

## A rheo-optical investigation of shear-induced morphological changes in biopolymeric blends

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(Received June 28, 2002)

### Abstract

In this paper, a rheo-optical methodology based on small angle light scattering and polarimetry is applied to investigate *in-situ* and on a *time resolved* basis the flow-induced structures in aqueous biopolymeric blends. Water-dextran-gelatin is chosen as an example. It is verified to what extent the laws and scaling relations, originally developed for synthetic polymer blends, are valid for the morphology development in this aqueous biopolymeric mixture. It was observed that under low shear rate conditions, the biopolymeric emulsion can be regarded as a conventional emulsion. However, at high shear rates flow induced homogenization occurs.

**Keywords** : biopolymers, rheo-optics, emulsions, flow-induced mixing

### 1. Introduction

Aqueous mixtures of biopolymers such as proteins and polysaccharides are widespread in the food industry as thickeners for low or zero fat foods. Due to the rather poor compatibility, generally a two-phasic structure is obtained (e.g. Antonov *et al.*, 1980; Blonk *et al.*, 1995; Norton and Frith, 2002). The morphology of such mixtures, which governs the sensorial properties and hence the ability of mimicking for example fat in food products, is altered during processing (Ross-Murphy, 1995; Langton *et al.*, 1999). Hence, a good understanding of the relation between the morphology development and the processing conditions is required to design products with desired properties.

The plastics industry faces a similar problem when two immiscible polymers are blended. The resulting microstructure, generated during the processing, is to a large extent responsible for the final properties of the plastic part. In the case of synthetic polymer mixtures, the relation between the morphology development and the processing conditions has been widely investigated (see for a recent review Tucker and Moldenaers (2002)). For simple droplet-matrix morphologies of Newtonian components most of the physical phenomena are reasonably well understood. Recent work suggests that biopolymer mixtures, that form water-in-water emulsions, are governed by the same physical principles as conventional mixtures containing synthetic polymers (e.g. Foster *et al.*, 1997; Wolf *et al.*, 2001).

However, some peculiarities of the water-in-water emulsions, such as the limited miscibility and the extremely low values of the interfacial tension may add extra complications to the processing.

The aim of this work is to verify to what extent existing models, originally derived to study the flow-induced morphologies of synthetic polymers, can be used to describe the morphology development in two-phasic biopolymer mixtures. For this purpose, an aqueous biopolymer mixture is investigated in shear flow. For mixtures of synthetic polymers, it is known that rheology is a powerful tool to examine the flow-induced structures (e.g. Tucker and Moldenaers, 2002). However, due to the extremely low interfacial tensions encountered in mixtures of biopolymers, the interfacial contribution to the rheometric response of the system will be negligible (Simeone *et al.*, 2002; Van Puyvelde *et al.*, 2002a; Scholten *et al.*, 2002). Hence, it becomes difficult to apply the rheological approach to obtain information about the structure development. An alternative rheo-optical methodology to investigate the morphology development during flow, originally developed to study immiscible synthetic polymer blends, will be used in this contribution (Yang *et al.*, 1998). It is based on polarimetry during flow, microscopy during flow and on small angle light scattering during flow.

### 2. Materials and methods

The gelatin-dextran-water system used in this study is chosen because of its low compatibility at the selected conditions and the liquid state of the coexisting phases over a

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wide range of compositions. The gelatin sample is an ossein gelatin type A 200 Bloom PS 8/30 (Lot 09030) produced by SBW Biosystems, France. The Bloom number, weight average molecular mass and the isoelectric point of the sample, as reported by the manufacturer are respectively 207, 99.3 kD and 8-9. A high molecular weight dextran T-2000 sample was purchased from Amersham Pharmacia Biotech AB (lot 275817). Its intrinsic viscosity in water at 293 K and weight average molecular mass; reported by the manufacturer, are 0.9 dl/g and  $2.10^6$  respectively. Preparation of the mixtures has been performed according to a procedure described in Van Puyvelde *et al.* (2002a).

Small angle light scattering experiments (SALS) have been performed on a Rheometrics Optical Analyzer (ROA) that has been modified to perform SALS measurements. The flow cell consists of a parallel plate device in which the shear flow results from the rotation of the upper glass plate of the cell. The gap between the plates has been set at 1 mm in these experiments and the temperature is kept constant at 318 K. In the present setup a He-Ne laser is used with wavelength 633 nm. The scattered light is intercepted on a screen that consists of a semitransparent paper with a beam stop. The resulting image is recorded on a CCD camera (Ikegami ICI-810P), which is mounted under the screen. The CCD camera is connected either to a frame grabber (Data Translation DT 3851) or to a video recorder to collect the scattering patterns. In addition, the ROA has been used to measure the transmitted light intensity. Microscopic observations have been performed on a Linkam

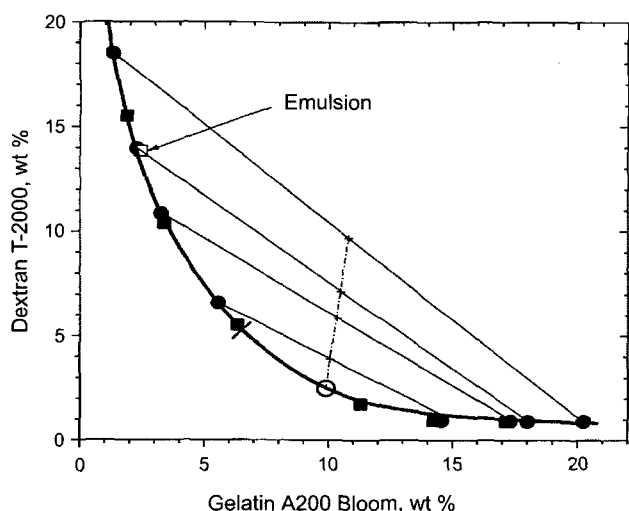
shearing cell mounted upon a Leitz Laborlux 12 PolS optical microscope using different magnifications.

### 3. Morphology development during flow

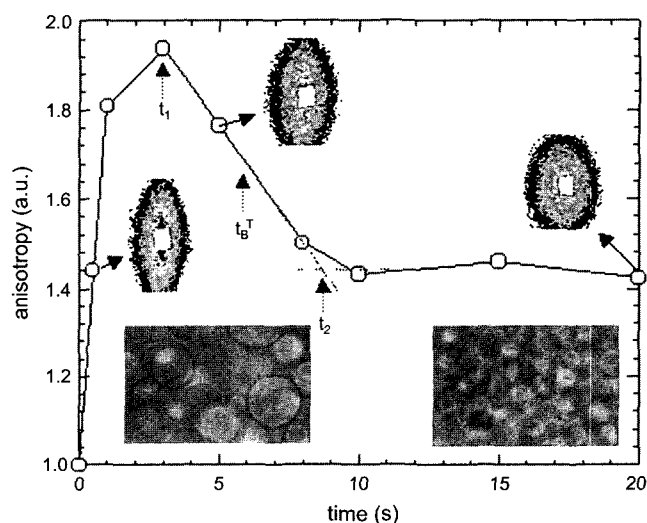
The phase diagram of the ternary system under quiescent conditions is shown in figure 1. It was obtained at isothermal conditions ( $T=318$  K),  $pH=5.0$  and ionic strength = 0.002. The procedure is adapted from Koningsveld and Staverman (1968) and Polyakov and colleagues (1980). The experiments shown in this section have been obtained on a water (83.72%)-gelatin (2.44%)-dextran (13.84%) emulsion. It contains 99 wt% of the dextran enriched phase and 1 wt% of the gelatin enriched phase. This emulsion is located in the two-phase region far from the critical point and close to the binodal line. It should be noted that both coexisting phases have about equal Newtonian viscosities at 318 K, i.e. 0.1 Pa.s and 0.08 Pa.s respectively. The interfacial tension, measured by a rheo-optical methodology, amounts to  $2.10^{-5}$  N/m (Van Puyvelde *et al.*, 2002).

#### 3.1. Low shear rate behaviour

The flow history used here consists of three parts. First a low shear rate is applied in order to wipe out any previous mixing history. Subsequently the shear rate is stopped and the droplets are allowed to relax to their spherical shape. Finally a start-up of shear flow is then performed and the evolution of the SALS patterns is recorded. The analysis of the light scattering patterns is performed by quantifying the degree of anisotropy of the pattern. Hereto, a second moment tensor is calculated from the measured light inten-



**Fig. 1.** Isothermal phase diagram of the water-dextran-gelatin mixture at 318 K ( $pH=5.0$ ; ionic strength 0.002). Thin lines correspond to the tie lines, the thick line is the binodal. O=critical point (9.5% gelatin, 2.5% dextran); X=threshold point (6.5% gelatin, 5.25% dextran). The emulsion used in this work is indicated on the phase diagram.



**Fig. 2.** Anisotropy as a function of time for a start-up to a shear rate of  $5\text{ s}^{-1}$ . Some of the SALS patterns are shown as well. The microscopy inserts display the morphology directly before application of the shear flow (on the left) and directly after stopping the shear flow (on the right).

sity on the 2D CCD array. A measure of anisotropy  $\varepsilon$  may be obtained from the difference between the eigenvalues of this tensor (Van Egmond *et al.*, 1997):

$$\varepsilon(\dot{\gamma}, t) = \frac{[(\int d\vec{q} q_x q_x I(q, \dot{\gamma}, t) - \int d\vec{q} q_y q_y I(q, \dot{\gamma}, t))^2 + 4[\int d\vec{q} q_x q_y I(q, \dot{\gamma}, t)]^2]^{0.5}}{\int d\vec{q} I(q, \dot{\gamma}, t)}$$

where the integration is performed over the complete surface of the CCD array,  $q_{x,y}$  being the components of the scattering vector.

Figure 2 shows examples of the SALS patterns as well as the accompanying evolution of the anisotropy as a function of time for a start-up in shear flow ( $\dot{\gamma}=5 \text{ s}^{-1}$ ). It can be observed that initially the SALS pattern becomes largely deformed, which is reflected in the increasing anisotropy. However, after some time the anisotropy decreases and will finally reach a steady state value. The SALS pattern at steady state conditions is elliptic, reflecting a slightly deformed structure.

A similar evolution of the anisotropy versus time has been observed for blends of synthetic polymers (Vermant *et al.*, 1998). It was shown that the initial part of the curve is associated with the deformation of the droplets. However after a certain deformation, the interfacial tension becomes important and the elongated fibrils will breakup. While breaking up, the anisotropy decreases which is indeed observed in the experiments. Recently, the breakup time  $t_b^d$  of droplets under flow, starting from their undeformed state, was determined unambiguously by measuring the linear conservative dichroism and its orientation angle in the velocity-gradient plane (Vermant *et al.*, 1998). It was shown that  $t_b^d$  is associated with the time halfway between the times corresponding to the maximum ( $t_1$ ) and the minimum values ( $t_2$ ) of the anisotropy. In addition it was demonstrated that the dynamics of the anisotropy calculated from the SALS patterns evolves in an identical manner as the dynamics of the dichroism. Hence the analysis of the evolution of the anisotropy, such as the one shown in figure 2, provides a very important structural characteristic, i.e. the time  $t_b^d$  at which droplets break under certain experimental flow conditions.

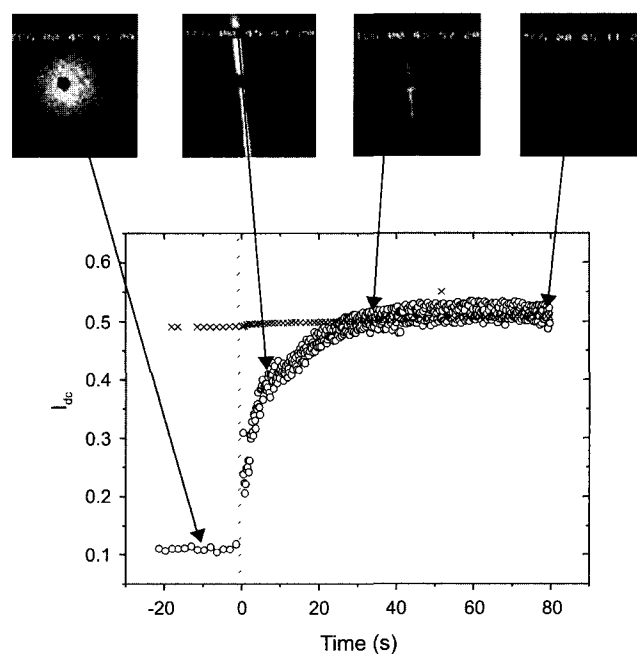
Based on the analogy discussed above, it is clear that the analysis of the SALS patterns during flow becomes a powerful tool to investigate the structural time scales in these biomaterials as well. The inserts in figure 2 indeed show that breakup has occurred. The microscopy image on the left represents the droplet structure just before imposing the shear rate of  $5 \text{ s}^{-1}$ . The microscopy image on the right represents the droplet structure after stopping the flow at  $5 \text{ s}^{-1}$ . When steady state conditions have been reached, it can clearly be seen that structure refinement has taken place during flow, as expected from the anisotropy curve. Two

conclusions might be drawn at this stage: firstly the techniques used to deduce morphological information of synthetic blends can, not surprisingly, be used to study the flow induced structures in aqueous biopolymer mixtures as well; secondly at the low shear rates as the one used in figure 2-the biopolymer mixture can be regarded as a conventional emulsion. This observation is fully discussed elsewhere (Van Puyvelde *et al.*, 2002b). This is an important result as such because it implies that a variety of structural models (see for instance the recent review of Tucker and Moldenaers (2002)) can be used to predict the flow-induced structures of aqueous biopolymer mixtures at low shear rates.

### 3.2. High shear rate behaviour

As demonstrated in section 3.1 aqueous biopolymer mixtures can be regarded as conventional emulsions when the applied shear rate is low. However during processing these materials are often subjected to high shear rates. Hence the question arises if other phenomena will interfere under high shear conditions.

Figure 3 shows the evolution of the SALS patterns and the transmitted light intensity for a start-up in shear flow to a shear rate of  $60 \text{ s}^{-1}$ . As in 3.1 the emulsion was pre-conditioned at a low shear rate to erase the shear history. Initially, the pattern in figure 3 is changed into a bright streak perpendicular towards the flow direction, indicative of very elongated structures in the flow direction. However,



**Fig. 3.** Evolution of the transmitted intensity after a start-up to a shear rate of  $60 \text{ s}^{-1}$ . Some of the light scattering pictures are shown as well. The transmitted intensity of the continuous dextran rich phase is shown as X.

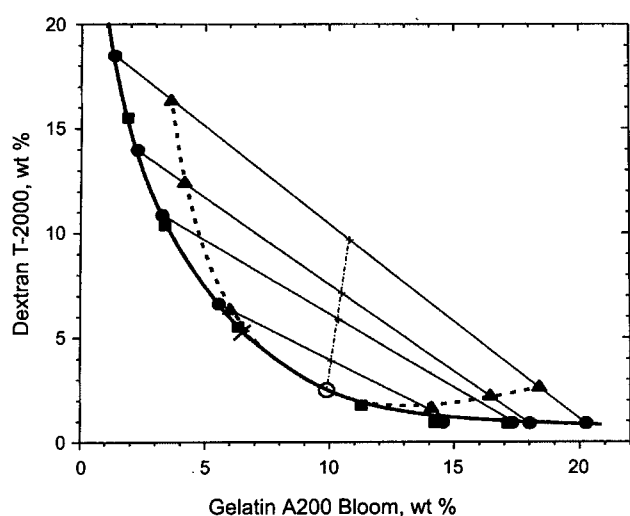


Fig. 4. Isothermal phase diagram at rest (thick line) and at a shear rate of  $60 \text{ s}^{-1}$  (dotted line). The thin lines correspond to the tie lines of the quiescent phase diagram.

during the application of the high shear rate, no evolution towards a steady state elliptic pattern is seen. Instead the streak gradually loses its intensity and finally the scattering pattern completely disappears. In addition the transmitted light intensity gradually evolves towards the value of the continuous dextran enriched phase. This observation indicates that the sample is homogenized on the length scales probed by light scattering. It needs to be stressed that if the system would still be in a two-phasic state, the expected droplet size at  $60 \text{ s}^{-1}$  would be well within the sensitivity range of the laser light used (wavelength  $633 \text{ nm}$ ). Hence, as no interaction is seen, the sample can be considered to be in an homogeneous state at  $60 \text{ s}^{-1}$ . This is an important result since it indicates that a flow field can have a drastic effect on the phase behaviour of the mixture. This is already known for mixtures of synthetic polymers (e.g. Gerard and Higgins (1999)) but has not yet been reported for biopolymer mixtures. Secondly, the rheo-optical methodology is capable of capturing the changing thermodynamics of the emulsion when moving towards higher shear rates. By repeating this procedure for a series of mixtures located along different tie-lines on the quiescent phase diagram, the phase diagram of the system under flow can be obtained.

The resulting binodal for the phase diagram of the ternary aqueous protein-polysaccharide system under a shear flow of  $60 \text{ s}^{-1}$  is shown in figure 4. The effect of shear on the binodal depends on the location of the system in the quiescent phase diagram. The higher the total concentration of biopolymers in the solution, the larger the concentration range in which a single phase system is observed. Close to the critical point the effect of the shear ( $\dot{\gamma}=60 \text{ s}^{-1}$ ) on the phase equilibrium is not significant.

## 4. Conclusions

In this paper, the effect of flow on the morphology in aqueous biopolymer mixtures containing gelatin and dextran in water has been investigated. A rheo-optical methodology based on small angle light scattering and polarimetry has been used. These methods were originally developed to study the flow-induced morphology in blends of synthetic polymers. Here it is shown that this rheo-optical methodology can also be used to investigate the flow-induced morphologies in aqueous biopolymeric mixtures.

As an example, the flow-induced structures during a start-up of flow have been investigated. It is demonstrated that at low shear rates, the biopolymeric emulsion can be regarded as a conventional emulsion. Hence, various structural models that are available in literature for the predictions of the morphology in these emulsions can also be used for the prediction of the structure in aqueous biopolymeric emulsions. However, at high shear rates, flow has a drastic effect on the phase equilibrium of the system. It is demonstrated that shear flow can homogenize the structure. The methodology is used to map out the effect of shear flow on the phase diagram of the water-gelatin-dextran system.

## Acknowledgements

PVP is indebted to the FWO-Vlaanderen for a postdoctoral fellowship. YA thanks the Research Council of the K.U.L. for a senior fellowship. This research has been partially funded by a GOA project (98/06) from the Research Fund K.U.Leuven.

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