Alkaline or Acidic Pretreated Gelatins; Effect on Rheological Properties of Gelatin-based Chewable Solid Emulsions

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ABSTRACT

Raw materials for the production of gelatin may either be pre-treated with acid or alkali to hydrolyze inter- and intramolecular bonds between and within the collagen mother molecules. The resulting gelatins are denominated type A or type B, respectively, and the main difference being a conversion of the acid amides (Asn and Gln) to their acid analogues (Asp and Glu) after alkaline pretreatment leading to a lowering of the pI. Gelatins also possess amphiphilic properties and will therefore be able to stabilize O/W emulsions. In this study, gelled O/W emulsions with varying oil contents have been prepared with the two different types of gelatins. Small strain oscillatory measurements combined with temperature sweeps were used for the determination of the gelling kinetics. The acid pretreated gelatins exhibited a steeper increase in modulus as function of increased oil contents as well as increased setting and melting temperatures. This behavior is suggested to stem from a hydrogen bond mediated flocculation of the oil droplets. Additionally, gelled emulsions were made applying a cold-water fish gelatin sample, which typically show inferior physical properties compared to their mammalian counterparts. At high contents of oil inclusion, these suboptimal properties were improved. Within certain limitations, these results suggest that the properties of gelatin-based solid emulsions can be manufactured to meet specific demands.

INTRODUCTION

Chewable oral formulation is gathering an increased popularity; particularly in the neutraceutical segment but also as pharmaceutical formulations[1]. The main reason for this is linked to different dysphagia challenges, especially amongst children and the elderly, which makes it challenging to swallow traditional oral formulations such as tablets and capsules.

Gelatins are especially preferred for such chewable formulations because of their long texture and melt-in-mouth properties. These properties are, however, exclusive to gelatins from mammalian sources as e.g. gelatin extracted from cold-water fish species has considerable lower setting and melting temperatures[2].

Another beneficial feature of applying proteins such as gelatins is that they are in general considerably more surface active compared to e.g. polysaccharides. In turn, this means that they can be exploited to stabilise emulsions without the need for additional emulsifiers. One example of this is that gelatin based chewable formulations are now made with a very high payload of long chain omega-3 fatty acids (DHA/EPA)[3].

Gelatins are categorized according to their gelling potential ("Bloom strength") as well as to the pre-treatment of the raw

material (e.g. pigskin) before the extraction of the gelatin. The former is in general linked to molecular weight, whereas the latter is linked to if acid or alkali is used as pre-treatment. Acid pre-treatment leads to a gelatin that is identical to the mother collagen from which it was extracted, whereas alkali pre-treatment renders the amino acid composition in that the acid amide (Asn and Gln) are converted to their acid analogues (Asp and Glu). This change will, in turn, lead to a considerable decrease in the isoelectric point (Ip) of the manufactured gelatin[1].

The question raised in this study is if the properties of chewable, gelatin-based solid emulsions are independent of which type of gelatin used.

MATERIALS AND METHODS

Gelatins with varying Bloom strength and type (A and B) were dissolved at 55C at a concentration of 25%. Sunflower oil was added to different concentrations (0 – 50% w/w), and emulsions were made by using a VDI 12 homogeniser (dispersing element type S12N-12S) at a mixing speed of 28 000 RPM for 3 min. Rheological analyses were performed using a 4/40 plate-cone geometry
in a strain controlled mode (0.005; 1 Hz). Viscoelastic properties were determined using a 2C/min temperature gradient; start and end temperature at 60C and a holding time of 15 min at 20 C. Setting and melting temperatures were determined as the temperature where the phase angle corresponded to 45^0 the cooling and heating process, respectively.

RESULTS AND DISCUSSION

Gelling kinetics of the emulsion gels showed an expected temperature dependent sol gel transition with a slight hysteresis for all samples except for the high Bloom (260) type A (Fig. 1). The same deviation was also observed for lower Bloom type A gelatins but at higher oil contents (data not included).

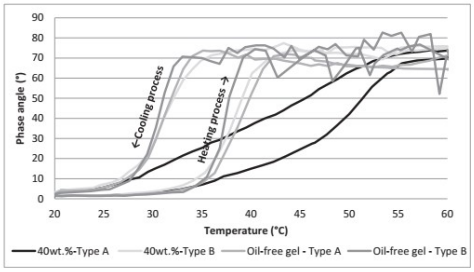

Figure 1. Phase angle development for gelled emulsions (40 wt.% corn oil) and oil-free gels prepared using acid (type A) or alkali (type B) pretreated 260 Bloom gelatin.

Type A-gelled emulsions all exhibited increased setting and melting temperatures at high oil content, but only small differences were observed for the gelled emulsions prepared with type B gelatins. This is most likely due to a physical interaction between the oil droplets. The main difference between type A and B gelatins is the conversion of glutamine and asparagine into their acid analogues for the alkaline treated samples, which leads to a lower IEP and a higher charge density for the type B gelatin. Presence of electrostatic effect was, however, ruled out as type B gelatin exhibited only small changes in setting and melting temperatures over a wide pH range (4-8).

A more solid-like behavior above the transition temperature for the type A emulsions rather suggests that hydrogen bonds may be involved. Asparagine is able to form hydrogen bonds with the peptide backbone[4]. Moreover, as only type A gelatin contains asparagine, it cannot be ruled out that these amino acids contribute to the formation of hydrogen bonds promoting flocculation of the oil droplets. Light microscopy examination of dissolved type A emulsion did indeed confirm the presence of

flocs above the helix-to-coil temperature of the gelatin (data not included). It is therefore assumed these flocks will stabilize type A emulsions by providing an additional network in addition to the pure gelatin-gelatin network leading to more solid like behavior.

This particular property of type A gelatin can also be utilized to improve sub-optimal properties of non-mammalian gelatins. Gelatins extracted from cold water fish species normally melts well below room temperature, but as Fig. 2 shows both gelling and melting temperature as well as mechanical properties can be rendered at high oil inclusions.

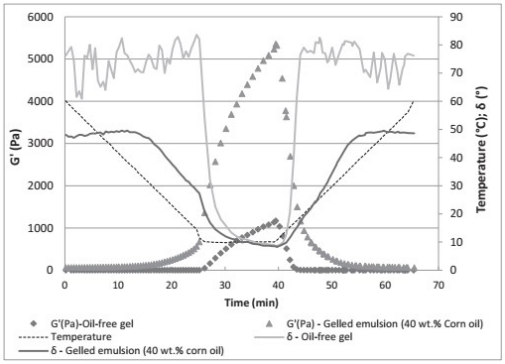

Figure 2. Phase angle and shear storage modulus (G') for a gelled emulsion (40 wt.% corn oil) and oil-free gels prepared with a high molecular weight cold water type A fish gelatin (25 wt.% gelatin of the aqueous phase).

The overall conclusion is that the properties of a gelatin based gelled emulsion depends both on the fraction of lipid, but also on the type of gelatin used. Type A will exhibit more solid like properties compared to type B due to the formation of flocks. This may also influence on the bioavailability of bioactives from chewable tablet formulations. But such an additional network can also be exploited to improve properties of non-mammal type A gelatins.

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