

Droplets Size Distribution Analysis in Suspension Polymerization of Methyl Methacrylate

Raluca Isopescu*, Paula Postelnicescu, Ruxandra Palau, Anca-Madalina Dumitrescu,
Ana Maria Josceanu
University POLITEHNICA of Bucharest,
Centre for Technology Transfer in Process Industries (CTTPI)
1-5, Gh. Polizu Street, Bucharest, Romania
r_isopescu@chim.upb.ro

For many applications, the size range of the particles is very important. For example, heat transfer rates to polymer particles during extrusion and mass transfer rates of plasticizers both depend on particle size. From a phenomenological point of view, the size of drops in suspension polymerization is the result of a dynamic balance between the occurrence of breakage by shear of turbulence forces and coalescence by surface tension or adhesion forces. Monodisperse, narrow, broad and bimodal droplet size distribution (DSD) are generally reported in suspension polymerization. In the present paper an experimental study for methyl-methacrylate suspension polymerization was carried on. A microscopic method was used to evaluate the drop/particle sizes and distribution. The analysis of experimental DSD led to the assumption that an intense droplet breakage occurs in the first period of the onset of polymerization reaction generating a small droplet mean diameter. The bimodal distribution revealed in the first stage of the polymerization may stand for the overlapping of breakage and coalescence. The DSD shifts toward larger sizes with increasing time. In the last stage of the process the shape of DSD and mean diameter do not vary any more, meaning that the breakage-coalescence process is no more important. A population balance model capable to describe the breakage and coalescence mechanisms is applied. The model allows the prediction of DSD in suspension polymerization. The kinetic parameters were identified by correlation of experimental data. The computed DSD was in good agreement with experimental measurements.

1. Introduction

In aqueous suspension polymerization processes, a liquid monomer is dispersed into droplets by a combination of strong stirring and small amounts of suspending agents. Polymerization occurs in the drops, which become more viscous as the conversion proceeds and they are transformed into solid particles by the end of the reaction. For many applications, the particle size range is very important. For example, both heat transfer rates to polymer particles during extrusion and mass transfer rates of plasticizers depend on particle size (Meyer and Keurentjes, 2005).

While the theoretical and experimental methodologies available for the estimation and measurement of the molecular weight distribution are well developed, the same can not be stated regarding the particle size distribution (PSD). Prediction and control of the final PSD is associated with the evolution of the droplets size distribution (DSD) of the monomer dispersion in the continuous phase. From a phenomenological point of view, the size of drops in suspension polymerization is the result of a dynamic balance between the occurrence of breakage and coalescence. Droplet size is determined as a result of a dynamic equilibrium between breakage by shear of turbulence forces and coalescence by surface tension or adhesion forces (Polacco et al., 1999).

Monodisperse, narrow, broad and bimodal PSD are generally reported in suspension polymerization (Jahanzad et al., 2005). In the present paper a population balance model able to describe the breakage and coalescence mechanisms is applied. The model allows the prediction of DSD in suspension polymerization, commonly used for producing commercially important polymers like poly(methyl-methacrylate). Experimental studies for methyl-methacrylate polymerization were performed in order to validate the theoretical models and identify the adjustable parameters.

2. Experimental

1.1 2.1 Experimental procedure

The experiments for free-radical polymerization of methyl methacrylate (MMA) were carried out using a glass stirred 250 cm³ vessel.

The ratio methyl methacrylate: distilled water was 1:4 in all experiments. Methyl methacrylate was purified by vacuum distillation in order to remove the inhibitor. The suspending agent was polyvinyl alcohol (PVA) with a hydrolysis ratio of 88 %; the initiator used was benzoyl peroxide (PBO). The PVA and PBO concentrations were 0.15 wt % (based on water phase), and 3.0 wt % (based on monomer phase) respectively. Initially, water and stabilizers were filled into the laboratory reactor. The reactor was heated; methyl methacrylate and the initiator were added at 70 °C. The reaction temperature was maintained at 70 °C, at a stirring speed of 480 rpm. During the methyl methacrylate polymerization process, DSD was measured by an optic method. At given time intervals, a drop from the reactor content was transferred to the microscope. The images obtained on the 10x microscope were analyzed using an image analyzer software. The software provides values for the particle size expressed as Ferret diameter, shape factor, volume and area. At least 400 particles were counted for each moment of time investigated. The DSP was represented by histograms which revealed the time evolution.

1.2 2.2 Experimental results

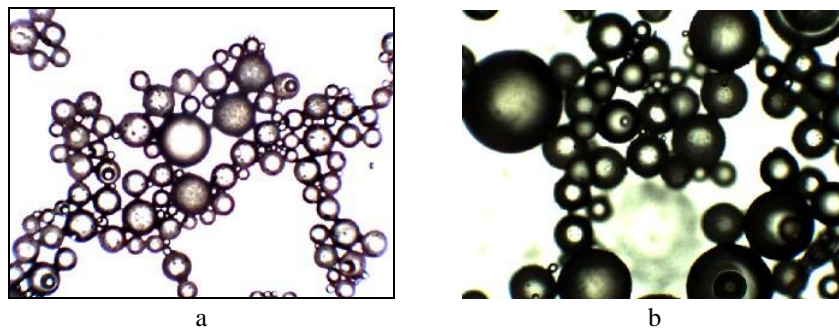
During the polymerization reaction, the variation of the properties in the dispersed phase influence the coalescence and the drops break up and, consequently, their diameter.

Characteristic images obtained by the microscope during the polymerization reaction, are presented in Figure 1. After 40 min, droplets characterized by a well defined contour can be observed. Between 100 and 170 min, the contribution of large droplets increased. The coagulation of these particles led to a final solid product with a large

mean particle size. As shown by Polacco et al. (1999), during the suspension polymerization, the viscosity of the dispersed phase increases and the interfacial properties also change, particularly in the gel-effect region. Then the DSD continues to change and the mean droplet size increases, as the polymer content of the drop increases.

The time variation of the mean droplets diameter is represented in Figure 2. It can be observed that after 110 min from the beginning of the polymerization process, the mean number based droplet diameter (D_{10}) has a very little variation around 78-80 μm . Because the glass effect appears, the droplets behave as rigid balls, so that breakage and coalescence decrease, and the mean droplets diameter becomes constant.

The time variation of DSD indicated that between 10-20 min, the dominant droplet size decreases. As Figure 3 shows, a narrow distribution centered on small droplets size is obtained after 20 min. This behavior can be explained by a very high droplets breakage rate. The DSD becomes wider with time increasing from 20 to 50 min, as droplets with larger sizes are formed by coalescence mechanism, which takes a leading role as compared to breakage.



1.3

a

b

Figure 1: Images of droplets distributions obtained by the microscope after: a) 40 min; b) 170 min

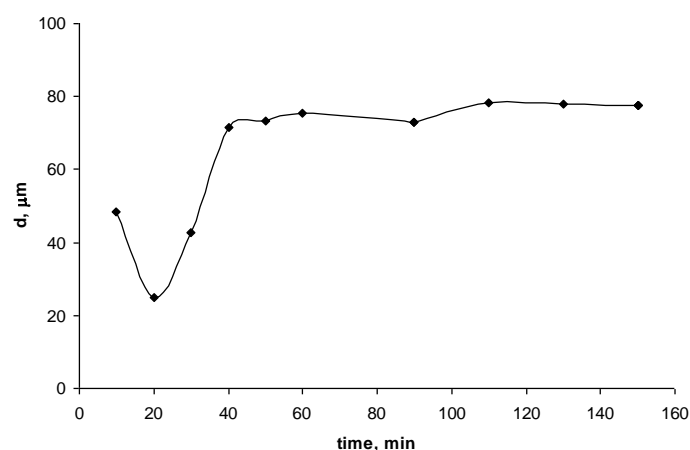


Figure 2: Time variation of droplets average diameter

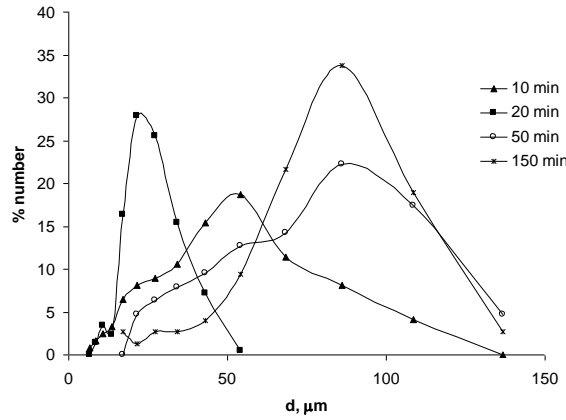


Figure 3: Droplets distribution along polymerization process

Population Balance Equation

The droplet/particle size distribution is controlled by drop breakage and drop coalescence rates. The relative importance of these two processes depend on hydrodynamic characteristics, continuous, and dispersed phase properties (viscosity, density), and interface tension. In general, the drop size distribution in a batch system can be described by the population balance equation (PBE):

$$\frac{\partial n(L,t)}{\partial t} = \int_L^{L_{\max}} b(L,y) \cdot g(y) \cdot n(y,t) dy + \int_{L_{\min}}^{L/2} \beta(L-y,y) \cdot n(L-y,t) \cdot n(y,t) dy - n(L,t) \cdot g(L) - n(L,t) \int_{L_{\min}}^{L_{\max}} \beta(L,y) \cdot n(y,t) dy \quad (1)$$

The left-hand side of equation (1) is the rate of change of number density function, $n(L,t)$. The first term in the right-hand side represents the generation of droplets in the size range $(L, L+dL)$ due to breakage, the second term reflects the generation of droplets by the coalescence of two droplets of size $L-y$ and y . The third and fourth terms represents the disappearance rate of drops of size L by breakage and coalescence respectively. In equation (1), $b(L,y)$ is the breakage probability function, $g(L)$ is the breakage rate of droplet of size L , and $\beta(L,y)$ represents the coalescence rate kernel for two drops of size L and y . The numerical resolution of PBE was realized using a discretization method based on successively larger interval sizes related by a constant geometric ratio between the drop volumes in class $i+1$ and i . A volume ratio of 2 was chosen, as defined for coalescence rate discretization by Hounslow et al. (1988), and for breakage rate by Hill and Ng (1995). For a volume ratio of 2, the ranges for drop diameters L_{i+1} and L_i should respect the ratio $2^{1/3}$. For each discretized interval the number of droplets in unit volume, N_i can be defined as:

$$N_i(t) = \int_{L_{i-1}}^{L_i} n(L,t) dL \quad (2)$$

The discretized PBE represents a system of nc ordinary differential equations, where nc is the number of discretized intervals:

$$\begin{aligned} \frac{dN_i}{dt} = & N_{i-1} \sum_{j=1}^{i-2} 2^{j-i+1} \beta_{i,j} \cdot N_j + \frac{1}{2} \beta_{i-1,i-1} \cdot N_{i-1}^2 - N_i \sum_{j=1}^{i-1} 2^{j-i} \beta_{i,j} \cdot N_j - N_i \sum_{j=i}^{nc} \beta_{i,j} \cdot N_j \\ & + \frac{3}{4} \sum_{j=i+1}^{nc} \left(2 \frac{L_i^3 - L_{i-1}^3}{L_j^3} \right) \cdot g_j \cdot N_j - \frac{1}{2} g_i N_i \end{aligned} \quad (3)$$

For the coalescence kernel, $\beta_{i,j}$, and breakage rate, g_i , size dependent forms were chosen:

$$\beta_{i,j} = \beta_0 \cdot (L_i + L_j) \cdot \left(\frac{1}{L_i} + \frac{1}{L_j} \right) \quad (4)$$

$$g_i = g_0 \cdot L_i^\alpha \quad (5)$$

The kinetic parameters β_0 , g_0 , and α must be adjusted from experimental data. As during the polymerization of MMA the physical properties of the dispersed phase vary in time due to the monomer conversion, these parameters values are not constant. In order to check the validity of the PBE model for our experimental MMA suspension polymerization study, the discretized PBE was integrated on short time intervals where the parameters values variation can be neglected. For each time interval the differential equations system was integrated using as initial conditions the experimental values N_i at the beginning of the time interval. The validation of coalescence-breakage mechanisms assumed and the estimation of corresponding kinetic parameters were accomplished by formulating the objective function:

$$1.4 \quad F = \sum_{i=1}^{nc} \left[\ln(N_{i,\text{exp}}) - \ln(N_{i,\text{comp}}) \right]^2 \quad (6)$$

The minimization was carried out using an adaptive-random search (Luus-Jaakola method) which is expected to give good results due to its capability to find the global optimum, even for multimodal objective functions. The mathematical model was solved for two time intervals: 10-20 minutes and 20-30 minutes.

The results are summarized in Table 1. For the final values of the optimized parameters the computed size distribution gives a good approximation of the experimental data (Figure 4). The values of kinetic parameters show that under the experimental conditions investigated, in the first polymerization stage, the coalescence rate is small and droplet breakage is dominant. Particle coagulation begins abruptly after 20 min from the beginning of the reaction without any transition period, as generally mentioned in literature (Jahanzad, 2005). This fact was also revealed by the time variation of mean droplet diameter (Figure 3) and may be caused by the low agitation speed and specific relative monomer and PVA concentration.

Table 1: Kinetic parameters

Time interval, min	$g_0, \text{s}^{-1} \mu\text{m}^{-\alpha}$	α	$\beta_0, \text{m}^3 \text{s}^{-1}$
10-20	$2.29 \cdot 10^{-7}$	2.86	$1.414 \cdot 10^{-21}$
20-30	$8.13 \cdot 10^{-4}$	1.69	$2.078 \cdot 10^{-14}$

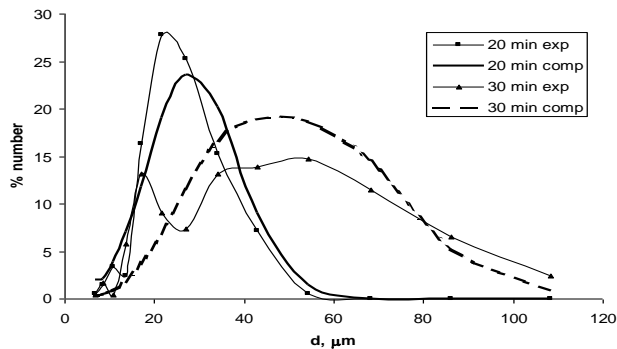


Figure 4: Experimental and computed droplet size distribution

4. Conclusions

The experimental and theoretical study of droplet size distribution for MMA suspension polymerization revealed that over the whole reaction time, breakage and coalescence are competing mechanisms. The computed DSD values are in good agreement with experimental data, proving that the PBE is an efficient instrument for modeling the DSD in suspension polymerization.

References

- Georgiadou, S. and Brooks, B. W., 2006, Suspension polymerization of methyl methacrylate using ammonium polymetacrylate as suspending agent, *Chem. Eng. Sci.* 61, 6892-6901.
- Hill, P. J. and Ng Ka, M., New discretization procedure for the breakage equation, 1995, *AIChE J.*, 41, 1204-1216.
- Hounslow, M. J., Ryall, R. L. and Marshall, V. R., 1988, Discretized population balance for nucleation, growth and aggregation, *AIChE J.* 34, 1821-1832.
- Jahanzad, F., Sajjadi, S. and Brooks, B. W., 2005, Characteristic intervals in suspension polymerization reactors: An experimental and modelling study, *Chem. Eng. Sci.* 60, 5574-5589.
- Meyer, T. and Keurentjes, J., 2005, *Handbook of Polymer Reaction Engineering*, WILEY-VCH Verlag, Weinheim, Germany.
- Polacco, G., Palla, M. and Semino, D., 1999, Measurements of particle-size distribution during suspension polymerization, *Polym. Int.* 48, 392-397.