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The viscosity influence study on poly(styrene-*Co*-divinylbenzene) beads diameter in suspension polymerization

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SUMMARY

Two theoretical models for the division of droplets in a turbulent flow were experimentally checked for high viscous liquids. The relationships found between the polymer beads maximum diameters and the aqueous phase viscosity cannot be described by an inertial breakup but are in good agreement with a viscous shear breakup.

INTRODUCTION

Suspension polymerization is an important industrial process which mainly consists in a dispersion of monomers as droplets. This dispersion is obtained and kept up by a mechanical stirring. The monomers containing the radicalar initiator polymerize into beads. The mean diameter of the beads is determinant for the transformation of polymers into manufactured products.

It is usually assumed (1) that the polymer beads diameters are those of the droplets during the reticulation. Therefore, the prediction of droplets diameters allows to determine the beads diameters.

Many papers have already been published on this subject, they are mostly reviewed by two main papers in 1976 (2) and in 1991 (3). Several relationships were established to precise the correlations between the mean diameter d and the interfacial tension, the kinematic viscosities of the continuous and discontinuous phases, the densities of the continuous and discontinuous phases, the volumic fraction of the discontinuous phase and the Weber's number (4) of the tank. The only relationships which are commonly proposed by different authors (5-9) are in the following general form :

$$d = a(1 + b\Phi)W_{e,t}^{-0.6} \qquad \text{(I)}$$

where a and b depend on the geometry of the reactor and the stirrer, Φ is the volumic fraction of the discontinuous phase and $W_{e,t}$ the Weber's number (dimensionless) of the

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tank defined by the relation:

$$W_{e,t} = (N^2 D^3 \rho_c) / \sigma \qquad \text{(II)}$$

where N is the stirring speed, D the stirrer length, pc the density of the continuous phase and σ the interfacial tension.
Thus, for a given reactor, the droplets mean diameter only depends on the interfacial tension at constant stirring speed :

$$d \propto \sigma^{0,6} \qquad \text{(III)}$$

This relation can be explained by a locally homogeneous and isotropic turbulence when particular scale conditions are verified (v. i. theoretical part). At the contrary, when the droplets mean diameter is depending on the viscosity, the experimental correlations published differ from one author to other (2-3). Nevertheless, the local isotropic theory of turbulence also predicts a relation when the viscosity is a determining factor for the droplets mean diameters. Relation which is :

$$d \propto [(\nu\sigma) / \rho c)^{1/3} \qquad \text{(IV)}$$

where v is the kinematic viscosity of continuous phase.
But at our knowledge, this relation was never experimentally tested. In an other way, the influence of the viscosity may also be discribed in terms of the theory of viscous shear breakup (*v. i.*).

In order to determine which of these two theories is suitable to describe the role played by the viscosity, we have carried out aqueous suspension polymerizations in a large interval of viscosities, including high viscosities.

THEORETICAL PART

1) Inertial breakup theory

In a mechanically dispersed system the flow is practically always turbulent. For a given point in the space the flow velocity, which is a random function of time, depends on three space coordinates. Thus, the determination of the mean velocities is impossible and therefore, the kinetic energy of a liquid globule at a given point of the turbulent flow is unknown. The eddies in a turbulent flow have very different sizes. The largest eddies of size close to that of the stirrer blade, D, transfer their energy to smaller eddies. These eddies again transfer their energy to smaller eddies and so on. Then, the smallest eddies transfer their energy in heat. Kolmogorov (10) stated the hypothesis that for the eddies which sizes are very small compared to D, the turbulent flow is locally isotropic and homogeneous (11).
Thus, for a liquid globule of diameter d, such as :

$$D >> d \qquad \text{(V)}$$

the laws governing the flow at this scale d must be those of an isotropic and homogeneous flow. As a consequence, the mean square velocity of such a liquid globule can be describe by a relationship independent of the macroscopic parameters of the turbulent flow. According to the values of d, D and η (Kolmogorov's scale) two different relationships are derived for the mean square velocity, $v^2(d)$,(11-12) :

for $D >> d >> \eta$ (VI)

$v^2(d) \propto (\varepsilon d)^{2/3}$ (VII)

for $D >> \eta >> d$ (VIII)

$v^2(d) \propto (\varepsilon / v)\, d^2$ (IX)

where $\eta = v^{3/4} \varepsilon^{-1/4}$ (X)

with ε power by mass unit.

The liquid globule breaks down for a limiting value ($W_{e,crit}$) of Weber's number:

$$W_{e,crit} = (v^2 max^d max,th\ \rho c) / \sigma \qquad \text{(XI)}$$

where v^2max is the maximum mean square velocity, and $d_{max,th}$ the corresponding largest diameter which is theoretically stable. By replacing the expression of v^2 (VII) in the relation (XI), we have:

$$d_{max,th} \propto (\sigma / \rho_c)^{3/5}\, \varepsilon^{-6/15} \qquad \text{(XII)}$$

Thus, $d_{max,th}$ is independent of the viscosity when relation (VI) is satisfied. With the expression v^2 (IX), the relation (XI) becomes:

$$d_{max,th} \propto [(\nu\sigma) / (\varepsilon\rho_c)]^{1/3} \qquad \text{(XIII)}$$

In this case, $d_{max,th}$ depends on both the viscosity and the interfacial tension, when relation (VIII) is satisfied.

2) Viscous shear breakup theory

Taylor (13) experimentally and theoretically studied the liquid drop breakage in a viscous flow. The drop deformation is defined by (L - B)/(L + B) where L is the lenght and B the width of the drop. When this ratio reaches a critical value, the drop breaks up in two parts. This critical ratio depends on a function $\phi(P)$, with P the ratio of the dynamic viscosity of the dispersed phase on the dynamical viscosity of the continuous phase (14). The relation between the viscosity and the maximum diameter is then:

$$[d_{max} / 2\, \sigma\xi] \propto (\mu\rho_c)^{-1/2} \qquad \text{(XIV)}$$

with $\xi = [(\phi(P)(P+1) / (1.19P+1)]$ (XV)

where μ is the continuous phase dynamic viscosity.

EXPERIMENTAL PART

1) Materials

Styrene purchased from Aldrich, was distilled under reduced pressure and conserved at 5°C. Divinyl benzene (mixture of meta, para isomer 55% and ethylvinylbenzene), benzoyl peroxide, acacia gum were purchased from Aldrich, and used without further purification. Sugar is a caster sugar for feeding use. All aqueous solutions were prepared in distilled water. The organic phases were prepared in chromatographic grade toluene from BDH.

2) Methods

In all experiments, polymer beads were prepared in a reactor (fig.1) using 100 g of organic solution and 350 g of aqueous solution. The temperature was maintened at 78 ± 0.5°C. The stirring speed was fixed at 270 rd/mn which dissipated a power by mass unit $\varepsilon = 0.53$ Watt/kg. After 5 minutes of mixing, the benzoyl peroxide was added. The gelification time was about 1 hour, nevertheless the polymerization was ran during 5 hours. The mixture was then filtered. Polymer beads were washed and purified by soxhlet using water and then methanol. The beads are finally dried under reduced pressure (0.1 mmHg) at 100°C.

The organic phase was constitued of 36% styrene, 8% divinyl benzene, 56% toluene (% in mass). The organic phase density and the dynamic viscosity are respectively : $\rho d = 832$ kg/m^3, $\mu d = 0.055.10-2$ Pl. Two aqueous solutions series were prepared : acacia gum solutions with concentrations from 1.9% to 40%, and sugar solutions with concentrations from 40% to 78.8%. These concentrations were needed in order to obtain high viscosities.

The dynamic viscosities of acacia gum, sugar solutions and organic phase were measured with an Ubbelhode type viscosimeters which diameters were adjusted to the viscosity of the solutions (0.5 and 2 mm). The accuracy was $\pm 10^{-4}$ Pl.

The interfacial tension has been measured with a pendant drop tensiometer at 78 ± 0.5°C. The method is based on an the integrated form of Laplace equation for all the point of the drop profile (15-16). The accuracy was ± 104 Pl.

The counting of about 500 beads for each experiment was done with an optic microscope. The maximum diameter was determined with the ten bigest beads.

RESULTS AND DISCUSSION

All the experiments were performed at constant temperature, constant power per unit mass and constant composition of the organic phase. The maximum diameters observed ($d_{max,obs}$) are given in table (I). The values of ρ, ν, σ were experimentally measured and η was determined from relation (X). P is the ratio of the dynamic viscosity of the discontinuous phase to that of the continuous phase. ϕ(P) was deduced from Karam's results (14).

Table (I) : Maximum diameters observed and experimental parameters ρ, ν, σ.
Units : ρ in kg/m^3, μ.10^2 in Pl, σ.10^3 in N/m, ν.10^6 in m^2/s, d_{max}.10^6 in m, η.10^6 in m.

% mass.	*first serie : acacia gum*								*second serie : sugar*				
	0	*1.9*	*7.4*	*14.4*	*27.4*	*31.5*	*34*	*40*	*40*	*60*	*76.25*	*77.5*	*78.8*
ρ	973	979	1004	1031	1086	1103	1114	1139	1148	1259	1361	1370	1379
μ 10^2	0.036	0.06	0.14	0.34	1.56	2.68	3.72	8.20	0.13	0.54	3.00	4.10	5.78
σ 10^3	34.1	12.8	10.3	9.8	9.6	9.5	9.3*	9.1	31.6	30.4	29.5	29.4	29.3
ν 10^6	0.37	0.61	1.4	3.3	14.4	24.3	33.4	72.0	1.1	4.3	21.8	30.1	41.4
$d_{max}10^6$	-	236	157	118	109	94	78	47	5000	1850	869	948	948
η 10^6	18	26	48	91	274	405	515	916	40	111	374	476	605
P	1.528	0.917	0.393	0.162	0.035	0.021	0.015	0.007	0.423	0.102	0.018	0.013	0.010
ϕ(P)	3.0	2.3	2.2	2.4	4.1	5.2	6.2	10.8	2.2	2.7	2.9	4.2	8.3

The inertial breakup theory leads to distinguish two cases : D >> η >> d (VI) and D >> d >> η (VIII).

The experiments carried out with sugar correspond to conditions (VI). In this case, the theoretical relation (XII) predicts that $d_{max,th}$ linearly depends on the ratio (σ/pc) at power 3/5. Nevertheless, when In $d_{max,obs}$ is drawn as function of In (σ/ρc) a linear correlation having a slope of 6.65 is found (see fig.2). This slope is much higher than the theoretical prediction: 3/5.

The experiments carried out with acacia gum correspond to relation (VIII), except for the three low concentrations acacia gum (1.9 to 14.4%). Thus, $d_{max,th}$ linearly depends on (σν/εpc) at power 1/3, relation (XIII). In fact, as it can be seen on fig. 3, there is no linear dependence of ln $d_{max,obs}$ on 1n (oν/εpc). Moreover, $d_{max,obs}$ decreases as (σr/εpc) increases. This is totally incompatible with relation (XIII). The inertial breakup theory does not describe the behaviour of $d_{max,obs}$ for high viscosities.

Let us consider now the viscous shear breakup theory which predicts that $d_{max,th}$ linearly depends on (μpc) at power -1/2. Fig.4 shows ln ($d_{max,obs}$/2σξ) versus ln (μpc) are quite linear. The slopes found are -0.66 for sugar and -0.52 for acacia gum.These values are in good agreement with the theoretical prediction (-1/2) in a large range of viscosities (from 0.6.10^{-6} to 72.10^{-6} m2/s).

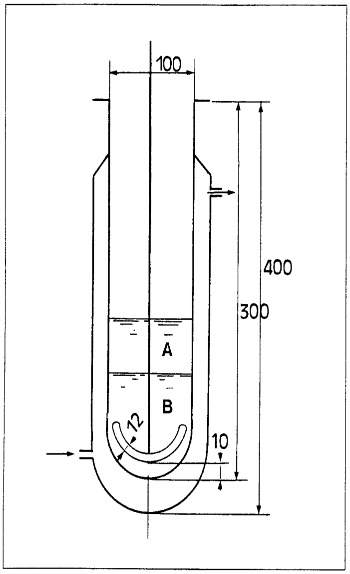

Fig. 1 : Reactor for suspension polymerisation
A : organic phase, B : aqueous phase

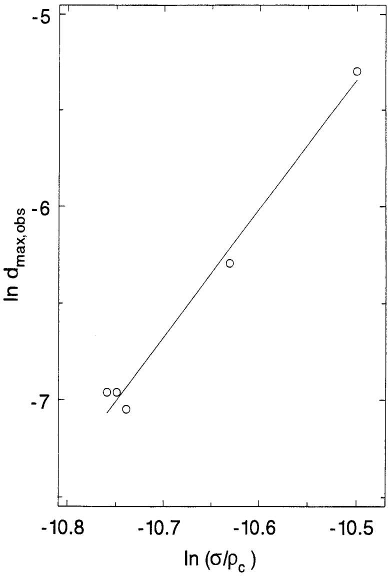

Fig. 2 : ln $d_{max,obs}$ versus ln (σ/p_c
for aqueous sugar viscosity

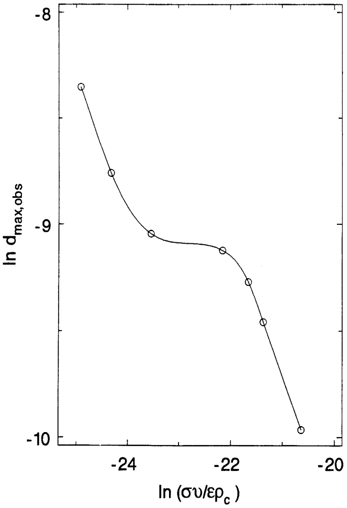

Fig. 3 : ln $d_{max,obs}$ versus ln ($\sigma\nu/\varepsilon\rho_c$)
for aqueous acacia gum viscosity

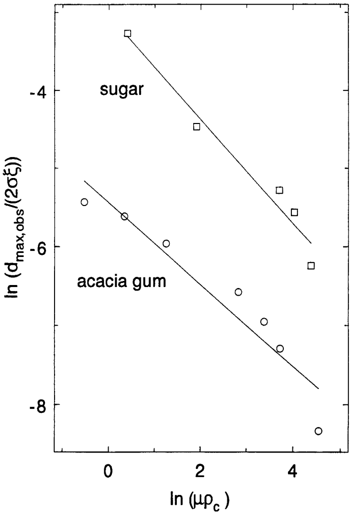

Fig. 4 : ln ($d_{max,obs}/(2\sigma\xi)$) versus ln ($\mu\rho_c$)
for aqueous sugar and acacia gum viscosities

From our results, we can reasonably conclude that the viscous shear breakup theory is valuable for the prediction of the beads maximum diameters. Further experiments will be performed in order to check these results for much higher viscosities.

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