CAPILLARY BREAKUP EXTENSIONAL RHEOLOGY OF MATRIX-SOLUTIONS USED IN MICRO-ENCAPSULATION

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In this work, Capillary Breakup Extensional Rheometer (CaBER) was used for studying the capability of two different polymeric solutions in creating dimensionally stable matrices for encapsulation purposes. Results were correlated to the final aspect of microcapsules obtained through a vibration-assisted encapsulator (Nisco), showing good perspectives for using CaBER for fast preliminary estimations of the final quality of the matrix-solutions.

Keywords: CaBER, microencapsulation, extensional rheology, vibrating nozzle

1. Introduction

Micro-encapsulation technology deals with the entrapment of small particles or droplets (core or internal phase) into a micrometric protecting shell of hard or soft soluble film (membrane or matrix), in order to reduce their dosing frequency or to prevent degradation under specific conditions.

The reasons for encapsulation are countless, from influencing embryonic or neural stem cell-fate in regenerative medicine to increasing solubility and stability of the molecules encapsulated in foods, pharmaceuticals and cosmetics, up to facilitating manipulation and liberation of drugs and pesticides in environmental science [1]–[5]. More precisely, the goal of this research has been to prepare matrix-capsule type microcapsules. The efficiency of the encapsulation process is sometimes triggered by the rheological quality of the matrix, which can rapidly be evaluated by the dimensional stability of the microcapsules[6].

In some cases, the elongational properties of the matrix could limit or disturb the even formation of droplets, leading to a high distribution in capsule diameter. Obtaining a suitable matrix composition is usually achieved by trial-

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and-error in equipment that requires large amount of sample and is energetically and time-costly. Research was mainly done in the field of shear rheology [7], [8]. On the other hand, capillary breakup extensional rheology was shown to be a very fast and effective technique in studying the uniaxial elongation of polymeric materials [9], [10]. Until present, at least from our knowledge, there is no information about probing matrix elasticity using an elongational device. The aim of this work was to study the rheological properties of two different polymeric matrices and to compare their capability in creating dimensionally stable microcapsules.

2. Materials and methods

2.1. Materials

Two matrices of 5% polymeric solution (A and B) were in-situ produced by adding the specific amount of polymer to preheated deionizer water (90 °C). Solutions were mechanically mixed until complete hydration and were let to cool down naturally at room temperature. All tests were performed at the same day.

2.2. Methods

Conventional shear rheological measurements were performed, at 25 °C, in a controlled stress rheometer (Haake, Thermo Haake GmbH, Karlsruhe, Germany), using a cone-plate geometry (CP 60mm/1°). Flow curves were determined in a shear rate range of 0.1-1000 s^{-1}. Additionally, small amplitude oscillatory shear tests in the linear regime were performed.

Elongational flow behaviour and full filament profile have been monitored using a high-speed camera (Photron Fastcam Mini UX100, Photron, USA) attached to a capillary break-up extensional rheometer (CaBER-1, Thermo Haake GmbH, Karlsruhe, Germany). The filament thinning of the samples was induced by separating the 6 mm diameter parallel plates of the extensional rheometer from an initial gap of 2.5 mm to a final gap of 11 mm, within 50 ms. Mid-filament diameter was measured with the standard laser micrometer of device and both filament evolution and breakup time were qualitatively and quantitatively compared. The device and its functionality are described elsewhere [11]–[14]. Shear measurements were done in duplicate, while extensional tests were performed in triplicate.

The two matrix solutions were also used to produce microcapsules using a laminar jet breakup via extrusion through a vibration agitated nozzle (NISCO, Nisco Engineering AG, Zurich, Switzerland). In order to manufacture the microcapsules, droplets of matrix solutions obtained through the nozzle were let to fall directly into a mildly stirred crosslinking solution. Device description and

performances are presented elsewhere [15], [16]. All tests were performed at 25 °C.

3. Results and discussion

Viscous flow and SAOS behaviour of the two analyzed samples (A and B) are shown in Fig. 1 and 2.

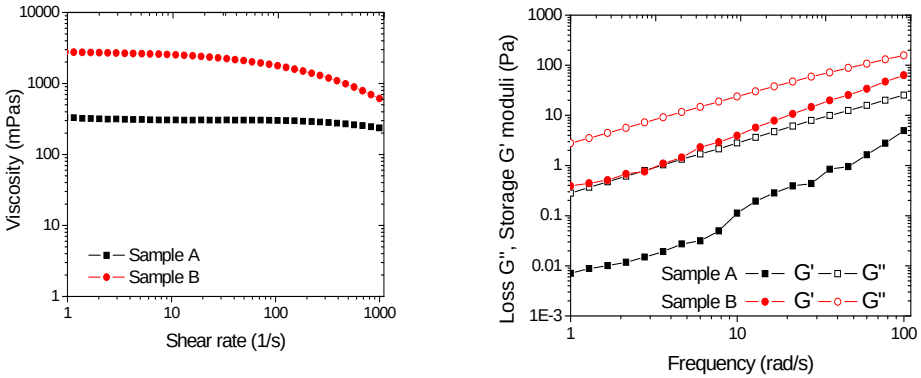

Fig. 1. Results for the two polymeric solutions (A) and (B): viscous flow curves, at 25 °C (a), and the evolution of the storage and loss moduli with frequency, at 25 °C (b)

Conventional shear rheological measurements performed on the two polymeric solutions reveals Newtonian behaviour, with a constant viscosity for sample A and a shear-thinning behaviour for sample B (Fig. 1a). Small amplitude oscillatory shear measurements highlighted a predominant viscous fluid behaviour for both matrix-solutions (G" >G'), although the elastic modulus values of sample B were higher in comparison to sample A (Fig. 1b).

On the other hand, uniaxial elongational behaviour of the two polymeric matrices is highlighted in Fig. 2.

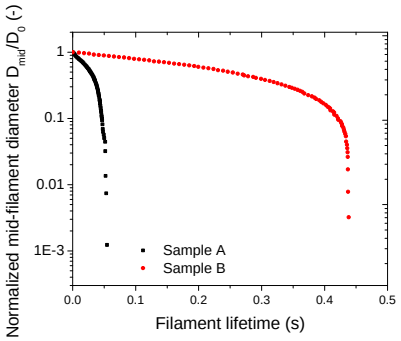

Fig. 2. Normalized mid-filament evolution of the two different polymeric solutions (A) and (B) tested in the CaBER device.

As can be observed, the filament diameter of sample A shows a linear decrease, specific to Newtonian fluids, while sample B shows an exponential filament decrease, widely described in the literature as a specific behaviour of viscoelastic fluids [12], [17]. Filament breakup time of sample B is one order of magnitude larger than the one of sample A. This increase in filament lifetime could be directly related to its viscoelasticity and inability to create even droplets throughout the encapsulation process. High-speed camera images of the two samples are presented in Fig. 3.

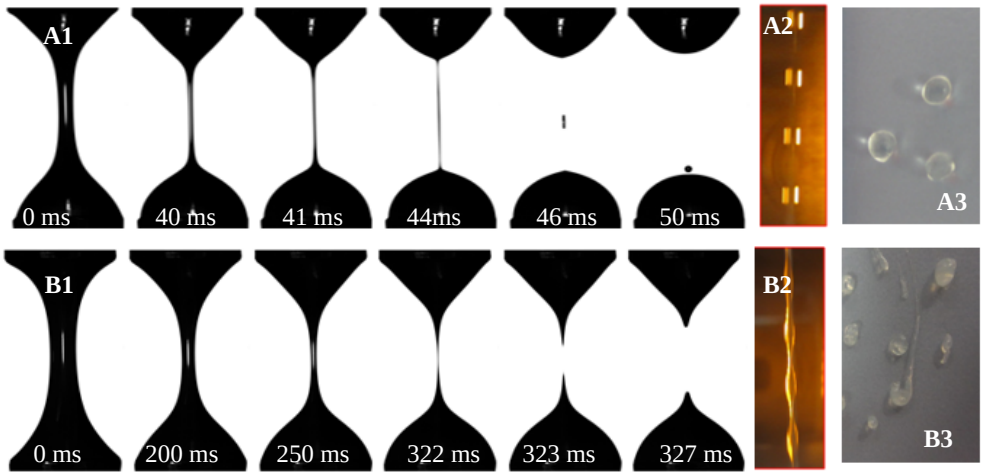

Fig. 3. Results for the two polymeric solutions (A) and (B): filament evolution in the CaBER device (1), laminar jet breakup obtained through a vibrating nozzle (2), and shape of the microcapsules obtained after gelling in the presence of a crosslinking solution (3)

Filament evolution and breakup is fast for sample A (46 ms), due to the lack of elasticity (Newtonian fluid) and provides its ability of creating satellite droplets (Fig.4. A1). Matrix solution B shows a more elastic behaviour, with a longer filament lifetime (323 ms) and slow rupture recovery (Fig. 4. B1). The long relaxation of sample B influences the even formation of droplets. In the case of matrix A (see Fig. 4: A2-A3), the laminar jet break-up created via extrusion through a vibration-agitated nozzle yields well defined droplets, which leads to spherical microcapsules. The viscoelastic properties of matrix B seem to restrict the droplet breakup in the vibration-assisted encapsulator and lead to highly deformed microcapsules (Fig. 4. B2-B3).

4. Conclusions

Differences in the rheological behaviour of the two analysed samples were seen in both, shear and elongational measurements. Viscoelastic characteristics could rapidly be estimated through a CaBER experiment (max 20 min), compared

to a shear measurement (minimum 60 min) or to the direct preparation and production of microcapsules (minimum 60 min). From the experimental results obtained, it is apparent that capillary break-up rheometry could be a very fast and useful tool to predict the quality of the encapsulation by measuring the elongational properties of the matrix-solutions. In addition, from an environmentally point of view, this study could suggest the ability of this technique in diminishing the amount of sample (which are sometimes expensive or could be toxic), energy consumption, cleaning efforts, and the time needed in a trial-and-error process as matrix-solutions can be pre-selected to those showing weakly elastic behaviour throughout CaBER experiments. Further investigations are needed in order to establish an optimal relation between elongational behaviour, breakup time and droplets dynamics in predicting the microencapsulation capabilities of different other matrix solutions currently used in industry.

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