeneous films could only be extruded at a limited pressure range, allowing no more variation than 0.3–0.4 MPa. As the die pressure exceeded the optimal pressure range, the films had inhomogeneous surfaces, featuring a flake-like structure of different colors, including nearly black and light brown spots. This was probably the result of phase separation of the two components, crambe and WG, which forms an immiscible polymer blend and obviously responds with different viscosities at a critical pressure value with constant temperature and composition. At die pressures below the optimum range, the films were not continuous due to insufficient material accumulating anterior to the die. Hence, the die pressure was shown to be an important process parameter, and all effects described and samples analyzed in this article refer to films produced within their optimum die pressure range if not indicated otherwise.

The effect of the die temperature was studied by maintaining the low T-profile for Zones 1–10 inside the extruder barrel. The results are shown in Figure 2. With die temperatures of 105°C –(105°C) and 110°C –(110°C) investigated at different die pressures and screw speeds, no continuous films could be extruded. The samples were light brown with an inhomogeneous and “scaled” surface. Again, phase separation was observed, indicating that these processing temperatures were below that needed for the two components to form a more intimate mixture. Raising the die temperature to 125°C –(115°C) improved the extrudate quality significantly. The best results were obtained at a die pressure of 3.4 MPa and a screw speed of 30 rpm. Long continuous films could be extruded, which felt strong and flexible. The samples were darker than those obtained with lower die temperatures but had a smoother surface. Although having a homogeneous overall appearance, small color variations, including darker and lighter spots, were detected when closely examining the surface and indicated slight phase separation. Applying a die temperature of 130°C –(120°C) yielded bubbles on the film surface accompanied by the loss of ammonia (from urea) at the die exit. The segments without bubbles appeared similar to the samples obtained with 125°C die temperature, although slightly darker in color. Die temperatures higher than 130°C could not be applied. Not only was the bubble formation intensified but the material also started burning at the die exit, leading to extensive ammonia-containing smoke.

During the extrusion experiments, it was observed that after the machine stops, the films having a uniform, nearly black color and a dense, homogeneous surface without any melt fracture were observed (Supporting Information Figure S3). This material exited the die at a high rate, and the extrudate felt strong and leather-like. This structure arose from the prolonged residence time in the barrel at high temperature. This sample indicated that it is possible to produce a fully dense homogeneous structure from the crambe and WG blend; however, the

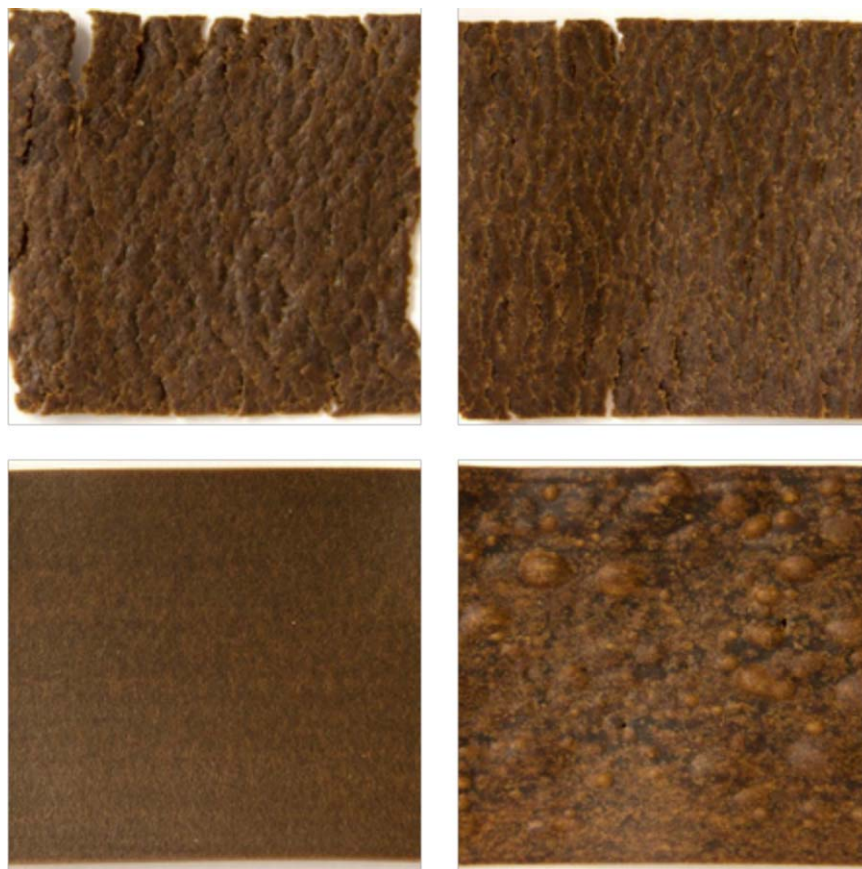


Figure 2. Effects of die temperature. Films extruded at a die temperature of 105 (top left), 110 (top right), 125 (bottom left), and 130°C (bottom right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

material, observed by the color change, was then somewhat degraded. It was attempted to obtain such films with continuous extrusion, by keeping the screw speed at 30 rpm and adjusting the temperature profile inside the barrel to higher temperatures (high T-profile). Long continuous films, which were significantly darker than the films extruded with the lower barrel temperature profile, were obtained with die temperatures of 125 and 130°C. However, the formation of bubbles and ammonia was extensive (Supporting Information Figure S3).

Once continuous films could be extruded with the low T-profile and die temperatures of 125 and 130°C, the effect of the screw speed became apparent. The best result, with respect to minimal melt fracture, was achieved with a screw speed as low as 30 rpm.

To keep the die pressure constant at its optimum value, uniform material feeding was required. As this was observed to be difficult by manual feeding, due to the tough dough, the material was pelletized from extruded strands prior to film extrusion. Generally, the extrusion of strands was far easier than the extrusion of films. The strand-extrusion die temperature that yielded the easiest pelletizing and the best film qualities was 85°C (for details refer to Supporting Information).

The dough of Material B (less urea) felt a bit drier and more powdery than the dough of the standard material A, but it was still quite hard and tough, whereas the dough of Material C

(less glycerol) was more brittle and easier to feed into the extruder (Supporting information Figure S2). However, because of the reduced amount of glycerol, the urea did not completely dissolve in the glycerol. The dough consistency of the materials with higher crambe content [D (70CR_30WG) and E (80CR_20WG)] was similar to that of Material A.

No continuous films could be extruded from Material B by applying a die temperature of 125°C and a screw speed of 30 rpm—the parameters that yielded the best results for Material A. The sample pieces had many cracks. It was assumed that the extrusion temperature was too high, as less urea was present, which would otherwise delay the crosslinking of the proteins prior to the die zone. The die temperature was therefore lowered to 115°C–(105°C). The film formation improved, but the film surface was still rough and flaky, with small holes present all over the extrudate. At this temperature, the material exited the die slowly due to the high viscosity because of a low total amount of plasticizer (glycerol and urea). To reduce the viscosity, Zone 11 was adjusted to 115°C. This improved the extrusion process slightly, but the material flow rate was still low and the film quality was still poor. Changing the screw speed or the die pressure did not improve the extrudate quality.

For Material C (less glycerol), extrusion of continuous films was not possible with an extrusion temperature of 125°C and a die pressure of 3.4–3.8 MPa, as the extrudate fractured in several



Figure 3. Films extruded from Material C with different die temperatures and pressures: 125°C_3.6 MPa (left); 125°C_5.2 MPa (middle), and 130°C_5.2 MPa (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

places (Figure 3). By successively raising the die pressure up to 5.6 MPa, phase separation was observed, which was more extensive than previously noticed with Material A (Figure 3). Fractured films were also obtained with a die temperature of 130°C and 3.4–3.8 MPa die pressure. However, at this temperature, an interesting observation was made, that is, by raising the die pressure to 5.2 MPa films with a smooth, dense, and homogeneous surface were observed, featuring even less melt fracture than observed for Material A (Figure 3). Evidently, a specific combination of die pressure, die temperature, and screw speed, different from that for Material A, led to high-quality films for Material C. Extruding the material at 115°C resulted in only little material exiting the die, probably due to the same reason as for Material B. Apart from a higher material viscosity, the lower flow rate at the die was possibly also caused by the lower amount of glycerol, which seemed to act as a lubricating agent at the die.

Extruding Materials D and E (higher crambe/WG ratio) with a die temperature of 125°C was possible. When compared with the Material A films, they were somewhat darker, especially Material E, probably caused by the higher fraction of crambe (Figure 4). They felt strong and flexible. Both materials exited the die evenly and significantly faster than Material A, although the die pressure (3.4–3.8 MPa) and the screw speed (30 rpm) were maintained the same. The lower amount of WG was probably the reason for the viscosity change. WG is more sensitive to crosslinking than crambe in the applied temperature range and may raise the overall viscosity if present at higher fractions. A drawback of the increased material flow rate at the die was

more extensive melt fracture than in the Material A films. To reduce the material flow rate and to consequently limit the melt fracture, the screw speed was lowered to 20 rpm, which improved the extrudate quality of both the D and E materials. Albeit the film quality was satisfactory, it was difficult to obtain long smooth extrudates, as cracks were present between homogeneous sections. It was assumed that the extrusion temperature was slightly too low for these formulations. Therefore, the die temperature was increased to 130°C, which improved the extrusion process significantly. Long continuous films without cracks were obtained. However, more dark spots appeared on the surface, indicating the different response of the components to the elevated temperature. Once again, the material behavior was quite sensitive to changes in the die pressure. The best extrudates were obtained at a die pressure of 3.3–3.5 MPa, whereas at ≥ 3.6 MPa, clear phase separation and bubbles occurred on the surface. The lower optimal die pressure range for Materials D and E when compared with that for Material A was attributed to their lower viscosity.

Postextrusion Processing and Compression Molding

The surface quality of A_125 films was improved significantly by additional compression molding. The films were flexible and appeared reddish and translucent with smooth surfaces. The places of melt fracture disappeared due to the material flow under the influence of additional heat and pressure. The most homogeneous films were obtained by pressing the extrudates at 110°C and 40.8 MPa for 20 min (Figure 5). Press temperatures of 120 and 130°C led to the formation of large bubbles on the surface, probably due to steam formation and decomposition of



Figure 4. Material D extruded at 125°C_20 rpm (left) and 130°C_20 rpm (middle), and Material E extruded at 125°C_30 rpm (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

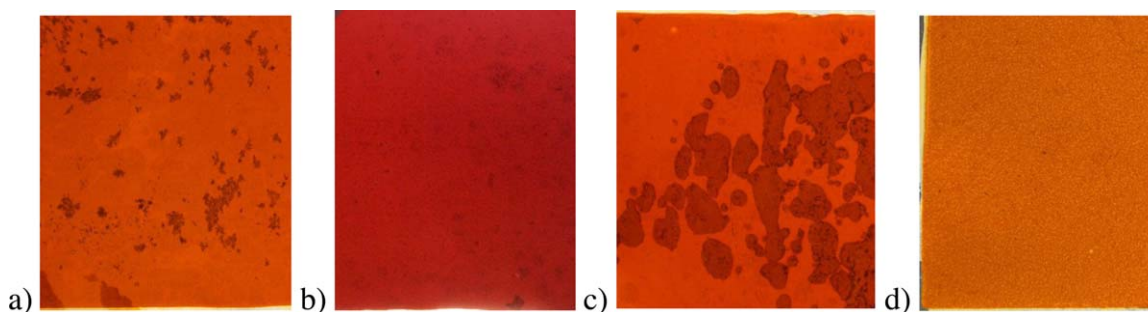


Figure 5. A₁₂₅ films after compression molding: (a) 110°C_20.4 MPa_10 min, (b) 110°C_40.8 MPa_20 min, and (c) 120°C_20.4 MPa_10 min; and the reference film directly from dough: (d) 110°C_20.4 MPa_10 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

urea. Reducing the pressure (20.4 MPa) or the time (5 and 10 min) at a 110°C press temperature resulted in films that were not completely homogeneous, exhibiting some darker spots (Figure 5). In contrast, no spots were detected in the reference films, pressed from freshly prepared dough at 110°C, even at a lower pressure (20.8 MPa) and shorter pressing time (10 min). However, bubbles occurred also for these films at plate temperatures above 110°C.

The comparison of the extruded and the reference material (Figure 5) supported the previously outlined effect of phase separation during extrusion. The dark areas, visible on the compression-molded extruded films, were originating from the crambe meal. As they were absent in the reference film, they must have formed from a phase separation during the extrusion step. Apparently, a high pressure and a long pressing time reduced the amount and size of these areas and improved the film homogeneity, possibly due to a fusion of the “phase-separated structures.” Compression molding the A₁₂₅ films without the aluminum frame resulted in thin films of 0.1–0.2 mm. The films were flexible, translucent, and yellowish. Again, spots were detected, which became less with increasing pressure and temperature. Interestingly, in contrast to the films obtained with a frame, no bubbles occurred for pressing temperatures above 110°C.

SEM Investigation

Figure 6 shows the morphology of extruded materials, extruded with their optimal process parameters. The SEM analysis showed that there was a high content of small holes present on the surface of the A₁₂₅ films, probably originating from melt fracture. The cross section contained a sizeable amount of particles and pores, preexisting or formed when breaking the specimen prior to SEM investigation. The particles occurred as a consequence of the immiscible blend of the two proteins and the nonprotein components. The pores were the result of insufficient adhesion between the components and from inclusion of air as the material exited the die. However, the pores were not interconnected through the film, which was beneficial for potential gas barrier applications. No evident difference in morphology could be detected for films with higher crambe content (Supporting Information Figure S6). The films that contained a low amount of glycerol had a more homogeneous surface with significantly smaller cracks (Figure 6, middle). The cross section

appeared denser with fewer pores than in the A₁₂₅ film, an effect of low glycerol content and/or higher extrusion temperature (130°C). It is possible, despite the lower glycerol content, that at higher temperature, glycerol becomes a more efficient plasticizer resulting in lower viscosity. Furthermore, at the higher temperature, it is possible that glycerol lubricates the material more efficiently at the die exit. The leftover material that was obtained after the machine stops had a homogeneous surface with only few surface defects (Figure 6, bottom). In addition, the cross section appeared slightly more homogeneous with less pores when compared with the A₁₂₅ film. This was, probably, the result of several mechanisms that occurs due to the prolonged exposure at elevated temperature, including protein crosslinking in parallel to protein degradation. It is here interesting to see whether any differences in moisture content of the doughs prior to extrusion had any effect on the extrudates. The moisture content was 14.5 (Dough A), 15.4 (B), 17.5 (C), 17.1 (D), and 14.5 wt % (E). It is clear that there is no unique correlation between moisture content and the extrudate quality. Materials D and E showed similar extrusion properties although having different moisture contents. The most difficult material to extrude was the B dough having an intermediate moisture content.

The surface quality of the extruded films was improved significantly after compression molding (Figure 7). The surface appeared much smoother, and the number of defects was reduced. However, previously present melt fractures were not completely erased, as indicated by the small cracks on the surface. Compression molding of thin films without the aluminum frame yielded similar surface quality as for the thicker films.

Mechanical Properties

Material A extruded with a die temperature of 105, 110 and 140°C could not be tested because they contained many cracks and was brittle. On the other hand, the films produced at 125 and 130°C were tested, which showed that these temperatures yielded similar stiffness and strength. The film produced at 125°C had a stiffness of 5.6 ± 1.8 MPa, a strength of 0.5 ± 0.1 MPa, and an extensibility of $14\% \pm 2\%$, whereas the corresponding values were 5.1 ± 0.6 MPa, 0.6 ± 0.1 MPa, and of $19\% \pm 2\%$ at 130°C.

No significant difference in tensile properties was observed for films that were extruded from fresh dough (A₁₂₅ films), from

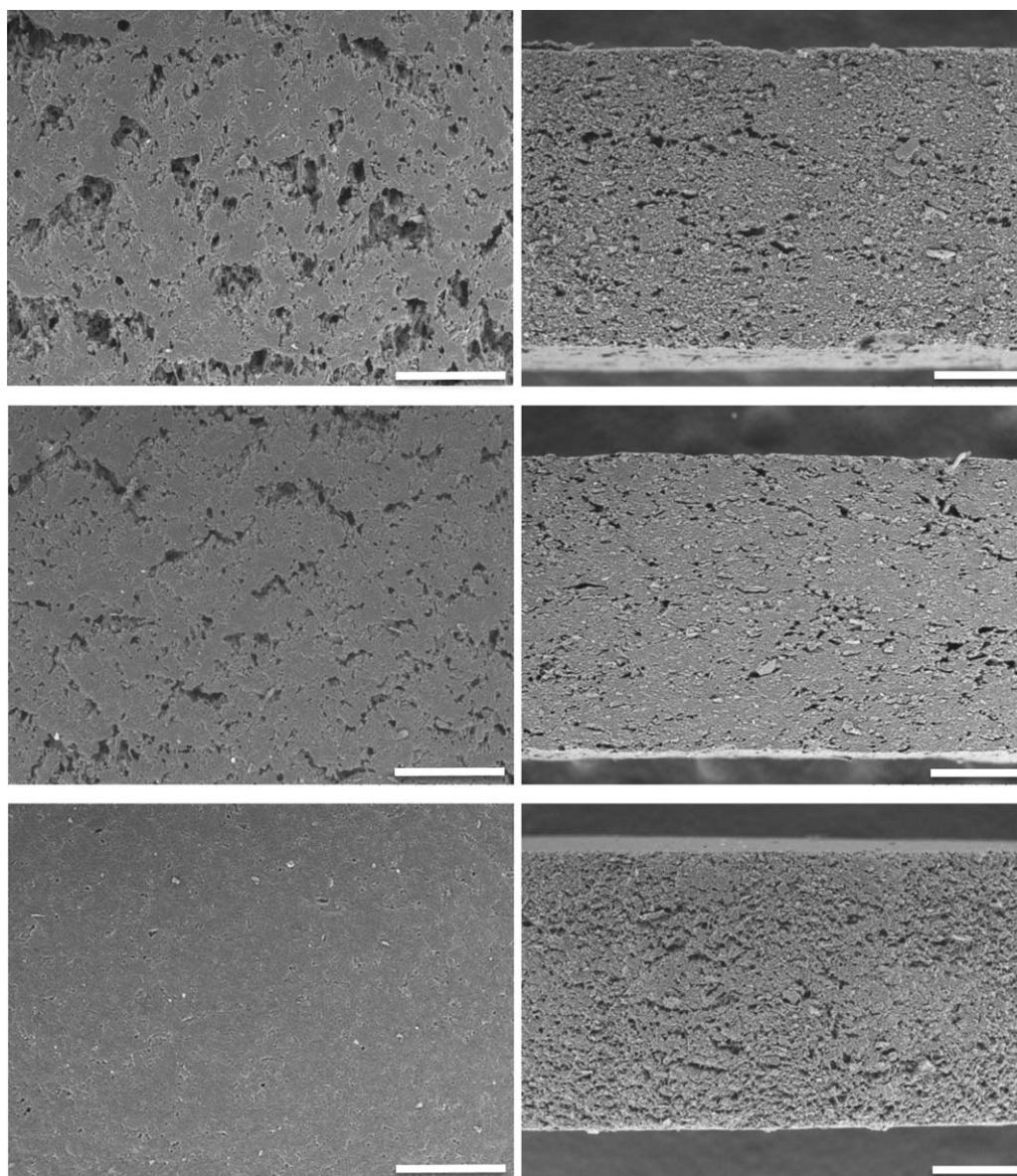


Figure 6. SEM images of the surface (left) and cross section (right) of films from Materials A (top) and C (middle) and the “leftover” piece (bottom). The scale bars are 500 μm .

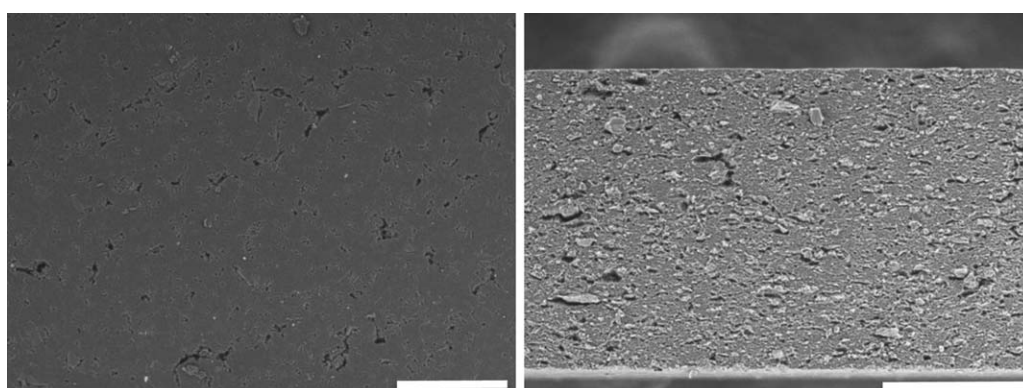


Figure 7. SEM images of the surface (left) of a compression-molded film (A_110°C_40.8 MPa_20 min) and its cross section (right). The scale bars are 500 μm .

Table III. Mechanical Properties of A₁₂₅ Films Compression Molded and Compression-Molded Dough

Material ^a	Modulus (MPa)	Maximum stress (MPa)	Strain at maximum stress (%)
A_110_20.4_10_extr	10.6 ± 0.4	0.8 ± 0.1	13 ± 2
A_110_20.4_20_extr	12.2 ± 1.1	1.1 ± 0.1	19 ± 3
A_110_20.4_20_dough	12.0 ± 0.7	1.0 ± 0.04	27 ± 3
A_110_40.8_10_extr	15.0 ± 0.6	1.1 ± 0.2	16 ± 4
A_110_40.8_10_dough	9.1 ± 0.8	0.9 ± 0.1	29 ± 4
A_110_40.8_20_extr	11.8 ± 0.8	0.6 ± 0.1	11 ± 4
A_110_40.8_20_dough	15.4 ± 2.3	1.2 ± 0.02	30 ± 2
A_125_extruded-only	5.6 ± 1.8	0.5 ± 0.1	14 ± 3

^aThe samples are coded as material_press temperature (°C)_pressure (MPa)_press time (min) previously extruded or from a dough (fresh).

A₈₅ pellets, and from pellets that were fed with the use of the volumetric feeding unit (data not shown). This implies that the additional extrusion step, required for pelletizing, did not impair the mechanical properties of the extrudate.

Although the films of Material B, containing a lower amount of urea, were too brittle to be tensile tested, the films containing a lower amount of glycerol could be tested (Material C). At a die temperature of 125°C, these films became more brittle than the corresponding Material A films having a higher glycerol content. On the other hand, at 130°C, there were no significant differences between the mechanical properties of these films. The film with less glycerol had a stiffness, strength, and extensibility of 5.4 ± 0.9 MPa, 0.7 ± 0.1 MPa, and 16% ± 2%, respectively. Note that Material A was difficult to extrude with a 130°C die temperature due to extensive bubble formation, which was not observed at a lower glycerol content (Material C).

The effects of different crambe contents (Materials A, D, and E) on the mechanical properties of films extruded with a die temperature of 125°C and 30 rpm screw speed are displayed in Table II. The lower screw speed (20 rpm), examined on films of Materials D and E, did not change the mechanical performance (Supporting Information Table S2). Table II shows that, with increasing crambe content, the strength and the extensibility decreased, whereas the stiffness was unaffected. An explanation for the decrease was the decreased amount of WG, which is known to account for improved extensibility in crambe–gluten blends.¹² A possible explanation is also that the die temperature of 125°C may have been too low to allow for sufficient crosslinking of crambe, reflected in the reduced strength.

The tensile results for the compression-molded A₁₂₅ films and compression-molded doughs are summarized in Table III. For nearly all examined extruder parameter combinations, the stiffness and strength of the extrudates were increased significantly, whereas the extensibility was essentially unchanged after the compression molding. The increase was possibly due to the increased compaction of the film (less pores) and also increased protein crosslinking due to the extra heat treatment. The density increased from 1220 to 1310 kg/m³ when the extruded sample was compression molded with a frame and to 1330 kg/m³ without a frame. The compression-molded doughs had a stiffness and strength similar to the compression-molded films, but

their extensibility was higher, probably due to a lower degree of protein crosslinking (only one heat treatment).

There were no direct correlations between the pressing parameters and the tensile properties. The compression-molded extrudate at the highest pressure and longest period of time (110°C_40.8 MPa_20 min) had the lowest strength and extensibility, although it appeared visually as the most homogeneous sample. A possible explanation is that the material components were partly degraded. The samples pressed with the same pressure but for a shorter period of time (110°C_40.8 MPa_10 min) and the samples pressed at a lower pressure (110°C_20.4 MPa_20 min) had a higher strength and extensibility. The most “gentle” pressing (110°C_20.4 MPa_10 min), on the other hand, resulted in the second lowest strength and extensibility.

The film quality after compression molding without a frame showed a strong dependence on the process parameters (Table IV). These thin films were not as strong as those molded in a frame; however, some films still reached values up to 0.7–0.8 MPa. Surprisingly, the extensibility was generally lower than both the thicker compression-molded and the extruded-only films. The stiffness was generally higher than the extruded/compression-molded films but lower than for the thicker compression-molded films (compare Tables III and IV).

Again, it appeared that the toughest processing conditions (high temperature and pressure) yielded poorer mechanical properties. The highest strength (0.8 MPa) was obtained with the most “gentle” condition (110°C_12.9 MPa_5 min), whereas the lowest strength (0.3 MPa) was obtained with the toughest condition (130°C_19.4 MPa_5 min), which indicated some material degradation.

Interestingly, when considering all the different samples, it was observed that the variation in extensibility was within the same material. This is somewhat surprising considering the heterogeneous structure of the material having a mixture of the proteins, hull components, fibers, and starches.

It is here interesting to compare the mechanical properties of the crambe/WG blends with those on crambe and WG reported previously, as well as other protein polymers. It must be stressed that the properties are a strong function of the glycerol content used. Newson *et al.*^{4,18} reported the mechanical properties of

Table IV. Mechanical Properties of A₁₂₅ Films with Additional Compression Molding without Aluminum Frame

Material ^a	Modulus (MPa)	Maximum stress (MPa)	Strain at maximum stress (%)
A_110_12.9_5	7.8 ± 0.5	0.8 ± 0.3	11 ± 3
A_110_19.4_5	6.4 ± 1.4	0.4 ± 0.1	10 ± 2
A_110_25.8_5	6.5 ± 1.3	0.5 ± 0.3	8 ± 1
A_120_12.9_5	8.6 ± 1.5	0.6 ± 0.1	10 ± 1
A_120_19.4_5	8.2 ± 1.4	0.5 ± 0.1	10 ± 2
A_120_25.8_5	9.3 ± 1.4	0.5 ± 0.1	8 ± 3
A_130_12.9_5	10.7 ± 1.1	0.7 ± 0.1	11 ± 1
A_130_19.4_5	8.4 ± 1.0	0.5 ± 0.1	10 ± 2
A_130_25.8_5	6.4 ± 0.7	0.3 ± 0.1	8 ± 2

^aThe samples are coded as material_press temperature (°C)_pressure (MPa)_press time (min).

compression-molded crambe (30% glycerol) in relation to the processing temperature and the additives used [e.g., bases (ammonium hydroxide and sodium hydroxide), acid (citric acid), radical producer (benzoyl peroxide), and diamine (cross-linker)]. The stiffness, strength, and extensibility were 20–60 MPa, 0.5–1.1 MPa, and 2–6%, respectively. Our samples contained 20–26% glycerol, which together with urea (contributes also, to some extent, as a plasticizer) becomes 35–40%. The stiffness, strength, and extensibility of the current extruded films were 5–6 MPa, 0.3–0.7 MPa, and 14–19%, respectively. The corresponding values for the extruded and compression-molded films were 6.4–15 MPa, 0.3–1.1 MPa, and 8–19%, respectively, and films compression molded directly from the dough were 9–15 MPa, 0.9–1.2 MPa, and 27–30%, respectively. Hence by mixing WG into the crambe meal, both the extruded and the compression-molded films became more extensible/ductile, while having a similar strength but a lower stiffness. The benefit of using WG is its high cohesion and elasticity. In a number of articles, we have reported the mechanical properties of extruded WG. Ullsten *et al.*^{19,20} extruded WG films with 30% glycerol, with or without sodium hydroxide/ammonium hydroxide and salicylic acid. The stiffness, strength, and extensibility were 9–96 MPa, 1.3–5.8 MPa, and 30–151%, respectively. Türe *et al.*,³ using 30% glycerol and 10–20% urea, produced films with a stiffness, strength, and extensibility of 3–5 MPa, 2.2–3.6 MPa, and 70–87%, respectively. With the addition of 1% montmorillonite clay, it was possible to reach an extensibility of 98% without sacrificing stiffness or strength.²¹ It is obvious here that WG has a higher extensibility than crambe, at similar plasticizer content, and that the blends have improved mechanical properties, again due to the higher cohesion and elasticity of WG. It should be noted that the mechanical properties of the crambe and crambe/WG materials were obtained with a strain rate of 10 mm/min, whereas those of WG were obtained at 100 mm/min.

Barone *et al.*²² obtained a stiffness, strength, and extensibility of extruded feather keratin (30% glycerol) which were 20–30 MPa, 2–3 MPa, and 0.1–0.5%, respectively. The corresponding values for extruded soy protein isolate (ca. 30% glycerol) were 180 MPa, 9 MPa, and 160%.²³ Wang and Padua²⁴ tensile tested extruded zein sheets produced with a high amount of oleic acid

(40%) as plasticizer. The stiffness was 100 MPa, and the strength was 3–4 MPa. The extensibility was 100–120%. The mechanical properties of gelatin films, extruded and compression molded with a relatively low content of glycerol (17%), were measured by Park *et al.*²⁵ The modulus, strength, and extensibility were 490 MPa, 17 MPa, and 216%, respectively. To conclude, when comparing the data of the four cases (keratin, soy protein isolate, zein, and gelatin) with the crambe/WG data, it is observed that the modulus and, often also, the strength were higher in the former systems. Surprisingly, some of these materials also showed a larger extensibility than the crambe/WG materials. It should be noted that the strain rate was significantly higher in the keratin, soy protein isolate, and gelatin cases (25–100 mm/min; for zein, the strain rate was not reported) than in the crambe/WG case (10 mm/min), which will lead to primarily higher stiffness and strength.²⁶

Oxygen Permeability

The oxygen permeability was examined for the extruded films of Materials A, C, and E and the compression-molded film from Material A (Table V). Although the A₁₂₅ films had an oxygen permeability of 36.1 [cm³ mm/day m² atm], subsequent compression molding reduced the oxygen permeability of the same material by ~ 50%. This was ascribed to the additional processing step, which reduced the number and size of pores (refer to the density data above).

Although the oxygen permeability of crambe-containing films could be measured, it was significantly higher when compared with the best values of the extruded WG films reported and compiled by Türe *et al.*³ Generally, the low oxygen permeability of protein films, like WG, is attributed to the presence of a high content of hydrogen bonds between the protein chains. The higher oxygen permeability of the crambe-containing films was not surprising, as its protein content (ca. 30 wt %), and amount of hydrogen bonds, was lower than for WG. Nevertheless, the increase in permeability, when increasing the amount of crambe from 60 to 80 wt %, was rather small (compare Materials A and E in Table V).

To our knowledge, the oxygen permeability has not been determined on extruded proteins, except by ourselves on WG-based materials. The reason is probably that the quality of the

Table V. Oxygen Permeability

Material	Processing method	Oxygen permeability [cm ³ mm/ (day m ² atm)]
A (60CR_40WG)	Extrusion, 125°C die temperature	36.1
E (80CR_20WG)	Extrusion, 125°C	38.7
C (less glycerol)	Extrusion, 130°C	^a
A (60CR_40WG)	Extrusion, 125°C die temperature, and compression molding with frame (110°C_40.8 MPa_20 min)	17.1

^a Too high to be measured.

extrudates is often quite poor, including voids, which leads to unmeasurably high values. The values reported for extruded WG varies between 0.2 and 213 cm³ mm/(day m² atm) depending on the content and type of additives included. The highest value is reported for WG with 30% glycerol, and the best values are obtained when WG is mixed with glycerol and ammonium hydroxide/salicylic acid or urea.³

CONCLUSIONS

It was shown here that glycerol-plasticized crambe meal, blended with WG and urea, could be successfully extruded as continuous, flexible plastic films, which exhibited oxygen barrier properties better than polyethylene and in the same range as those of glassy amorphous polymers like poly(butylene terephthalate)/polycarbonate blends and polyetherimide.¹ For the first time, to our knowledge, oxygen permeability could be measured on films that contained crambe.

By the means of the “standard” formulation by Henne,¹² it was shown here that this crambe blend also had the potential to be processed in a continuous way with master batches. Pellets, produced by pelletizing pre-extruded strands, could be fed automatically into the extruder by using a volumetric feeder and then extruded into films.

Table VI. Summary of Optimal Extrusion Parameters for Each Blend (A–E)

Material (CR_WG_GLY_UR) (wt %)	Die temperature (°C)	Die pressure (MPa)	Screw speed (rpm)
A (35.7_23.8_25.5_15)	125–(115)	3.4–3.8	30
B (38.7_25.8_25.5_10)	115–(115) ^a	-	30
C (38.3_25.6_20_16.1)	130–(120)	5.2	30
D (41.6_17.9_25.5_15)	130–(120)	3.3–3.5	20
E (47.6_11.9_25.5_15)	130–(120)	3.3–3.5	20

^a No satisfying film quality could be obtained within the invested parameter range. With the temperature given here, the “best possible” result was obtained.

It was demonstrated that the optimal process parameters, for the formation of continuous and homogenous films, depended on the actual formulation. It is known that significant protein network formation (crosslinking) may occur in the extruder and should be “balanced” to obtain high extrudate quality.²⁷ The “optimal” extrusion parameters for each investigated material composition are summarized in Table VI. Generally, a die temperature of 125–130°C, a die pressure of 3–5 MPa, and a screw speed of 20–30 rpm yielded the best extrudates.

It was shown that it is possible to increase the content of crambe in the formulation, without lowering the surface quality of the films. The strength and the extensibility were, however, reduced as the crambe content increased. It was also shown that there was no clear correlation between the dough moisture content and the extrudate quality.

By compression molding the extruded films, it was shown that the surface and cross-sectional homogeneity of the films were improved. The mechanical effects of compression molding were not entirely conclusive, except that the film stiffness increased, and depended on the final film thickness (with or without the frame).

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