Interfacial and rheological properties of gelatin based solid emulsions prepared with acid or alkali pretreated gelatins

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A B S T R A C T

In this study gelled emulsions (10, 20, 40 and 50 wt.% corn oil) and oil-free gels have been prepared using either acid (type A) or alkaline (type B) pre-treated gelatins with varying Bloom values and molecular weights. The gelling kinetics of the gels were monitored by performing small strain oscillatory measurements in combination with a temperature sweep. Increasing setting and melting temperatures as a function of oil content were obtained for the gelled emulsions prepared with type A gelatin. The shear storage moduli for the gels were determined after curing at 20 °C for 15 min and compared to estimated values using a simplified version of the van der Poel's formula. A steeper increase in moduli as a function of oil content was obtained for the gelled emulsions prepared with the acid pretreated gelatins, also overshooting the estimated values. It is suggested that the higher moduli and setting and melting temperatures are caused by a hydrogen bond mediated flocculation of the oil droplets. Measurements of interfacial tension between gelatin solutions and corn oil, indicated that type A gelatin samples were more surface active compared to type B gelatin samples. This was attributed to the assumed presence of minor contaminants in the acid pre-treated gelatin samples, which were able to adsorb and reduce the interfacial tension at a faster rate. Finally, gelled emulsions were prepared using a cold water fish gelatin. It was observed that by the introduction of oil droplets, potentially improved physical properties may be obtained for these gels.

1. Introduction

Gelatin is a biopolymer obtained from the partial hydrolysis of the parent collagen molecule. A characteristic property of gelatin is its ability to form a thermoreversible gel with a low degree of thermal hysteresis. Gelatin is also amphiphilic due to the presence of both hydrophilic and hydrophobic amino acids (Ward & Courts, 1977). These properties enable gelatin to be an excellent stabiliser of gelled emulsions, as it may both adsorb at oil-water interfaces and form a polymeric network. Gelatin is prepared from collagen by pretreating it with either acid or alkali, in which the final gelatin is referred to as type A or type B gelatin, respectively. The pretreatment leads to hydrolysis of the inter- and intramolecular bonds within and between the collagen molecules. After pretreatment,

gelatin is extracted using hot water or diluted acid, and the soluble fraction after this step is usually referred to as gelatin (Stainsby, 1985). By alkali pretreatment, a conversion of glutamine and asparagine to glutamic and aspartic acid occurs, giving a shift in the isoelectric point (IEP) from 7–9 to ~5. The molecular weight of the final gelatin may also vary, depending on the raw material and preparation procedure. As its precursor collagen, gelatin may interconvert between a helix and random coil. Gelatin is however soluble above the helix-to-coil temperature in water and it will partially regain the triple helical structure below this temperature (Schrieber & Gareis, 2007; Veis, 1964; Ward & Courts, 1977).

Gelatin based gelled emulsions are used extensively within food and confectionary, and have also been suggested as a possible delivery vehicle for lipid-based nutraceuticals and pharmaceuticals (Hattrem, Dille, Seternes, & Draget, 2014; Haug et al., 2011; Sato, Moraes, & Cunha, 2014; Thakur et al., 2012). For all of these applications the mechanical properties of the gelled emulsions are of crucial importance. In general, the mechanical properties of gelled emulsions vary strongly depending on the fraction and modulus of the dispersed phase, type and concentration of polymer and

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interaction between the dispersed droplets and the polymer matrix (Chen & Dickinson, 1999; Chen, Dickinson, Langton, & Hermansson, 2000; van Vliet, 1988). The structural network of gelled emulsions may be formed either by aggregation of dispersed filler, known as a particle gel, and/or by a structural network formed by polymers in the continuous water phase. Gelatin based emulsions would represent the latter, in which the solid like behaviour is mainly determined by the polymer matrix (Dickinson, 2012). The mechanical properties of such gels are known to be highly influenced by the interaction between the droplets and the gel matrix. A structural reinforcement (an increase in the composite modulus) may be obtained if there is a strong interaction between the droplet interfacial layer and the polymer matrix, in which the filler is referred to as being active. This may either occur by the adsorption of the gelling polymer at the droplet interface or by a molecular interaction between the emulsifying agent and the polymer matrix, e.g. electrostatic interaction. Usually, a prerequisite for an increase in composite modulus is that the droplets' modulus (G_{filler}), given by the Laplace pressure (equation (1)), is higher than the modulus of the polymer matrix.

$$G_{filler} = \frac{2*\gamma_{oil-water}}{droplet\ radius} \qquad (1)$$

As seen in equation (1), the G_{filler} is proportional to the interfacial tension ($\gamma_{oil-water}$) between the oil and water. If there is no/weak interaction between the interfacial layer and polymer matrix, a reduction in the overall modulus would be expected regardless of the Laplace pressure of the dispersed droplets. The filler of such gels is referred to as being inactive (Chen & Dickinson, 1999; Kim, Renkema, & van Vliet, 2001; van Vliet, 1988).

The mechanical properties of gelatin based gelled emulsions have earlier been characterized (Dickinson, Stainsby, & Wilson, 1985; Lorenzo, Checmarev, Zaritzky, & Califano, 2011; Sala, Van Aken, Stuart, & Van De Velde, 2007; Sala, van Vliet, Stuart, van de Velde, & van Aken, 2009). In the study by Dickinson et al. an increase in modulus as a function of oil content was observed. However, at lower gelatin concentrations a minimum in the shear modulus was obtained at a specific fraction of oil. This was suggested to be caused by an adsorption of gelatin at the droplet interface leading to a depletion of gelatin available for gelling in the continuous water phase (Dickinson et al., 1985). Studies by Sala et al. investigated both Young's modulus and stress and strain at fracture for a whey protein stabilised emulsion, in which the droplets were encapsulated in a gelatin matrix (Sala et al., 2007; Sala, van Vliet, Stuart, van Aken, & van de Velde, 2009; Sala, van Vliet, Stuart, van de Velde, et al., 2009). These droplets behaved as active fillers, leading to an increase in Young's modulus with increasing fraction of oil. Additionally, a decrease in both the fracture stress and strain were observed with increasing amount of filler. In a recent study, Lorenzo et al. investigated the influence of the molecular weight of the gelatin on the gelling properties of gelled emulsions. Increased elastic properties were obtained for the gelled emulsions with increasing molecular weights of the gelatin (Lorenzo et al., 2011).

Although there have been several studies on the mechanical properties of gelatin based emulsions, the influence of using either acid or alkali pretreated gelatin have not yet been reported. The difference in both molecular weight distribution and IEP between type A and B gelatin may influence their ability to adsorb at and stabilise oil-water interfaces. It is further known that minor contaminants (mucosubstances, proteins and fats) with potential surface active properties may remain in the gelatin samples after preparation. These contaminants are reported to be present in larger amount in type A gelatin samples (Schrieber & Gareis, 2007; Ward & Courts, 1977). As the modulus of the dispersed phase is suggested to be proportional to the interfacial tension (equation (1)), this may further influence the mechanical properties of the gelled emulsions. The scope of the present paper was to investigate if the gelatin type influenced the rheological and interfacial properties of gelled emulsions. Type A or type B gelatin with varying reported bloom values and molecular weight distributions were used to prepare gelled emulsions and oil-free gels. Dynamic interfacial tension was measured for different gelatin solutions, and small strain oscillatory measurements and puncture testing were performed on the resulting gels.

2. Materials and methods

2.1. Materials

Acid and alkali pretreated gelatins with reported Bloom values of 160, 200 and 260 g were kindly supplied by Gelita (Eberbach, Germany) and used without further processing. Information about the different gelatins is listed in Table 1. Corn oil and trizma base were purchased from Sigma Aldrich (Seelze, Germany). Acetic acid was provided by VWR international (Darmstadt, Germany). High molecular weight cold water fish gelatin (batch 8004) was supplied by Norland Products (New Jersey, USA). All experiments were performed using deionised water (MQ-water).

2.2. Preparation of gelatin based emulsions and oil-free gels

A gelatin solution was prepared by dissolving 25 wt.% gelatin (160A, 160B, 200A, 200B, 260A or 260B gelatin — see Table 1 for information) in MQ-water at 55 °C. The present gelatin concentration was chosen in order to give a surplus of gelatin in the bulk phase of the finalised emulsion, reducing potential bulk depletion effects due to gelatin adsorption at the droplet interface. Corn oil (10, 20, 40 or 50 wt.%) was added to the gelatin solution and this sample was further equilibrated at 55 °C for 10 min. An oil-in-water emulsion was prepared by mixing the two liquids using a VDI 12 homogeniser (VWR International, Darmstadt, Germany) equipped with a dispersing element (type S12N-12S, VWR International, Darmstadt, Germany) at a mixing speed of 28 000 RPM for 3 min. The homogenization process resulted in a small increase in temperature (~5 °C) of the finalized emulsion and the sample was therefore subsequently equilibrated back to 55 °C. The oil-free gels were not homogenized, since small strain oscillatory measurements (see Section 2.6) gave insignificant differences in rheological properties between homogenized and non-homogenized samples. Air bubbles were removed by degassing the prepared samples in a vacuum chamber (Nalge company, Rochester, New York, USA) connected to a vacuum pump (Diaphragm Vacuum Pump, Wertheim, Germany). Oil-free gels were prepared by the same

Table 1
Information about the different gelatins used in this study, with reported Bloom strength given by Gelita. Molecular weights for the gelatins have earlier been reported (Hattrem, Molnes, et al., 2014). The sample names listed are used throughout this work.

Type	Source	Bloom (g)	Batch number	Sample name	Mn[a]	Mw[a]
A	Pig skin	160	629586	160A	36.1	90.9
A	Pig skin	200	630396	200A	59.4	148.2
A	Pig skin	260	628305	260A	88.7	191.3
B	Limed bovine bone	160	630473	160B	58.1	161.1
B	Limed bovine bone	200	626440	200B	73.0	174.6
B	Limed bovine bone	260	630507	260B	118.8	217.2

[a] These values have earlier been reported by (Hattrem, Molnes, et al., 2014).