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In-Line Monitoring of Size Distributions in Liquid-Liquid Dispersions and Suspension Polymerizations by Focused Beam Reflectance Measurements

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Summary: This work studies the use of Focused Beam Reflectance Measurements (FBRM) for monitoring of size distributions in liquid-liquid (styrene-water) dispersions and styrene suspension polymerizations performed in stirred tanks. The effects of the suspending agent concentration, stirring rate and presence of external light sources on the FBRM performance were evaluated during the in-line monitoring of average size chords and chord length distribution (CLD). It can be stated that FBRM is sensitive to variations of particle sizes and, therefore, that FBRM is suitable for evaluation of CLDs in real time in suspension polymerization systems.

Keywords: CLD; dispersion; FBRM; polymerization; suspension

Introduction

Several techniques have been developed since the second half of the 20th century to characterize the particle/droplets/bubbles size distributions in heterogeneous systems[1–3] in order to understand and control the evolution of these distributions.[4] These techniques are often based on laser spectroscopy, capillary spectroscopy,[5] laser diffraction,[6] near-infrared spectroscopy[7] and backscattered lighting.[8–10]

Reflection constitutes the basis of the *Focused Beam Reflectance Measurement* (*FBRM*) technique. Basically, FBRM uses a laser beam, which rotates with known constant velocity and is directed towards a set of lenses that is in contact with the sample. When the beam is intercepted by a droplet/particle, light is reflected and does not reach the detector. Assuming that the laser wavelength and the reflection time are known, it is possible to determine the chord-length of the particle (and the chord length distribution, CLD, if a sufficiently large number of particles are considered). More detailed description of FBRM is presented elsewhere.[11,12] As the CLD can be related to the actual particle size distribution (PSD) of heterogeneous systems, FBRM can be used for monitoring and control of particle sizes in many different applications, including crystallization,[8] characterization of biomass in cell cultures,[9] monitoring of gas hydrate formation,[10] among many others.

Some studies have developed techniques to formally convert the CLDs obtained by FBRM into PSDs,[13,14] but these techniques are usually complex and require the adjustment of various parameters.[12,15] Nevertheless, for most applications the formal transformation of CLDs into PSDs is not necessary, as CLDs can be used as surrogate variables for proper monitoring and control of PSDs. For example, some direct FBRM results, such as particles counts (frequency of particles that interrupt the laser beam), can be directly related to the mechanisms of breakage and coalescence of droplets. For this reason, transformation of CLDs into PSDs is not pursued here and CLDs and number average chord lengths are used in the present study for

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monitoring of liquid-liquid dispersions and suspension polymerization systems.

Previously published papers showed that the mean sizes and size distributions of droplets/particles suspended in liquid-liquid dispersions and suspension polymerization reactions are sensitive to many operation variables, including the concentration of suspending agent, particle holdup (fraction of the dispersed phase), impeller geometry, agitation speed, reactor size and presence and design of baffles.[16,17] The main objective of the present study is to evaluate how measured FBRM values respond to modification of some of these operation variables (surfactant concentration, agitation speed and the presence of external light sources) in order to use FBRM for monitoring and control of particle sizes in liquid-liquid (styrene-water) dispersions and styrene suspension polymerization reactions.

Experimental Part

Materials

Styrene (99.5%) stabilized with tert-butylcatechol was supplied by NITRIFLEX Resins S/A (Rio de Janeiro, Brazil). Benzoyl peroxide (BPO) was provided by VETEC Fine Chemicals (São Paulo, Brazil), containing 25% of humidity. Poly(vinyl alcohol) (PVA) was supplied by VETEC Fine Chemicals (São Paulo, Brazil), with degree of hydrolysis of 88% and weight-average molar mass (Mw) of 78000 g/mol. All chemicals were used as received. Water was distilled prior to use.

Experimental Setup

The preparation of styrene-water dispersions and styrene suspension polymerizations were conducted in a jacketed 1-liter glass reactor equipped with flat rectangular baffles and a reflux condenser. Reactions were conducted as described in the literature.[17] Unless stated otherwise, the volume fraction of the dispersed phase was kept equal to 0.25; the BPO concentration was kept equal to 1.95% (w/w) in respect to monomer in the polymerizations runs; PVA concentrations ranged from 1.0 to 5.5 g/l (above the CMC[19]) in the aqueous phase; and dispersion experiments and reactions were carried out at 80 °C. Table 1 summarizes the operation conditions used in all experiments performed in the present work.

The Lasentec D600L FBRM instrument was used in all experiments. The focal point of the probe tip was positioned at 0.02 mm from the sapphire window, as recommended by the manufacturer[18] in order to minimize the effects caused by the unavoidable differences between the refractive indices of the sapphire window and of the dispersed phase. The probe tip was located in a region of high turbulence, just above the impeller, in order to maximize the number of particle hits in the FBRM lens.

Results and Discussion

Liquid-Liquid Dispersions

Techniques used for measuring sizes of droplets/particles based on use of laser beams or light may require the isolation of the system from external light sources. This may be necessary to guarantee that the measured light signal comes from a single light source. However, it is not clear whether the ambient light can affect FBRM measurements, as this has not been reported in previous works. It must be observed that isolation of the measuring system can constitute a major drawback for implementation in real production sites.

Figure 1a shows FBRM results for experiments performed with and without the presence of external light. Isolation from external light sources was attained by placing the experimental setup inside a black box and covering of the experimental setup with black plastic films. Differences between FBRM results obtained in presence and absence of external light can be regarded as negligible, so that it does not seem necessary to isolate the measuring system from external ambient light to make proper measurements. This encourages the development of the FBRM technique for real production sites.

As one can see in Figure 1a, at the beginning of the dispersion process (transition

Table 1.
Operation conditions used in the experiments performed in the present work.

Experiment	Type of Experiment	Suspending Agent Concentration (g/L)	Agitation Speed (rpm)	Absence of External Light Source
E1	Dispersion	5.5	800	No
E2	Dispersion	5.5	400	No
E3	Dispersion	5.5	200	No
E4	Dispersion	5.5	800	Yes
E5	Dispersion	5.5	400	Yes
E6	Dispersion	5.5	200	Yes
E7	Dispersion	5.5	700	No
E8	Dispersion	–	800	No
E9	Dispersion	–	400	No
E10	Polymerization	5.5	600	No
E11	Polymerization	1.0	600	No
E12	Polymerization	5.5	700	No
E13	Polymerization	1.0	700	No

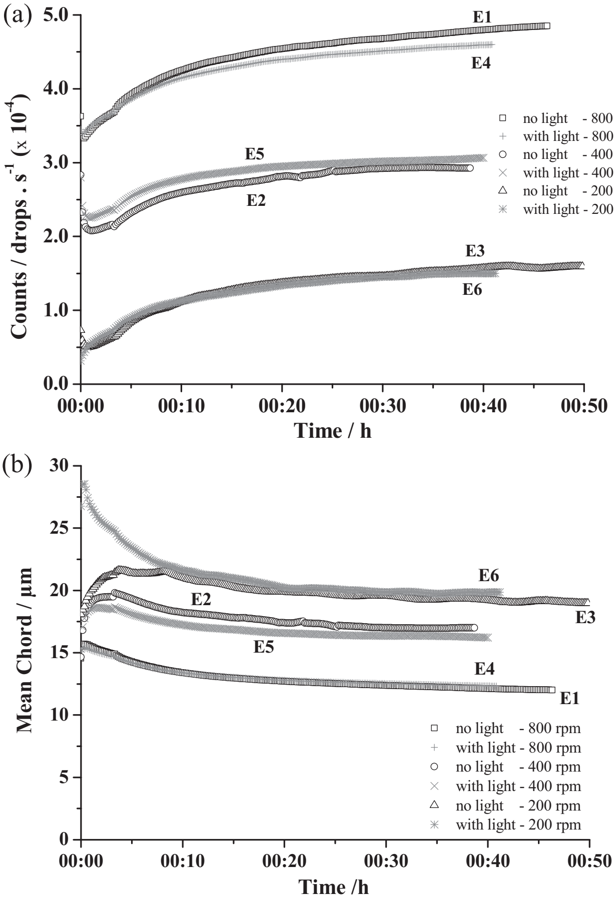

Figure 1.
Evolution of the particle count (a) and number average chord length (b) in dispersion experiments that were isolated and non-isolated from external light sources.

stage) the total number of droplets increases, due to breakage of the suspended styrene droplets, leading to formation of smaller particles (and smaller chords). As the process evolves and the number of particles increases, the coalescence rate increases and a dynamic equilibrium is reached, leading to stabilization of the number and size of the droplets in the system. The duration of these characteristic dispersion process stages depends on the operation conditions.

Figures 1a and 1b show the effect of the stirring speed on the dispersion process. As the stirring speed increases, higher rates of particle breakage are expected due to the increased shear rates. As a result, the number of droplets is also expected to increase, with the simultaneous reduction of the average chord length, as shown in Figures 1a and 1b. This shows that FBRM is able to capture changes in the system due to modification of the stirring speed.

Suspending agents affect the nature of the interface between the dispersed and continuous phases, leading to formation of a protective film on the interface and reducing the interfacial tension, which regulate the dynamics of breakage and coalescence in dispersed systems. Dispersion experiments were conducted in absence and presence of the suspending agent, as shown in Figure 2.

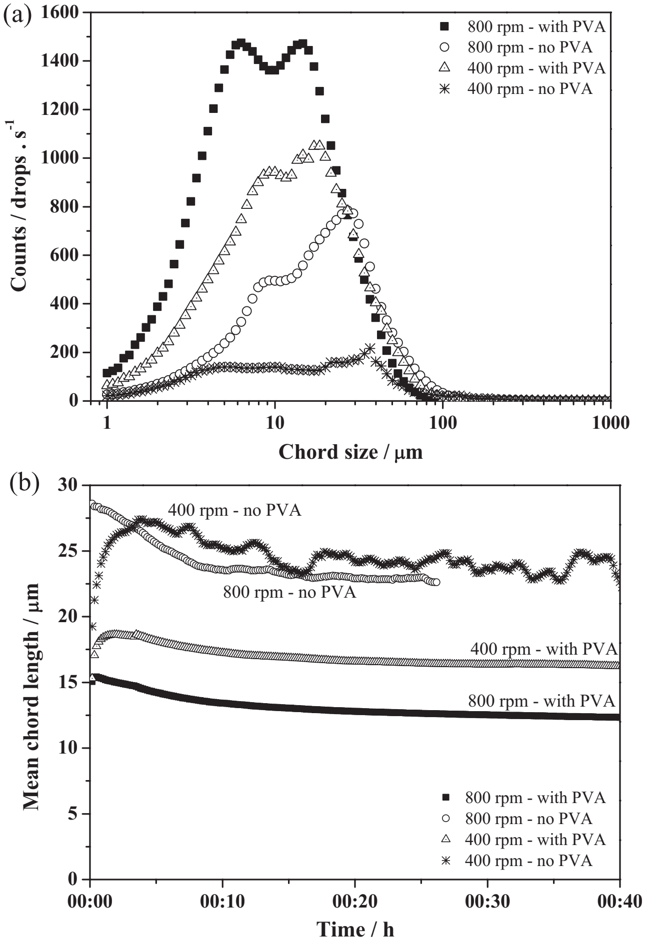

Figure 2.
CLDs (a) and number average chord length (b) in dispersion experiments performed with different suspending agent concentrations.

The chord length distribution obtained at the end of each experiment shows the excellent sensitivity of the FBRM technique to changes of the PVA concentration. As the PVA concentration increases, the CLD becomes broader and bimodal, with the pronounced increase of the mode positioned at smaller chord sizes, as one might already expect. This shows that FBRM is able to capture changes in the system due to modification of the suspending agent concentration and that addition of suspending agent reduces the rates of coalescence and promotes the increase of the droplet population.

Styrene Suspension Polymerization

Styrene suspension polymerizations were performed and monitored by FBRM. The effects of two operating variables were analyzed: the stirring speed and the suspending agent (PVA) concentration. As well discussed in the open literature[1,4,17] and also observed in the previous set of experiments, the reduction of the suspending agent concentration induces the formation of larger drops, since coalescence is favored at low PVA concentrations. As shown in Figure 3, FBRM can detect such effects when experiments E12 and E13 are compared to each other. It is possible to observe the higher rates of particle breakage in the first 40 minutes of reaction in both experiments, especially in experiment E12, performed with higher PVA concentrations.[20] As monomer conversion increases, the particle viscosity also increases, leading to reduction of breakage rates. This effect is detected by FBRM, as one can observe a significant decrease of the number of particles after 80 minutes of reaction. When the monomer conversion becomes sufficiently high (>60%), the particles become rigid and rates of particle breakage and coalescence fall dramatically, leading to stabilization of the number of particles and average chords-length after 2 hours of reaction. At the end of the polymerization, when the monomer conversion reaches 90%, one can observe the sudden change of FBRM values, due to polymer fouling on the probe lens.

It is expected that the increase of the stirring speed in suspension polymerizations will cause the same qualitative effects observed in liquid-liquid dispersion experiments, as shown in Figure 4. The higher stirring speed (700 rpm) causes a slight reduction of the number average chord length. After 60 minutes, one can observe a slightly lower coalescence rate in experiment E12 (performed at 700 rpm), when

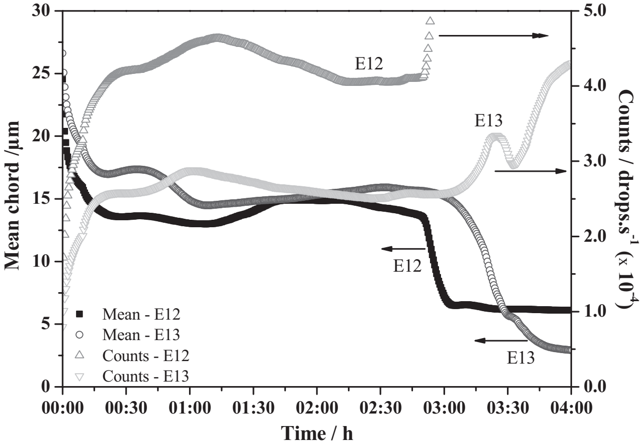

Figure 3.
Evolution of the average chord length and number of counts during suspension polymerization of styrene in reactions E12 and E13.

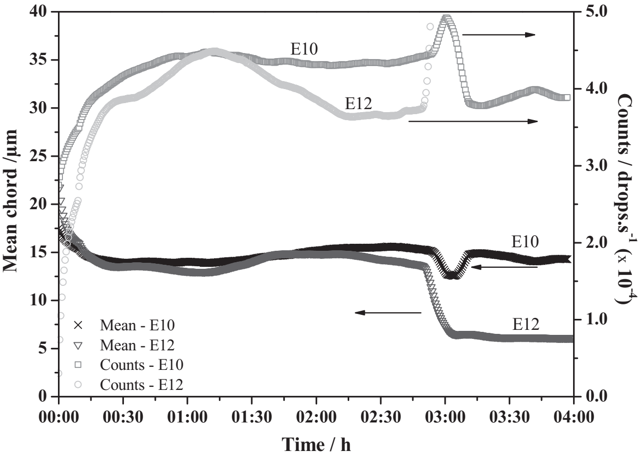

Figure 4.
Evolution of the average chord length and number of counts during suspension polymerization of styrene in reactions E10 and E12.

compared to experiment E10 (performed at 600 rpm). The total number of particle counts did not change significantly until 3 hours of reaction, when agglomeration of particles on the probe 'window' took place. The small variation of the average chord size and number of particles can be explained in terms of the small difference between the analyzed stirring speeds (600 and 700 rpm).

Conclusion

Focused beam reflectance measurements (FBRM) were used for monitoring of liquid-liquid (styrene-water) dispersions and styrene suspension polymerizations. The evolution of the chord length distributions of suspended droplets/particles and of the number of suspended particles (particle counts) was conducted in real time and it was concluded that the technique is reliable and sensitive to changes of the stirring speed and suspending agent concentrations, used at plant sites to control particle sizes in suspension polymerization reactions. As shown through dispersion experiments and suspension reaction runs, FBRM is capable of monitoring the initial particle breakage stage (when the number of particles increases and the average particle sizes decrease) and the attainment of the final breakage/coalescence equilibrium in dispersion experiments. Additionally, FBRM is also capable of monitoring the coalescence stage in suspension polymerizations, when coalescence rates control the evolution of particle sizes (when the number of particles decreases and the average particle sizes increase, due to the increasing droplet viscosity). A major drawback, however, is the frequent agglomeration of polymer onto the probe lens when monomer conversions are around 90%, which may require the implementation of special cleaning operations at plant site. Despite that, it is clear that FBRM can find very useful applications at polymerization sites, allowing for the in-line and *in situ* monitoring and control of particle sizes in suspension polymerizations.

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[1] R. A. F. Machado, J. C. Pinto, P. H. H. Araújo, A. Bolzan Braz, *J. Chem. Eng.* **2000**, 17, 395.
[2] A. W. Pacek, A. W. Nienow, I. P. T. Moore, *Chem. Eng. Sci.* **1994**, 49(20), 3485.

[3] R. P. Borwankar, S. I. Chung, D. T. Wasan, *J. Appl. Polym. Sci.* **1986**, *32*(7), 5749.

[4] A. F. Santos, E. L. Lima, J. C. Pinto, *Polímeros* **1999**, *9*, 39.

[5] J. H. Bae, L. L. Tavlarides, AIChE Journal, **1989**, **35** 7 1073.

[6] E. G. Chatzi, *Ind. Eng. Chem. Res.* **1991**, *30*(6), 1307.

[7] J. M. Faria, Jr., E. L. Lima, J. C. Pinto, F. Machado, *Polímeros* **2009**, *19*(2), 95.

[8] J. Heinrich, J. Ulrich, *Chem. Eng. Technol.* **2012**, *35*(6), 967.

[9] J. Whelan, E. Murphy, A. Pearson, P. Jeffers, P. Kieran, S. McDonnell, B. Glennon, *Bioproc. Biosyst. Eng.* **2012**, *35*(6), 963.

[10] H. L. Ba, A. Cameirão, J. M. Herri, M. Darbouret, J. L. Peytavi, P. Glénat, *Chem. Eng. Sci.* **2010**, *65*(3), 1185.

[11] R. G. Sparks, C. L. Dobbs, *Part. Part. Syst. Charact.* **1993**, *10*, 279.

[12] M. Kempkes, J. Eggers, M. Mazzotti, *Chem. Eng. Sci.* **2008**, *63*(19), 4656.

[13] A. Ruf, J. Worlitschek, M. Mazzotti, *Part. Part. Syst. Charact.* **2000**, *17*(4), 167.

[14] M. N. Pons, K. Milferstedt, E. Morgenroth, *Chem. Eng. Sci.* **2006**, *61*(12), 3962.

[15] N. Kail, W. Marquardt, H. Briesen, *Chem. Eng. Sci.* **2009**, *64*(5), 984.

[16] A. W. Pacek, C. C. Man, A. W. Nienow, *Chem. Eng. Sci.* **1998**, *53*(11), 2005.

[17] F. Machado, E. L. Lima, J. C. Pinto, *Polímeros* **2007**, *17*(2), 166.

[18] FBRM Control Interface User's Manual, Version 6.7.0, Mettler-Toledo AutoChem, EUA, 2005.

[19] R. Olayo, E. Garcia, B. G. Corichi, L. S. Vasquez, J. Alvarez, *J. Appl. Polym. Sci.* **1998**, *67*, 71.

[20] F. Jahanzad, S. Sajjadi, B. W. Brooks, *Chem. Eng. Sci.* **2005**, *60*, 5574.