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Plasticization effect of solubles in fishmeal

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ABSTRACT

The influence on glass transition (T_{gMid}) and flow-starting (T_f) temperatures of water soluble dry matter (WSDM) in fishmeal has been assessed combined with moisture content by use of a central composite design and response surface modeling. Established models with $R^2 > 0.951$ showed significant additive effects of WSDM and moisture on T_{gMid} and T_f without interaction. The effect of WSDM on T_{gMid} could also be modeled based on the Gordon–Taylor equation. The main effects on T_{gMid} and T_f were 3.1 and 1.2 times higher, respectively, for each percent increase in moisture compared to WSDM. However, on a molar basis the effect of solubles addition will be higher compared to moisture. The plasticization effect can be attributed to the content of low molecular N-compounds and also influences the viscosity reduction of temperature increase in the rubbery phase. Fishmeal has a lower T_{gMid} compared to casein and plant proteins. Combined, the observed physicochemical properties might contribute to explain reported unique functional properties of fishmeal with positive impact on physical pellet quality and open up the possibility to obtain a satisfactory thermomechanical transformation in the extrusion process at reduced moisture level.

1. Introduction

Large scale manufacture of compounded fish feed is extensively based on thermomechanical transformation of proteins and starch by extrusion processing. The extrusion process involves use of high temperature achieved by steam injection and mechanical energy dissipation, and transforms the feed mix into a plasticized and flowable material that can be shaped through a die and cut into pellets. The bulk density of the product is controlled by the temperature behind the die, expansion by flashing of steam over the die, the viscoelastic properties of the material during cool-down, and final fixing of the structure at a temperature of about 30 K above the glass transition temperature (Arhaliass, Bouvier, & Legrand, 2003; Fan, Mitchell, & Blanshard, 1994). Proteins have a high plasticization temperature and might decompose or form covalent crosslinking (disulfide bonds) at elevated temperature (Matveev, Grinberg, Sochava, & Tolstoguzov, 1997; Matveev, Slade, & Levine, 1999; Opstvedt et al., 2003). Normally a plasticizer is added to avoid such detrimental effects and enable the use of more gentle processing conditions.

A plasticizer is a low molecular compound incorporated into an amorphous polymer that depresses both the glass transition (T_g) and flow-starting (T_f) temperatures by screening off intermolecular attractive forces and increase the free volume and chain mobility (Abiad, Carvajal, & Campanella, 2009; Cuq, Gontard, & Guilbert, 1998; di Gioia & Guilbert, 1999; Fujio, Hayashi, & Hayakawa, 1991; Igura, Nakashima, Hayakawa, & Fujio, 1997). Water is the most commonly used plasticizer in the extrusion process (Akdogan, 1996; Bhattacharya & Hanna, 1987; Blanche & Sun, 2004; Chen, Wei, Zhang, & Ojokoh, 2010; Lam & Flores, 2003). The application of other plasticizers like polyols (Pouplin, Redl, & Gontard, 1999), sugars (Carvalho & Mitchell, 2001), organic acids (Pommet, Redl, Guilbert, & Morel, 2005), fatty acids (di Gioia & Guilbert, 1999; Pommet, Redl, Morel, & Guilbert, 2003), amines (Irissin-Mangata, Bauduin, Boutevin, & Gontard, 2001), and monodiglyceride esters (di Gioia & Guilbert, 1999) has been extensively studied in plant protein model systems or with relevance to the manufacture of biodegradable thermoplastics, however, to our knowledge not with relevance to fish feed extrusion mainly due to formulation constraints.

Several techniques have been developed to measure T_g in polymers, food and pharmaceutical products (Abiad et al., 2009). The selection of a proper method should be based on the response of interest. Closed-chamber capillary rheometry enables the measure of both T_g and T_f at elevated moisture levels and high pressure and temperatures (Fujio et al., 1991; Igura et al., 1997) and reflects the softening of the material and resistance to flow through a die encountered in the extrusion process. The Phase Transition Analyzer (PTA; Strahm, Plattner, Huber, & Rokey, 2000) is a closed-chamber capillary rheometer developed for this purpose and gives values consistent with the information obtained from differential scanning calorimetry, dynamic mechanical thermal analysis and capillary rheometry (Bengoechea, Arrachid, Guerrero, Hill, & Mitchell, 2007).

Fishmeal is produced by wet rendering of fish or by-products from the fish fileting industry (Schmidtsdorff, 1995). The raw material is heated to above 90 °C in a continuous cooker and mechanically dewatered by use of a screw press. Most of the suspended solids in the press liquid are removed by a decanter centrifuge before separation

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of excess oil. The obtained stickwater or solubles are concentrated before mixing with the press cake and decanter solids and dried to fishmeal. The fish solubles contain most of the water soluble nitrogen compounds (protein, peptides, amino acids, nucleotides etc.), vitamins and minerals in the raw material and shown to stimulate growth in Atlantic salmon given high plant protein diets (Kousoulaki et al., 2009). Extrusion trials have documented a positive association between the water soluble protein level in fishmeal and obtained specific mechanical energy, starch gelatinization and physical pellet quality (Samuelsen, Mjøs, & Oterhals, 2013, 2014). As distinct from moisture, a higher level of water soluble protein in the fishmeal gave increased specific mechanical energy during extrusion cooking and improved pellet hardness (Samuelsen & Oterhals, 2014). Water soluble protein and moisture content depressed both T_{gMid} and T_f in the extrudate and the observed extrusion effects reflect differences in the influence on rheological properties of the plasticized material and establishment of macromolecular interactions during extrusion processing and drying of the extrudate. The added water soluble protein is not removed during drying of the extrudate and will also influence the viscoelastic properties, improve binding properties and contribute to nutrients in the final feed pellet (Samuelsen & Oterhals, 2000, 2014).

Solubles are an intrinsic component in fishmeal but might be influenced by the raw material quality, processing conditions and the extent to which the stickwater is included in the drying process. This study was designed to: 1) Assess the effects of solubles combined with moisture level on T_{gMid} and T_f in a fishmeal model system and 2) characterize the main chemical composition of the added solubles to quantify compounds with possible effects on phase transition temperatures in protein ingredients. The results are discussed with specific application in the fish feed extrusion process but have a broad and general relevance in bio-based plastic formulation and food technology.

2. Materials and methods

2.1. Materials

Hot air dried press cake fishmeal (PCM) and stickwater concentrate (SWC) were obtained from a Norwegian fishmeal plant. The PCM was produced by shutting down the addition of SWC to the dryer. The production was based on blue whiting (*Micromesistius poutassou*) raw material preserved on board a fishing vessel by a combination of acetic acid addition (2 g kg^{-1}) and chilling by circulation of fresh/seawater mixture. Raw material quality during processing was (N = 4): ammonia: 14.0 ± 2.0 mg N 100 g^{-1}, trimethylamine (TMA): 19.5 ± 2.6 mg N 100 g^{-1} and trimethylamine N-oxide (TMAO): 23.3 ± 5.2 mg N 100 g^{-1}. Ethoxyquin FEQ 500 was provided by LL Chemie AB, Helsingborg, Sweden. Peptide standards were purchased from Sigma-Aldrich (Oslo, Norway) except lysozyme (Fluka Biochemika, Buchs, Switzerland) and Alberta standards (Alberta Peptide Institute, Department of Biochemistry, University of Alberta, Edmonton, Canada). All solvents and reagents for the analyses were of analytical grade.

2.2. Preparation of experimental fishmeal samples

To ensure an even distribution of solubles the experimental fishmeal (EFM) samples were prepared by addition of SWC to 350–500 gram PCM in a kitchen blender followed by drying in a hot air Retsch TG1 fluid bed dryer (Retsch GmbH, Haan, Germany) at 70 ± 3 °C. The drying curve was followed based on loss in weight and water removal stopped at a final dry matter content of 92–93%. The ratio of SWC to PCM was on a wet weight basis: 0.021, 0.316, 1.239, 2.656, and 3.493 in EFM #1–5, respectively. The experimental fish meal samples (Table 1) were stabilized by the addition of ethoxyquin to 200 ppm before drying and grinded on a Retsch ZM-1 Centrifugal Mill (Retsch GmbH, Haan, Germany) with a ring sieve aperture of 0.5 mm.

Table 1
Chemical composition of the experimental fish meal samples (g kg^{-1} DM).

	Materials		Experimental fish meal (EFM#)				
Composition	PCM	SWC	1	2	3	4	5
Moisture	74	3386	78	75	80	89	98
Fat	67	86	63	67	76	78	80
Protein (Nx6.25)	792	785	783	784	783	780	780
Water soluble protein (protein basis)	90	823	97	142	254	363	412
Water soluble protein	71	646	76	111	199	283	322
Water soluble dry matter	102	741	95	137	240	338	380
Ash	153	171	154	151	153	157	158
Water soluble ash	20	162	24	33	56	81	88
Sodium chloride	13	101	12	18	31	46	50
Putrescine	<0.10	0.57	<0.10[a]	0.04[a]	0.13[a]	0.22[a]	0.26[a]
Cadaverine	0.20	1.58	0.21[a]	0.30[a]	0.52[a]	0.75[a]	0.84[a]
Histamine	<0.10	<0.10	–	–	–	–	–
Total volatile nitrogen	1.2	5.7	1.2	1.5	2.1	2.4	2.5

PCM — presscake meal; SWC — stickwater concentrate; EFM — experimental fishmeal.
[a] Calculated based on composition data and ratio between PCM and SWC.

2.3. Chemical analysis

Moisture content was measured gravimetrically after drying at 103 ± 1 °C (ISO 6496). Ash was determined by combustion of organic matter at 550 °C and gravimetric measurement of the residue remaining (ISO 5984). Fat content was determined based on ethylacetate extraction (NS 9402) in SWC and petroleum ether Soxhlet extraction (AOCS Ba 3-38) in fishmeal samples. Crude protein (Nx6.25) was analyzed by the Kjeldahl method (ISO 5983-2) in SWC and the Dumas method (AOAC 990.03) in fishmeal. Water soluble protein content was determined by extraction of a 10 g sample with 150 ml boiling distilled water for 30 min, cooling and adjusting the volume to 250 ml, filtering through a Whatman 589/1 black ribbon paper (Whatman, Dassel, Germany) and quantification of nitrogen in the filtrate based on the Kjeldahl method (ISO 5983-2). Water soluble dry matter and ash contents were determined by the same extraction procedure and quantification in the filtrate. Total volatile nitrogen (TVN) in EFM was determined by distillation (AOAC 920.03). Ammonia, trimethylamine N-oxide (TMAO) and trimethylamine (TMA) in fish raw material were determined based on the micro-diffusion technique described by Conway and Byrne (1933). The biogenic amines cadaverine, histamine and putrescine were measured by HPLC according to Mietz and Karmas (1978). Sodium chloride (NaCl) was determined based on measurement of water soluble chloride (AOAC method 937.09). All analyses were run in duplicate.

2.4. Amino acid composition and peptide size distribution

Total amino acid composition was measured by HPLC after hydrolyzing in 6 N HCl for 22 h at 110 °C, using the Waters Accq-Tag method and fluorescence detection with excitation/emission at 250/395 nm (Cohen & Michaud, 1993). Cysteine and cystine were determined after performic acid oxidation. Tryptophan was chemically determined by the method of Miller (1967). Free amino acids were measured in the water soluble SWC extract by HPLC using Waters Pico-Tag method and UV-detection at 254 nm (Bidlingmeyer, Cohen, Tarvin, & Frost, 1987).

Peptide size distribution was measured by combining results from HPLC size exclusion chromatography using a Superdex™ Peptide 10/300 GL (I.D. 10 mm × 300 mm) (GE Healthcare, Upsala, Sweden) column (measuring range 200–20 000 Da) and a TSKgel G2000SW (I.D. 7.5 mm × 300 mm) (Tosoh, Tokyo, Japan) column (measuring range 2000–70 000 Da). Detection was based on UV adsorption at 214 nm and 210 nm, respectively. The water soluble SWC extract was diluted to approximately 150 mg/ml with the eluent (30% acetonitrile, 0.1% trifluoroacetic acid in water) and filtered