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# Improving the emulsifying properties of whey protein isolate-citrus pectin blends by a novel reactive extrusion approach

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ABSTRACT

In this study we used a new experimental setup to improve the emulsifying capacity of whey protein isolate-citrus pectin (WPI-HMCP) blends during extrusion processing. In this setup, the extruder serves as pump, while the reaction takes place mainly in a 380 mm long slit die which is attached at the end of the extruder. Using this setup, it is possible to improve the emulsifying capacity of WPI-HMCP blends: The Sauter mean diameter of emulsions stabilized by the extruded blends could be reduced compared to those stabilized by the untreated blend. The smallest Sauter mean diameter was measured when the WPI-HMCP blend was treated at 120 °C for 46 s residence time in the reaction die (corresponding to a total mass flow rate of 19.4 kg/h). It was halved compared to the untreated blend. Structural analyses of the reaction products showed that at constant reaction die temperature and increasing total mass flow rate the formation of disulfide bonds is favored, while the formation of non-disulfide covalent cross-links is inhibited.



## 1. Introduction

The ever-expanding consumer awareness of health and nutrition leads to a growing demand for natural-based food ingredients. Biopolymers such as whey proteins are often applied in food products due to their functional properties (e.g., emulsifying, stabilizing and foaming properties) (Thompson et al., 2009). However, whey proteins are very sensitive to changes in temperature, concentration of ions and pH. This can result in a loss of their functional properties and limits their industrial application to a specific range (Damodaran, 2007). In recent years, research focused on the functionalization of whey proteins. It has been shown that a covalent linkage of whey proteins with high molecular weight polysaccharides (e.g., citrus pectin) can improve emulsifying, foaming and stabilizing properties of whey proteins (e.g., Einhorn-Stoll et al., 2005; Mishra et al., 2001; Neirynck et al., 2004; Schmidt et al., 2016). These covalently linked molecules are formed during the initial step of the Maillard reaction and are referred to as protein-polysaccharide conjugates (Maillard, 1912).

Conjugates are commonly formed by incubation of either lyophilized protein-polysaccharide powders (referred to as dry-heating) (Kato et al., 1989) or protein-polysaccharide aqueous solutions (referred to as wet-heating) under controlled conditions (Zhu et al., 2008). Other recently published conjugation methods include ultrasonic treatment (e.g., Li et al., 2014; Mu et al., 2010), treatment with pulsed electric fields (Sun et al., 2011), enzymatic treatment (e.g., Flanagan and Singh, 2006; Song and Zhao, 2014) and thermomechanical treatment via extrusion processing (Guerrero et al., 2012; Koch et al., 2017a).

Extrusion is a continuous process running at a throughput of up to several hundred tons per hour and residence times of a few minutes. During extrusion processing, the material is subjected to elevated temperatures and high mechanical stresses generated by the rotation of screws (Riaz, 2000). Up to now, only a few studies focused on protein-polysaccharide conjugation by using extrusion processing and therefore less is known about the influence of the extrusion conditions on the reactions taking place (Guerrero et al., 2012, 2014; Koch et al., 2017a). Guerrero et al. (2012) concluded that the moisture content and the type of sugar affect molecular changes. The results of our previous study suggest that extrusion temperature, mechanical stresses and residence time affects the reactions proceeding (Koch et al., 2017a). However, thermal and mechanical stresses are coupled to each other and thus their influence on the reactions taking place can not be considered separately. Moreover, local extrusion conditions vary widely and the

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material is not treated homogeneously (Emin et al., 2016; Emin and Schuchmann, 2013).

To get more information about the influence of thermal and mechanical stresses on structural changes in highly concentrated systems, as found during extrusion processing, investigations under controlled, extrusion-like conditions were conducted in previous studies (Emin and Schuchmann, 2016; Habeych et al., 2009; Koch et al., 2017c, 2017c; Madeka and Kokini, 1994; Madeka and Kokini, 1996; Pommet et al., 2004). In our recent study, we investigated the influence of treatment temperature, shear rate and treatment time on structural changes of highly concentrated whey protein isolate-citrus pectin blends (i.e., 28% moisture content) in extrusion-like conditions (Koch et al., 2017c). It could be shown that the formation of disulfide bonds is increasing with temperature (i.e., 80 °C - 140 °C) and is accelerated with the application of shear. Non-disulfide covalent cross-links (i.e., isopeptides and Maillard reaction products) were determined at 120 °C and 140 °C already after 0.75 min, while shear seems to have an adverse effect on their formation. Besides the structural changes investigated in this paper, pectin degradation reactions which can be followed by polymerization reactions (e.g., caramelization) can also take place (Axelos and Branger, 1993; Morris et al., 2002; Schols and Voragen, 2002).

Even with this information on the chemical reactions at typical extrusion conditions, it is still a great challenge to design the extrusion process for a targeted functionalization of whey protein isolate-citrus pectin (WPI-HMCP) blends. As long as the exact thermomechanical stress profile is not known and can not be controlled, we are not able to define exact processing parameters for a tailor-made functionalization of raw materials. A possible approach is the detailed characterization of the extruder including all local extrusion conditions which allow the control of the reactions taking place, which is described on more detail in (Emin and Schuchmann, 2016). This paper focuses on an alternative approach based on a new extruder setup. In this setup, the extruder mainly serves as pump whereas the reaction is induced and controlled in a so-called reaction die being attached at the end of the extruder (see Fig. 1). The reaction die enables us to set defined reaction conditions (such as reaction temperature and time) and a homogenous material treatment. From a technological point of view, this setup has the advantage of a relatively simple scale up by the adaptation of die dimensions.

This study aims at analysis of the feasibility of this setup. We run the reaction die with WPI-HMCP blends and varied the influence of the two main process parameters: (1) total mass flow rate in order to control residence time and (2) reaction die temperature to control material temperature. We analyzed structural changes (i.e., covalent cross-links) and the emulsifying capacity of the extruded blends.

## 2. Material and methods

### 2.1. Materials

Whey protein isolate (WPI), Volactive UltraWhey 90, with typically 93% protein on dry matter basis was provided by Volac International Limited (Orwell, Royston, Hertfordshire, United Kingdom). According to the supplier, WPI contains about 2.5% lactose, 0.3% fat, 2.0% ash and 4.5% moisture. Highly methylated citrus pectin (HMCP), Classic CU-L 009/13, was kindly supplied by Herbstreith & Fox, Neuenbuerg/Enz, Germany. The HMCP used exhibits a moisture content of 7.5%, a degree of esterification of approximately 70%, and an average molecular weight of 79.8 kDa determined by intrinsic viscometry. Commercial rapeseed oil (FLOREAL Haagen GmbH, Saarbrücken, Germany) was used for the preparation of the emulsions.

### 2.2. Extrusion process

The extruder setup is depicted in Fig. 1. The reaction die is attached directly at the extruder outlet und replaces the commercial extruder die.

Extrusion experiments were carried out using a co-rotating twin-screw extruder ZSK 26 Mc (Coperion, Stuttgart, Germany) with screw diameter of 25.5 mm and length to diameter ratio (L/D) of 29. The extruder barrel consists of 7 sections which can be heated separately, except the first one.

The reaction die has dimensions of 15 × 30 × 380 mm (H x W x L) and is thermoregulated (up to 200 °C). Die dimensions were chosen to adjust comparable shear rates and residence times like in our previous study where structural changes were investigated under controlled, extrusion-like conditions in a closed-cavity rheometer (Koch et al., 2017c).

In this setup, the extruder mainly serves as a pump setting total mass flow rate and thus residence time in the reaction die. Chemical reactions are minimized in the screw section. For this we used the screw configuration that generated minimum structural changes defined in our previous study (Koch et al., 2017a), see Fig. 2.

To investigate the influence of temperature in the reaction die on the final products, extruder barrel temperature and temperature of the reaction die were varied during the experiments as shown in Table 1. Barrel temperature of section 2–6 was increased up to a temperature 10 K below the reaction die temperature. This procedure allowed us heating the material to the reaction temperature at the end of the extruder screw. The material temperature was measured along the extruder and the reaction die using thermocouples type J (Ahlborn, Holzkirchen, Germany). The reaction die

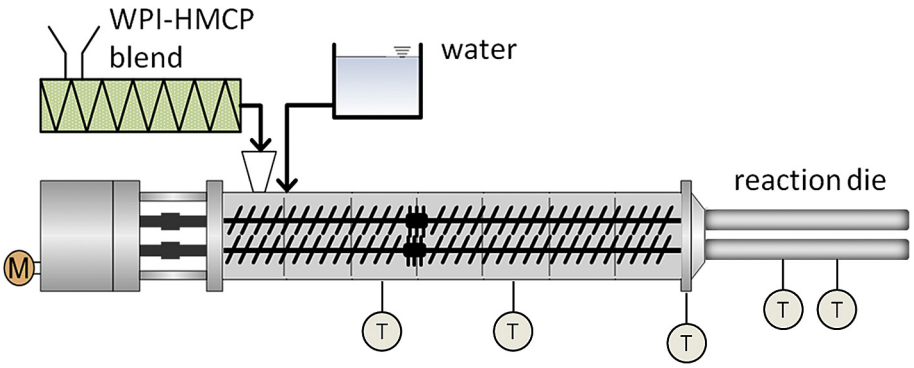


**Fig. 1.** Schematic illustration of the experimental setup.

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