

Influence of Agitation on the Creation of Coagulum during the Emulsion Polymerization of the System Styrene–Butylacrylate–Acrylic Acid

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Synopsis

This paper gives the results of the estimated coagulum content in the final sample of a dispersion based on styrene–butylacrylate–acrylic acid, prepared by semicontinuous emulsion polymerization. The results were gained from experiments on 25 L and 5 m³ reactors. The dependence of the amount of coagulum on the agitation intensity was studied. It was found that it is necessary to divide the results into two regions: (a) for specific power input smaller than 80 W/m³; (b) for specific power input greater than 80 W/m³. It was found that polymerization scaling up from the point of constant coagulum content in the system studied is possible under the conditions of constant specific power input. The specific power input varied in the range from 5 to 3000 W/m². For the first region was gained the empiric correlation $Y = 2.16(\phi_V)^{-1}$ and for the second region the equation $Y = 3.5 \times 10^{-5}(\phi_V)^{1.5}$, where Y is the amount of coagulum (wt %). For the existence of two regions we propose the following hypothesis according to which increasing mixing intensity improves the temperature and concentration nonuniformity which results in the decrease of coagulum content. From the certain value of specific power input, which is specific for each system, the amount of coagulum starts to increase due to increasing shear stress.

INTRODUCTION

During studies of the emulsion polymerization course, we often encounter the creation of dispersion systems, which consist not only of individual particles of polymerized monomer but also of doublets or triplets and sometimes of larger amounts of basic polymer particles, coagulated into larger aggregates than the triplets mentioned. These aggregates sometimes attain considerable dimensions, compared with the basic particles in the dispersion, their diameter being, for most dispersions, based on monomers derived from acrylic or methacrylic acid, up to 1 μm . The diameter increase of these aggregated particles corresponds to the 100–1000 multiple of the basic dispersion particle diameter. These aggregates (from here on we shall use the summary designation coagulum) to a large extent decrease the quality of the manufactured dispersion. One of the goals in the research and production of

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individual types of dispersions is to decrease the coagulum content in the final product to a minimum.

The creation of coagulum during emulsion polymerization brings up a complex problem. Besides the composition of the monomer mixture which is being polymerized, the creation of coagulum is governed by other factors, e.g., the reaction temperature, the concentration and chemical structure of surfactants, the concentration of monomer mixture in the emulsion being polymerized, the conduction of polymerization (batch, semicontinual, continuous), the possibilities of heat removal from the system, and the means and intensity of agitation during polymerization. Due to the influence of a large surface interphase between the polymerizing monomer phase and the water phase, the dispersion of the originating polymer from the thermodynamic point of view, had low stability and exhibits a tendency to aggregation or coagulation of individual polymer particles. This process is supported by the mechanical influence of the agitator. Our attention in this article is focused particularly on this problem, although we are aware that systems stabilized by surfactive substances, which create micelles with monomers (as in our case), the creation of coagulum due to the influence of mechanical stress is less pronounced than with systems stabilized with the aid of colloids.

PROBLEM ANALYSIS

Some aspects of the influence of agitation on emulsion polymerization have been discussed in our article¹ where we gave some information on the problem of coagulum formation. The scope of this problem is very broad, and it has been discussed recently by various authors.²⁻⁴ Their papers deal with the behavior of dispersion systems under both static and flowing conditions and introduce some basic relations describing the creation of aggregates, as, e.g., the relation of Smoluchovsky or Kolmogorov and the relations arising from the description of shear stress during the movement of liquid. These relations are the basis of the theory describing the creation of coagulum during the preparation of polymer dispersions by way of emulsion polymerization. The problem of coagulum creation due to forces, existing in the reacting system with respect to agitation is mentioned in some basic publications from the field of emulsion polymerization, e.g., monography by Šňupárek and Formánek⁵ or a chapter by Vannderhoff in the book of Basset and Hamielec.⁶ Probably the first information from this field is in Hölscher's⁷ publication. An interesting paper was published by Parts and Elbing⁸ on the coagulation of particles during the polymerization of acrylonitrile under the influence of large centrifugal forces. Although different authors discuss the possibilities of coagulum formation during emulsion polymerization due to tangential or shear stress, which originates in a liquid due to the agitation, literature has very little information on quantitative experimental data in this field. A comprehensive paper by Lowry et al.⁹ treats experimental data from Lehigh gained during the emulsion polymerization of styrene and from Rubens gained during the emulsion polymerization of vinylchloride and ethylacrylate, both batchwise. Lowry uses the energetic balance for colloid systems, that is, from energy interaction of two particles of this system, which is qualified with the

aid of the so called DLVO theory (Derjagin–Landau–Verway–Overbeck). A similar approach is described in the comprehensive work of Kriechbaumer.¹⁰ Herold's¹¹ paper deals with the coagulum creation due to the shear stress of the agitator. A presented graph shows the dependence of coagulated particle size (max. size $5 \times 10^3 \mu\text{m}$) on the size of shear stress up to the value of 10 N/m^2 .

Lowry's work is the one most closely related to our problem, and we can summarize his findings as follows. Particles can coagulate if they collide with an energy of collision sufficiently greater than the potential energy barrier. This barrier is the consequence of attractive forces (mainly Vandervaal's forces) and repulsive forces, which are above all the function of the surface potential and mutual distance. Particles gain kinetic energy either by Brown's movement or in mechanically agitated systems due to the flow which is developed by the rotating agitators. Great importance is given by the author to the shear stress. He comes to the relation describing the coagulation rate for spherical particles:

$$dN/dt = (4\tau\phi/\pi W)N, \quad (1)$$

where

$$N = N_0(1 - C) \quad (2)$$

We can see that the estimation of shear stress τ is of essential importance. However, in an agitated reactor, where the velocity gradient is created by the agitator, the shear stress in the liquid is a function of its position in the reactor. For this reason the author recommends as a characteristic parameter the mean value of shear stress. For Newtonian liquids and small values of Reynolds number, the mean value of shear stress is directly proportional to the speed of rotation:

$$\tau = k \cdot n \quad (3)$$

where the constant k is valid always only for a certain impeller type and system geometry.

For high values of Reynolds criterion Lowry uses Kolmogorov's theory of isotropic turbulence for the local dissipation rate of mechanical energy \mathcal{E}_i

$$\mathcal{E}_i = (15/2)\nu \cdot (\tau_i)^2 \quad (4)$$

From this relation he determines the mean shear stress in agitated reactors, which is given by the equation

$$\tau = (2\mathcal{E}/15\nu)^{1/2} \quad (5)$$

where

$$\mathcal{E} = P/V_R. \quad (6)$$

Since $\mathcal{E} \sim n^3$, then $\tau \sim n^{3/2}$, which means that the mean value of shear stress increases in a system of a given size, geometry, the same viscosity and density with the impeller speed to the power $3/2$.

EXPERIMENTAL

The goal of our experiments was to find the explanation for two questions:

(a) What is the real dependence of the amount of created coagulum on the rotational speed of the agitator at Reynolds numbers as they come into question for dispersion production?

(b) Is it possible to scale up this operation using the small geometrical models of production plant reactors?

To check up these questions we undertook the semicontinuous emulsion polymerization of the monomer system styrene-butylacrylate-acrylic acid.

All experiments were carried out in a 25 L reactor made from stainless steel of the same quality as the 5 m³ reactor which is installed on the production line in CHZ, Sokolov. The experimental apparatus was the geometrically similar model of the production equipment including the agitator, which is schematically pictured in Figure 1. During the experiments on the model apparatus we kept the chemical thermal and technological similarity to the process on the production apparatus.

All experiments were carried out with the following composition of the charge (for 25 L reactor).

total composition: water phase	48 wt %
monomer phase	52 wt %

The emulsion of monomers for feeding the reactor was prepared separately

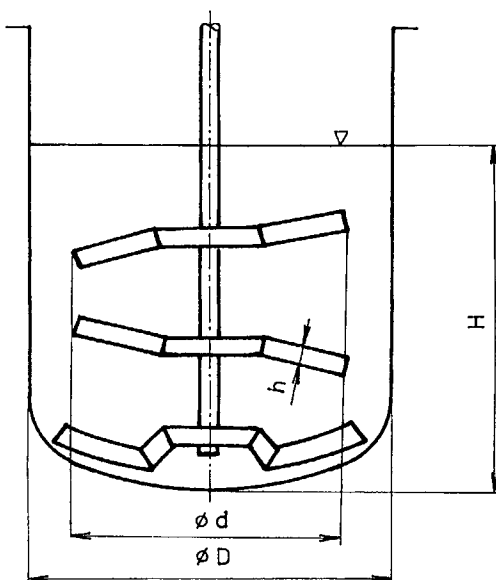


Fig. 1. The scheme of the reactor. Impeller "HAGEMANN," $d = 0.76D$, $h = 0.06d$, $H = D$.

with the following ratio of components:

styrene	4.78 kg
butylacrylate	4.31 kg
acrylicacid	0.28 kg
water	4.80 kg
Disponil SUS 87 (30%)	0.75 kg

Initiator solution:

$(\text{NH}_4)_2\text{S}_2\text{O}_8$	0.056 kg
water	0.94 kg
$\text{Na}_2\text{S}_2\text{O}_5$	0.028 kg
water	0.94 kg

The following compounds were weighed before feeding the reactor

water	1.50 kg
Disponil SUS 87 (30%)	0.18 kg

The emulsion and initiator dosing into the reactor was carried out at the temperature $80 \pm 1^\circ\text{C}$ for 3 h. At the end of the dosing the temperature in the reactor was increased to $85\text{--}90^\circ\text{C}$ and kept constant for 1 h.

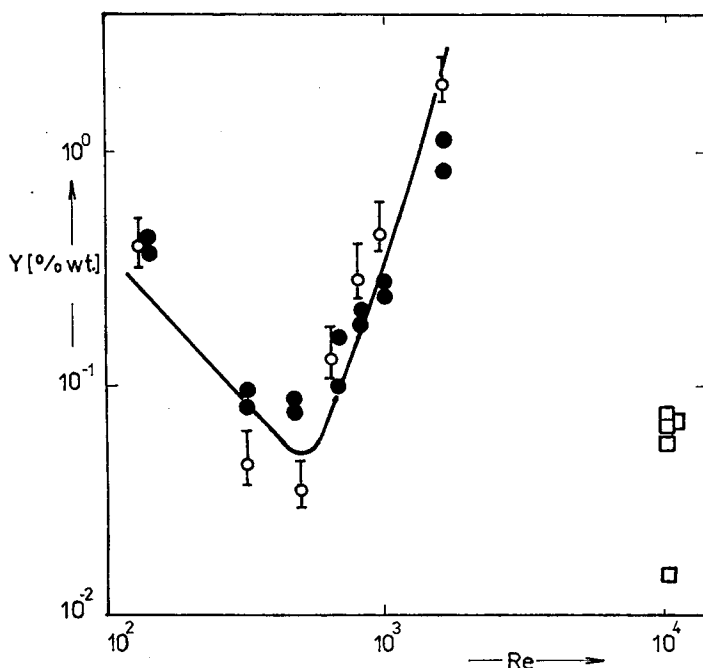


Fig. 2. Dependence of the coagulum content vs. Reynolds number: (○) 25 L reactor, basic technological regulation; (●) technological regulation with modified charging (see text); (□) 5 m³ reactor, basic technological regulation.

After the reaction we estimated the weight of the created coagulum in a sample of the dispersion in accordance with the published method. The sieve used for the filtration of the dispersion had a mesh size of 0.04 mm. Since the whole experiment was arranged into a statistical scheme, we included besides the main variable factor, i.e., rotational speed of agitator, two other factors. One was the charging of the reactor on five levels which were 0.8-, 0.9-, 1-, 1.1-, and 1.2-multiples of the basic charging and the second variable factor was the charging time again on five levels, which were 0.67-, 0.84-, 1-, 1.17-, and 1.33-multiples of the basic charging time.

From the statistical evaluation of the experimental scheme resulted that the creation of coagulum is on the significance level 95%, influenced only by another main factor, i.e., impeller speed. It can be stated that we did not find any significant interaction between the measured factors.

The results interpreted as the dependence of the coagulum content on the Reynolds criterion are plotted in Figure 2. Experimental results marked \circ correspond to those measurements which were carried out at the basic filling of the reactor which as a model corresponds to the production plant charging of the 5 m³ reactor. The intervals distinguished around these points mark the confidence limit of the measured values at 95% probability, based on the estimation of experimental error. Points marked \bullet were gained at other regimes than the basic one. Results marked \square were gained from production line readings during the manufacture of the dispersion on the 5 m³ reactor.

In order to compare agitation regimes of both reactors from the energetic point of view, the power input characteristic of the used agitator was measured. Results are given in Figure 3. With the use of this diagram we could then convert the obtained results to obtain the dependence of the coagulum content vs. the specific power input, i.e., on the value P/V_R , which corresponds to the relation (5), which was derived for the turbulent region of agitation. The results are given in Figure 4.

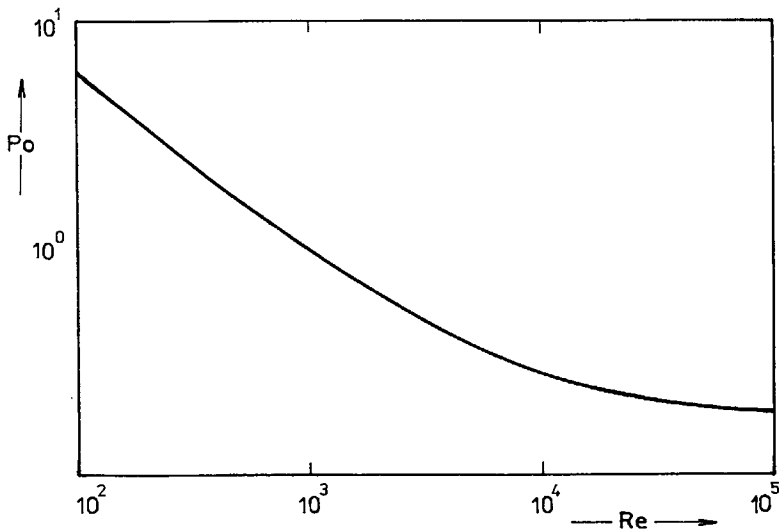


Fig. 3. Impeller power characteristic.

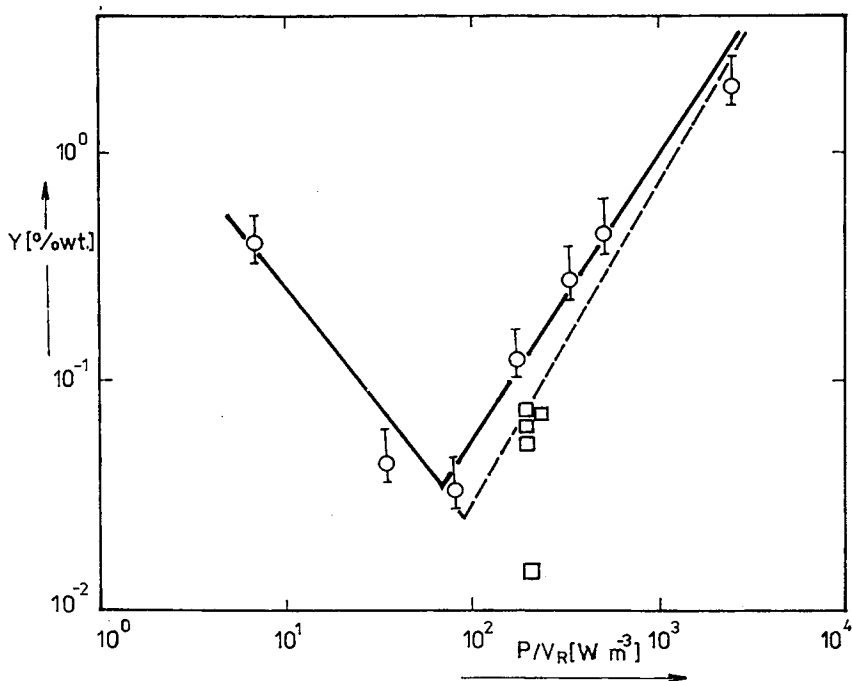


Fig. 4. Dependence of the coagulum content vs. specific impeller power input: (○) 25 L reactor, (□) 5 m³ reactor, both basic technological regulation.

DISCUSSION AND CONCLUSION

The dependence shown in Figure 2 is evaluated for the preparation of the tested dispersion in the 25 L reactor. From the results of the measurements (Fig. 2), we can conclude that the dependence of the coagulum content in the dispersion on impeller speed passes through a minimum. The plotted dependence shows practically the dependence on impeller speed n ; because it corresponds to one dimension of the apparatus, density and viscosity were the same during all experiments. The curve corresponding to the calculated regression function is represented in Figure 2 by the full line. From the values shown in Figure 2 we can further see that a change in the polymerization regime caused by a change in the charging of the reactor and in the feeding rate of the emulsion, which deviates from the basic recipe, does not assert itself in the coagulum content. Another observation is that the results gained during the manufacture on the 5 m³ reactor, plotted in Figure 2, lie far away from the measurements gained on the 25 L reactor. To generalize the results of scale-up, we used a method having its rationalization in Kolmogorov theory of turbulence and Lowry's work. We expressed the values of coagulum content in their dependence on the specific input P/V_R in accordance with the empiric power equation:

$$Y = A \cdot \mathcal{E}_v^\alpha = A(P/V_R)^\alpha \quad (7)$$

The results arranged in this manner are plotted in logarithmic coordinates

(Fig. 4). From these it is apparent that for practically the same value $P/V_R = 200 \text{ W/m}^3$ which we are working with on the production line reactor, we receive the same results in the final coagulum content in the dispersion prepared on the model 25 L reactor. It can be therefore stated that the course of coagulum content can be modeled on a geometrically similar apparatus under the conditions of constant specific power input. There is a great difference between our results and the results of Lowry. Our dependence goes through a minimum at the value $P/V_R = 80 \text{ W/m}^3$, while Lowry does not mention such a course. Our explanation for this minimum is that, at lower specific inputs than is stated above, the charged raw materials are badly homogenized in the reactor volume and the created coagulum is the result of a nonuniform emulsion polymerization. An increase of impeller speed is accompanied by a decrease of coagulum content because of better temperature and concentration uniformity. In the second region characterized by the value of specific power input greater than is the value $P/V_R = 80 \text{ W/m}^3$, our findings are practically in accordance with Lowry's conclusions. With increasing specific input the shear stress also increases in the agitated reaction liquid, and the content of created coagulum increases, consequently.

We made an attempt to express the gained results by means of an empiric equation. For the region $P/V_R < 80$, we received the relation (8)

$$Y = 2.16(P/V_R)^{-1} \quad (8)$$

For the region $P/V_R > 80$, we evaluated the results from the 25 L reactor and obtained the relation

$$Y = 1.71 \times 10^{-4}(P/V_R)^{1.25} \quad (9)$$

and, respecting also the results from the 5 m³ reactor, we have the overall correlation

$$Y = 3.5 \times 10^{-5}(P/V_R)^{1.5} \quad (10)$$

Predictions by eqs. (8) and (9) are shown in full lines in Figure 4, while prediction by eq. (10) by a dashed line.

We can therefore judge that it is possible to scale up under the conditions of constant specific power input, the polymerization studied on the 25 L reactor, with good reliability and from such measurements make conclusions on the coagulum content in the larger, production scale reactors. It is necessary to emphasize that our results are only related to the tested system of semi-continuous emulsion polymerization of a three component mixture styrene-butylacrylate-acrylic acid in the region of specific power inputs $P/V_R = 5\text{--}3000 \text{ W/m}^3$.

Appendix: Nomenclature

- C* ratio of coagulated particles to the whole sum of particles
- d* impeller diameter (m)
- D* vessel diameter (m)

H	liquid depth (m)
k	constant in eq. (3) ($\text{W m}^{-2} \text{s}$)
n	impeller speed (s^{-1})
N	number of particles in a volume unit of the system in time t (m^{-3})
N_0	number of particles in volume unit in time $t = 0$ (m^{-3})
P	impeller input (W)
Po	power number, $\text{Po} = P/\rho n^3 d^5$
Re	Reynolds number, $\text{Re} = nd^2/\nu$
t	time (s)
V_R	liquid volume in reactor (m^3)
W	stability factor of system
Y	weight ratio of coagulum (wt %) based on monomers
\mathcal{E}	specific power input of agitator related to the weight unit of the charge ($\text{W kg}^{-1}, \text{m}^2 \text{s}^{-3}$)
\mathcal{E}_i	local value of dissipation speed of energy ($\text{m}^2 \text{s}^{-3}$)
\mathcal{E}_V	specific power input per volume unit of the charge $\mathcal{E}_V = P/V_R$ (W m^{-3})
ν	kinematic viscosity (m s^{-1})
ρ	liquid density (kg m^3)
ϕ	volume fraction of particles in the system
τ	shear stress (s^{-1})
τ_i	local value of shear stress (s^{-1})
$\bar{\tau}$	mean value of shear stress (s^{-1})

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