DEVELOPMENT OF A NEW GRANULATION TECHNIQUE. II

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Summary

Based on theoretical considerations, the authors came to conclusions regarding the expected trend of the parameters of the dropping granulation technique. The experimental work was intended to check whether the actual results agree with those expected from the theoretical considerations. The results allow to assume the correctness of these considerations.

Introduction

In a previous paper [1] we reported on the results attained with a new granulation technique, a novel variation of the drop method. (A patent has been applied for the technique [2]).

To introduce the technique into practice, many preliminary tests are required for each individual case, since the properties and interactions of the numerous substances in question may significantly affect the technological parameters of the process.

In order to be able to predict the trends to be expected in these parameters for products made from various components, and thus reduce the experimental work required before starting their manufacture, we analyzed the process, based on theoretical considerations, and subsequently checked the conclusions experimentally.

In the present paper we deal with our investigations concerning the factors influencing the parameters of the drop technique.

Theoretical aspects

We interpreted the drop formation mechanism taking place in the drop granulation technique analogously to the method measuring drop mass to determine surface tension [3]. In conformity with the Tate law we assumed that the maximum weight of a viscous paste drop dropping from a capillary

under the effect of kinetic energy will keep equilibrium with the surface forces. Hence — assuming a spherical drop with the mass M_{dr} — the weight of the drop can be expressed as follows:

$$M_{dr} \cdot g = W_{dr} \cdot g \cdot \rho = \frac{d_{dr}^3 \pi \cdot g}{6} \rho = 2R\pi\gamma \tag{1}$$

where W_{dr} and d_{dr} are the volume and diameter of the drop, resp., ρ is the average density of the paste, R is the external radius of the dropping capillary and γ is the surface tension of the paste.

It follows from Eq. (1) that

$$d_{dr} = \sqrt[3]{\frac{12R\gamma}{g} \frac{1}{3}} \tag{2}$$

and the volume of the drop W_{dr} is

$$W_{dr} = \frac{2R\gamma}{g} \frac{1}{\rho} \tag{3}$$

Eqs. (2) and (3) indicate that the diameter (and volume) of the drop are directly proportional to the external radius R of the capillary (a technological parameters) and to the surface tension of the paste, and reversely proportional to the average density of the paste. The latter two values can be predicted for multi-component systems, if one assumes that the surface tension of the paste is proportional to the surface tension of the liquid phase in the paste, and that the average density is composed additively from the densities of the components in proportion to their respective volumes.

Our drop technique is characterized by the feature that the solvent, miscible with the precipitating bath, diffuses into the latter from the drop. In the ideal case, the solid granule with the volume W_{gr} formed from the drop with the volume W_{dr} is also spherical. Its volume W_{gr} is, however, less by the amount of solvent diffusing into and mixing with the precipitating bath. Hence, assuming that the solid granule is spherical, its volume will be

$$W_{gr} = W_{dr} - W_{dr}(1 - x_A - y_S)(1 - z_P)\frac{\rho}{\rho_0} \tag{4}$$

where x_A and y_S are the mass fractions of the active agent and the support material, resp., in the paste, z_P is the mass fraction of the polymer in the solvent, and ρ_0 is the density of the solvent. Correspondingly, the diameter of the granule is

$$d_{gr} = \sqrt[3]{\frac{6W_{gr}}{\pi}}. \tag{5}$$

It is this latter value that can be determined experimentally, and if our considerations are correct, it should depend, on the one hand, on composition (surface tension, density), and on the other hand, on technological parameters (external radius of the dropping capillary).

The considerations can be correct, however, only in the case when the kinetic energy of the pastes flowing through the given capillary (internal radius r, length *l*) is identical in all cases. In this case the volume Q flowing out in the time interval t is constant:

$$\frac{Q}{t} = const. \tag{6}$$

The ratio Q/t defined by Eq. (6) depends essentially on the rheological properties of the paste. Presumably — like almost all suspensions — the pastes to be applied in the drop granulation technique belong to the systems termed plastic systems in rheology [4, 5, 6]. Insofar as they are <u>Bingham</u> bodies, the constant Q/t can be expressed, for the slip-free case, by [4, 5]

$$Q/t = \frac{\Delta P \cdot r^4}{8l \cdot \eta_{pl}} \left[1 - \frac{4\tau_f \cdot 2l}{3\Delta P \cdot r} + \frac{1}{3} \left(\frac{\tau_f \cdot 2l}{P \cdot r} \right)^4 \right] \tag{7}$$
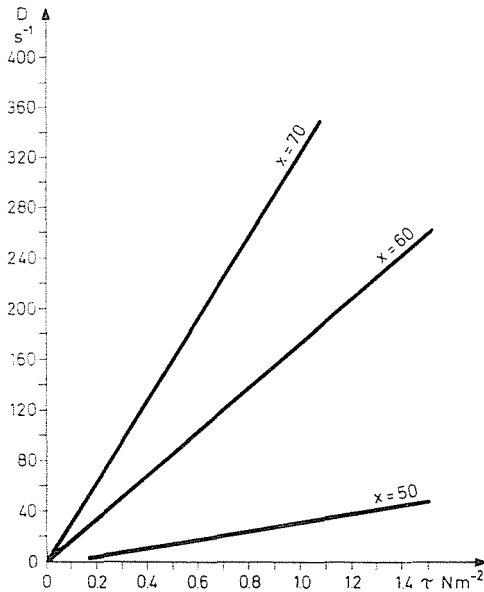

Fig. 1. Schematical flow curve of Bingham bodies

τ_f, the flow limit is the intercept on the abscissa axis of the flow curve (flow rate gradient D vs. shear stress), and the plastic viscosity η_{pl} is the reciprocal of the slope of this curve (Fig. 1).

Assuming that the pressure ΔP is significantly higher than the flow limit of the paste, the term on the fourth power in Eq. (7) may be neglected. Assuming further that the length l of the capillaries applied is identical, Eq. (7) will be reduced to the simpler form

$$Q/t = \frac{r^3}{\eta_{pl}} (A\Delta P \cdot r - B\tau_f) \tag{8}$$

where

$$A = \frac{\pi}{8l} \quad \text{and} \quad B = \frac{\pi}{3}. \tag{9}$$

Eq. (8) demonstrates that identical kinetic energy, that is, constant Q/t values can be attained for pastes with differing flow limits and plastic viscosities by varying the pressure and/or the internal diameter of the capillary. If the internal diameter is constant, higher pressures will be needed for pastes with higher plastic viscosities or flow limits.

Experimental

Our experiments served the purpose to check the correctness of the above conclusions.

The materials used were

Atrazin (A) and Propachlor (P), active agents [7]; bentonite (B) and kieselguhr (K), supports; cellulose acetate (CA) dissolved in dimethylformamide (D).

The amount of active agent (applied in the form of a fine powder) was 10% relative to the (assumedly dry) final product, and the amount of the support material was 90% (the amount of the polymer CA was neglected in the calculations). The components of the solid phase are marked with the above-noted symbols and with figures indicating their percentages. The figure following the symbol of cellulose acetate indicates its per cent by mass in its solution in dimethylformamide, and the figure following the symbol of dimethylformamide indicates the percentage of the liquid phase in the paste (suspension). E.g. the mark P1OB9OCA3D70 is a paste consisting of 10% Propachlor and 90% bentonite as internal phase and 70% liquid phase which is a 3% solution of cellulose acetate in dimethylformamide.

We measured the surface tension of the liquid phase of the pastes at different CA contents, recorded the flow curves of the pastes in a Rheotest
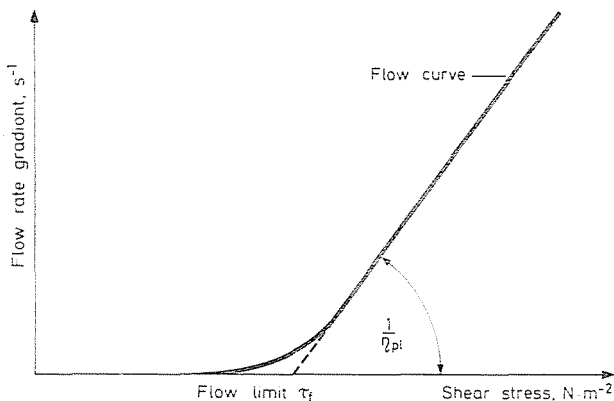
Fig. 2. Flow curves of the pastes marked P1OB90CA5Dx (x = percentage of the liquid phase in the system)

rotational viscosimeter at ambient temperature and performed dropping tests in an apparatus similar to the one reported in our earlier paper [1]. In this apparatus the capillaries could be changed and the pressure recorded. The drops fell into a bath consisting of water with 1 g/l TWEEN 80 emulsifying agent. After drying the products, we measured the mass and diameter of the spherical granules and calculated the averages of the measured values.

Our results will be presented on the example of Propachlor-containing products.

The rheological measurements confirmed that the pastes are in fact Bingham bodies. This is demonstrated, by way of example, in Fig. 2.

From the measurements obtained with the Rheotest instrument we determined the flow limit and plastic viscosity values of the pastes. The values obtained for Propachlor-containing pastes are listed in Table 1, indicating that both increase by raising the percentage of the solid phase in the suspension, and — at a constant value of this percentage — with growing cellulose acetate concentration in the external liquid phase.

The following conclusions can be made from the results of the drop experiments:

1. At identical pressure, using one and the same paste, the average diameter of the granules in the final product increases with the internal diameter of the capillar (Table 2/a);

2. At identical pressure and capillary diameter, identical composition, but varying ratio of the external (liquid) phase to the internal (solid) phase, the average diameter of the granules decreases with the decreasing ratio of solids in the paste (involving the decrease of the flow limit, the plastic viscosity and the calculated density). (Table 2/b);

Table 1

Changes of flow limit, plastic viscosity and calculated density with composition of the paste

Mark	τ_f, N·m^{-2}	η_{pl}, Pa·s	ρ, kg·m^{-3}
P10B90CA1D70	. . .	. . .	1148.2
P10B90CA1D60	0.012	0.0002	1234.5
P10B90CA1D50	0.111	0.0041	1334.5
P10B90CA3D70	0.0131	0.0007	1155.4
P10B90CA3D60	0.0125	0.0017	1241.7
P10B90CA3D50	0.102	0.0093	1341.9
P10B90CA5D70	0.010	0.0024	1162.8
P10B90CA5D60	0.027	0.0058	1249.0
P10B90CA5D50	0.148	0.023	1349.0
P10B90CA7D70	0.005	0.0076	1170.2
P10B90CA7D60	0.064	0.0155	1256.3
P10B90CA7D50	0.149	0.0380	1456.1

Table 2

Results of dropping experiments. Pressure 106.6 kPa

(a) Mark of paste: P10B90CA3D60
Calculated density of paste: 1242 kg·m^{-3}
Plastic viscosity of paste: 0.0017 Pa·s
Flow limit of paste: 0.013 N·m^{-2}

Internal diam. of capillary, mm	Average diameter of granules, cm
0.5	0.197
0.75	0.207
1.0	0.220

(b) Internal diameter of capillary: 1.0 mm

Mark	Flow limit, N·m^{-2}	Plastic viscosity, Pa·s	Calcd. density, kg·m^{-3}	Average diam. of granule, cm
P10B90CA5D50	0.148	0.0230	1349	0.245
P10B90CA5D60	0.027	0.0058	1249	0.225
P10B90CA5D70	0.010	0.0024	1162	0.208

(c) Calculated average density of paste: 1249 kg·m^{-3}
Internal diameter of capillary: 1.0 mm

Mark	Flow limit, N·m^{-2}	Plastic viscosity, Pa·s	Surface tension of ext. phase, mN/m	Average diam. of granule, cm
P10B90CA3D60	0.013	0.0017	69.3	0.220
P10B90CA5D60	0.027	0.0058	74.5	0.225
P10B90CA7D60	0.064	0.0160	83.3	0.243

3. At identical pressure and capillary diameter, close to identical calculated density and identical ratio of the solid to liquid phases, increasing concentration of cellulose acetate in the liquid phase, involving the rise of the surface tension, flow limit and plastic viscosity, results in an increase of the diameter of the granules (Table 2/c).

These results indicate that the conclusions made from the theoretical considerations agree — in their trends — with the measured data. It hence appears feasible to predict the technological parameters of the drop technique on the basis of the above-discussed theoretical considerations. However, the results also indicate that — owing to the large number of variables and affecting conditions — the parameters to be in fact applied should, by all means, be rendered more reliable by preliminary tests.

List of symbols

d_{dr}	diameter of drop, cm
d_{gr}	diameter of granule of the final product, cm
D	flow rate gradient, s^{-1}
l	length of capillary, cm
M_{dr}	mass of drop, g
M_{gr}	mass of granule, g
ΔP	pressure, $N \cdot m^{-2}$
Q	volume of paste discharged from the capillary, cm^3
r	internal radius of capillary, cm
R	external radius of dropping capillary, cm
t	time, s
W_{dr}	volume of drop, cm^3
W_{gr}	volume of granule of final product, cm^3
x_A	mass fraction of active agent in the paste, $g \cdot g^{-1}$
y_S	mass fraction of support in the paste, $g \cdot g^{-1}$
z_P	mass fraction of polymer in the solution, $g \cdot g^{-1}$
γ	surface tension of paste, $mN \cdot m^{-1}$
η_{pl}	plastic viscosity, $Pa \cdot s$
ρ	average density of paste, $kg \cdot m^{-3}$
ρ_0	density of solvent, $kg \cdot m^{-3}$
τ	shear stress, $N \cdot m^{-2}$
τ_f	flow limit, $N \cdot m^{-2}$

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