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Shear-induced coalescence in aqueous biopolymer mixtures

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Abstract

This work is focused on the investigation of coalescence under shear flow in aqueous mixtures of Na-alginate and Na-caseinate. Shear flow was generated in a parallel plate apparatus coupled with an optical microscope. Drop size distribution was measured as a function of time by computer controlled 3D optical sectioning of the sample and offline image analysis. Automated procedures of image analysis, based on out-of-focus components subtraction and drop contour detection, were implemented to measure a large number of drops, as required to minimize sampling errors. The effects of dispersed phase volume fraction and shear rate on the flow-induced evolution of the drop size distribution were explored. Finally, 3D reconstruction of the locations of the drops within the sample was performed to evaluate possible wall and sedimentation effects.

Keywords: Drop; Imaging; Emulsions; Coalescence; Microstructure; Biopolymers

1. Introduction

Aqueous–aqueous two-phase systems are widely used in the food industry as thickeners for low fat food. The flow history applied during processing influences the morphology of the mixture, which, in turn, modifies its rheological and sensorial properties, and its ability to mimic fat in food products. In order to design a product with the desired properties, a good understanding of the relation between mixture morphology (i.e., average drop size) and flow history applied during processing is essential (Ross-Murphy, 1995). A similar problem is faced in the plastic industry when two immiscible polymers are blended together and a well-defined morphology is desired or when aqueous/oil emulsions have to be created by proper mixing (Vinckier et al., 1998; Pacek et al., 1999; Sajjadi et al., 2002). Recently, a number of studies have concluded that the morphology evolution of aqueous–aqueous two-phase systems is governed by the same physical principles as the ones that govern polymer blends and oil/water emulsions (Van Puyvelde et al., 2003; Guido et al., 2002; Wolf et al., 2001; Foster et al., 1997). On the other hand, some evidence that the analogy between aqueous–aqueous and aqueous/oil dispersions can be rather limited was provided by Pacek et al. (2001).

Although different techniques, from rheology (Simeone et al., 2002) to small angle light scattering (Van Puyvelde et al., 2003), have been applied to measure the average drop size in aqueous–aqueous dispersions, direct measurement of drop size via optical microscopy and image analysis remains as a benchmarking technique, capable of providing, along with the averaged values, also the entire drop size distribution. From the experimental point of view, the main difficulties that limit the application of direct measurement of drop size via optical microscopy and image analysis can be summarized as follows. Imaging two-phase systems is hindered by the high turbidity associated with the typically small average drop size of the dispersed phase. The contribution of out-of-focus components in the plane of observation (which is due to drops located at different depths) can lead to rapidly increasing image degradation with optical penetration in the sample. A possible way to overcome this problem is to quench the sample at given times in the course of the experiment and to observe selected sections by electron

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microscopy. The main drawback of this approach is the possible artefacts introduced both by the quenching procedure and the sample preparation required by electron microscopy. A second problem is the detection of a number of drops high enough to guarantee statistically significant results. In most studies, a few hundred drops are manually identified at each time point and the calculated average drop size is considered representative of the whole population of drops in the dispersed phase. However, as shown by Paine (1993) in a recent study on error estimates in sampling from particle size distributions, the inferred parameters can be affected by large intrinsic errors, especially in the case of higher order moments (such as volume based averages). According to Paine's analysis, which is based on a log-normal distribution, there is a critical number of particles which must be counted or else the error may blow up catastrophically. Such a critical number is quite sensitive to the width of the distribution, and its dependence on the geometric standard deviation can be estimated by following Paine's approach.

In this work, we present a methodology to investigate the time evolution of the drop size distribution in aqueous–aqueous dispersions under shear flow in a parallel plate apparatus. The proposed approach is based on optical sectioning and 3D motorized scanning of the sample in the course of the experiment, followed by an off-line analysis of the acquired images.

The optical sectioning methodology was applied to investigate the evolution of drop size distribution as a consequence of shear-induced coalescence. The effects of shear rate and dispersed phase volume fraction were investigated.

2. Experimental part

2.1. Materials

Na-alginate is a salt of alginic acid, which is extracted from brown seaweeds (Smidsrød, 1970, 1974) and is used as a thickening, emulsifying, film forming and gelling agent in food and in pharmaceutical products (Johnson et al., 1997). It was purchased as powder from Sigma. Several grades, labeled according to the viscosity of a 2% Na-alginate solution in water at 25 °C, were available with the manufacturer. The Na-alginate sample used in this work was of a medium viscosity grade, with a nominal viscosity of 3.5 Pa s (the actual viscosity was 2.92 Pa s). The molecular weight of the sample was estimated by measuring its intrinsic viscosity, according to Haug and Smidsrød (1962) and was equal to 112,000 Da. The water content of the Na-alginate powder was determined by drying under vacuum at 70 °C for 2–3 days and was about 6%. Such value was used to calculate the actual concentration of Na-alginate in solution.

Aqueous solutions of 2% Na-alginate were prepared by dispersing the powder in bi-distilled water ($Ca < 0.01\,mg\,l^{-1}$) under stirring and by heating to 70 °C for 30 min in order to facilitate dissolution. The solution was then cooled down to room temperature and stirred again for a few hours until complete dissolution was obtained. To prevent bacterial contamination, sodium azide was added to the solution at a concentration of 0.03%. The value of pH was adjusted to 7.0 by using NaOH 0.1 M.

Na-caseinate is a derivative of casein, which is the main protein component of milk (Fox and Mulvihill, 1982). Caseinates are frequently used as emulsifiers in oil/water systems, their interfacial properties resulting from the presence of both hydrophilic and hydrophobic amino acid residues. It was purchased as powder from Sigma. Water content was determined by drying under vacuum at 70 °C for 5 h, according to the procedure recommended by Browne (1919) and was ca. 3%. As before, the concentration of Na-caseinate in solution will be referred to as water-free powder.

Aqueous solutions of 12% Na-caseinate were prepared by adding the powder in small amounts (to avoid lump formation) to bi-distilled water and stirring at room temperature. Dissolution was a slow process, especially at concentrations above 10% (the highest content of Na-caseinate that could be dissolved in water was around 20%). The solutions, even at low concentrations, showed a white, turbid appearance, which did not change with time. The opacity was due to the presence of minute, insoluble particles, which could be removed by centrifugation. Solutions of NaOH from 0.1 to 1 M were used to bring pH to 7.0. As for the Na-alginate solutions, sodium azide (0.03%) was added for sample preservation.

2.2. Mixture preparation

Aqueous mixtures containing 1% Na-alginate and 6% Na-caseinate were prepared by blending equal amounts of solutions of the pure components. The mixtures were stirred for several hours and then allowed to equilibrate for 1 day at room temperature. The value of pH was then checked again and corrected, if necessary, to 7.0. The so prepared mixtures are well within the biphasic region according to the phase diagrams reported in the literature (Antonov et al., 1980; Blonk et al., 1995; Simeone et al., 2004) and separate into a Na-alginate rich phase (A-RP) and a Na-caseinate rich phase (C-RP). To separate the two equilibrium phases, samples of the mixtures were loaded in transparent test tubes and centrifuged at $100,000g$ for 15 h, keeping the temperature at 23 °C. After centrifugation the samples looked clear and separated in two distinct layers with the A-RP on top of the C-RP. In order to prepare mixtures with the desired volume fraction of C-RP, in the range 5–15%, the equilibrium phases were re-mixed together in proper amounts.

2.3. Equilibrium phases characterization

After centrifugation, the two phases were carefully withdrawn by means of a syringe and analyzed as described in detail in a prior work by Simeone et al. (2004). It is worth