Rheological Parameters of Polyolefin Suspensions

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Synopsis

Effects of rheological parameters of polyolefin suspension were studied to better understand stirred tank polymerization reactors and their engineering principles. Experimental results have been fitted into a quadratic model. Consistency index and behavior index have been determined as functions of solids concentration, temperature, and particle size.

INTRODUCTION

Slurry polymerization is used in ethylene, propylene, and heavier olefin polymerization. Modern slurry processes are relatively simple and are used for production of a wide range of products.[1-4]

In a slurry process, the formed solid polymer particles are suspended in a liquid hydrocarbon, the suspension medium may also be a mixture of an inert hydrocarbon dissolving the monomer, or only the monomer. The latter case is called bulk polymerization.

In the end of the process the suspending medium is separated from the polymer and recycled.

The volume of recycle stream is strongly dependent on the highest allowable slurry concentration in the reactor, which has to be such that good agitation and heat transfer is assured, while plugging problems are avoided. The highest possible slurry concentration can be affected by agitator design, but finally it is a question of suspension properties.

The slurry concentration in the reactor should be maximized, while agitation is still assured, because the maximum allowable slurry concentration (g of polymer/dm^3 of slurry) is of primary importance to process economy. Too high a slurry concentration causes a dramatic increase in the slurry viscosity, which raises the reactor temperature, even causing plugging problems and possibly a runaway.

Maximum slurry concentration is dependent on particle size and shape. Spherical form particle processes have typically slurry concentrations of at least 300 g/dm^3, if the particles are nonspherical, the value will easily be halved.[2,5] The maximum slurry concentration can roughly be estimated by polymer bulk density (ASTM D 1895). Regulation of polymer powder bulk density is a central objective in catalyst development.[5]

In the CSTR the slurry concentration can be regulated by catalyst feed rate, inert medium and monomer feed rates, and mean residence time.

The polymer, which is present in high concentration must be kept in suspension and distributed through the liquid. Agitation power of a polymer

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slurry depends substantially on the solid polymer viscosity of the slurry.[15] The slurry behaves like a non-Newtonian fluid.[7,8]

Rheology research in the polymer field is primarily concentrated on polymer melt research, which supports polymer processing. There is little research on the rheological properties of reacting polymer slurries. Michael and Reichert[8] have studied polyethylene suspension and provided a graph, showing the relative viscosity of slurry expressed as a function of solid material concentration. Nicodemo et al.[9] have studied the dependence of the viscosity of polyisobutylene suspension on shear rate.

Several references discuss the factors affecting the suspension viscosity. Jinescu[10] has studied the dependence of slurry viscosity on temperature, particle size, and particle size distribution. Clarke[11] has studied the effect of particle shape and Jeffrey and Acrivos[12] have studied the effects of intramolecular forces on the slurry viscosity.

This paper discusses the rheological properties of polyolefin suspension and their dependencies on different process variables. In this study a novel experimental model has been determined for the calculation of rheological parameters—consistency index and behavior index—by using different polyolefin suspensions. Some notes on the time dependence of rheological parameters have also been done.

THEORETICAL PART

For pseudoplastic and dilatant fluids the following equation is valid:

$$\tau = k(-dw/dy)^{n'} \tag{1}$$

Metzner and Otto[14] have shown that the Reynolds number for pseudoplastic and dilatant fluids in a tube is:

$$\mathrm{Re} = dw\rho \frac{(8w/d)^{1-n'}}{K} \left(\frac{4n'}{3n'+1} \right)^{n'} \tag{2}$$

thus the apparent viscosity is defined as:

$$\mu_a = \frac{K}{(8w/d)^{1-n'}} \left(\frac{3n'+1}{4n'} \right)^{n'} \tag{3}$$

In agitation where a fluid rotates tangentially in a cylindrical vessel, the apparent viscosity can be calculated by the equation of Calderbank and Moo-Young.[15] In that the constant in Eq. (3) is displaced by term B, which can be measured empirically.

$$\mu_a = \frac{K}{(B \cdot N)^{1-n'}} \left(\frac{3n'+1}{4n'} \right)^{n'} \tag{4}$$

For all major agitator elements, except anchor, the constant B is 11 ± 1.1, provided that the fluid is pseudoplastic ($n' < 1$) and the ratio of vessel diameter to agitator impeller (S) is over 1.5.

For dilatant fluids ($n' > 1$), when $S < 3.0$, constant B can be calculated for all agitators by equation:

$$B = \frac{22 \cdot S^2}{S^2 - 1} \tag{5}$$

The accuracy of Eq. (5) is ± 15%.

EXPERIMENTAL

Polyethylene and poly-1-butene powders were used as model polyolefins. Apparent viscosities of polyolefin slurries were experimentally measured by LVTD-viscosimeter (Brookfield Engineering Laboratories Inc., Massachusetts, USA). The rheological parameters of polyolefin suspensions, such as consistency index and behavior index, were studied as function of solid material concentration, temperature, and particle size. Additionally, the change of rheological parameters of poly-1-butene suspension were studied as function of time at different temperatures.

The polyolefin suspension was held at a constant temperature for 15 min before the measurements were started. Suspension was assured by sufficient agitator speed. The viscometer spindle was in the suspension during the heating period.

The viscosity measurements were performed with eight viscometer spindle speeds, from 0.005 to 1 s^{-1}.

The viscosity of suspension was measured immediately after agitation ceased, and the flow had become laminar. This had to be done before the particles started to settle. This period is rather short because of the settling velocities of particles. Viscosity measurement was repeated up to four times with each viscometer spindle. The suspension was well agitated between the repetition.

A 2 dm^3 cylindrical vessel (diameter = 128 mm) was immersed into a water bath. In the cylinder were agitator and rotor of the viscosimeter, as is shown in Figure 1. The agitator was 4-pitched-blade turbine (45°), and had a diameter of 42 mm. Heptane was used as liquid and the total volume of the suspension was 1.85 dm^3.

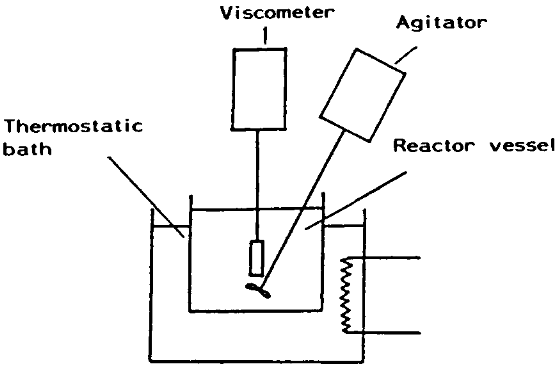

Fig. 1. Experimental arrangement.

The average Sauter diameter of polyethylene particles was from 0.300 to 1.205 mm. The average Sauter diameter of poly-1-butene particles was constant, 0.602 mm. Dry polyethylene and polybutylene powders had bulk densities 220 and 270 g/dm^3.

RESULTS AND DISCUSSION

Because no theoretically derived mathematical model for the experiments was found, the results were fitted into a quadratic equation in order to determine the rheological parameters for the polyethylene and poly-1-butene suspensions.

Quadratic equations for the rheological parameters of poly-1-butene suspensions were:

$$n' = 11.83 - 128.3 \cdot C_s - 0.1137 \cdot \Theta + 481.6 \cdot C_s^2 + 0.003377 \cdot \Theta^2 - 0.6405 \cdot C_s \cdot \Theta \tag{6}$$

$$K = -2.832 + 27.77 \cdot C_s + 0.05189 \cdot \Theta - 104.4 \cdot C_s^2 - 0.001205 \cdot \Theta^2 + 0.1490 \cdot C_s \cdot \Theta \tag{7}$$

The equations have been verified experimentally in the range:

$$0.128 \text{ kg/dm}^3 \le C_s \le 0.171 \text{ kg/dm}^3$$

and

$$25°\text{C} \le \Theta \le 35°\text{C}$$

and the correlation coefficients were calculated to be $R^2 = 0.94$ and $R^2 = 0.82$, correspondingly.

The quadratic equations for polyethylene suspensions were:

$$n' = 3.625 + 0.8213 \cdot d_p + 18.96 \cdot C_s - 0.2528 \cdot \Theta + 0.1736 \cdot d_p^2 - 15.47 \cdot C_S^2 + 0.003954 \cdot \Theta^2 - 8.284 \cdot d_p \cdot C_s + 0.01120 \cdot d_p \cdot \Theta - 0.3250 \cdot C_s\Theta \tag{8}$$

and

$$K = \exp\big(15.28 - 1.231 \cdot d_p + 23.91 \cdot C_S - 1.313 \cdot \Theta - 0.6153 \cdot d_p^2 + 200.1 \cdot C_s^2 + 0.03162 \cdot \Theta^2 + 74.47 \cdot d_p \cdot C_s - 0.3233 \cdot d_p \cdot \Theta - 3.495 \cdot C_s\big) \tag{9}$$

Equations (8) and (9) have been experimentally verified in the range:

$$0.129 \text{ kg/dm}^3 \le C_s \le 0.228 \text{ kg/dm}^3$$

$$30°\text{C} \le \Theta \le 40°\text{C}$$

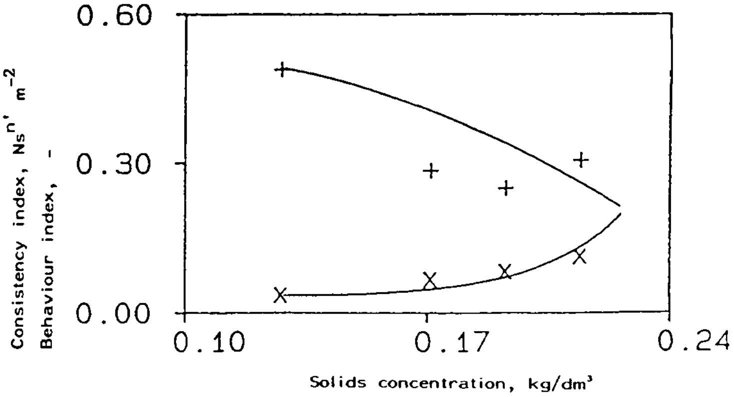

Fig. 2. Consistency index and behavior index of polyethylene suspension as a function of solid material concentration. Average particle diameter 0.605 mm, temperature 35°C. + = Behavior index; × = Consistency index; — = Calculated.

and

$$0.300\text{ mm} \leq d_p \leq 1.205\text{ mm}$$

The correlation coefficients for the equations were determined to be: $R^2 = 0.62$ and $R^2 = 0.78$, correspondingly.

The effect of solid concentration in the polyethylene suspension was studied with particle size 0.605 mm at temperature 35°C. The results are presented in Figure 2. The values calculated by quadratic equation are also shown. The corresponding information for poly-1-butene suspension is shown in Figure 3.

Figures 2 and 3 show, that consistency index, K, increases and behavior index, n', decreases when solid material concentration increases, which usually happens with slurries. However, at higher concentrations poly-1-butylene slurries consistency index remains almost constant and behavior index increases. This is caused by low solid material concentrations used. Polyolefin

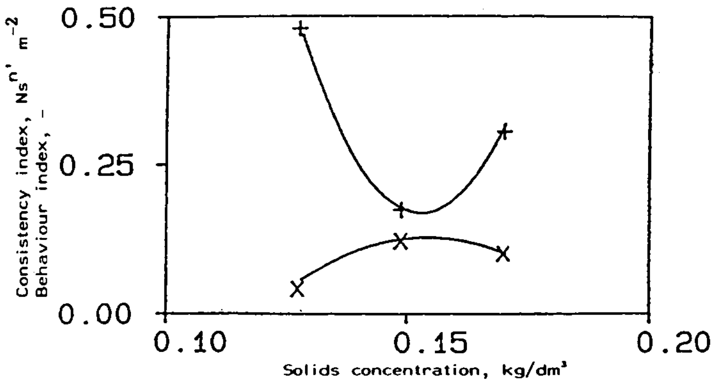

Fig. 3. Consistency index and behavior index of poly-1-butene suspension as a function of solid material concentration. Average particle diameter 0.602 mm, temperature 30°C. + = Behavior index; × = Consistency index; — = Calculated.

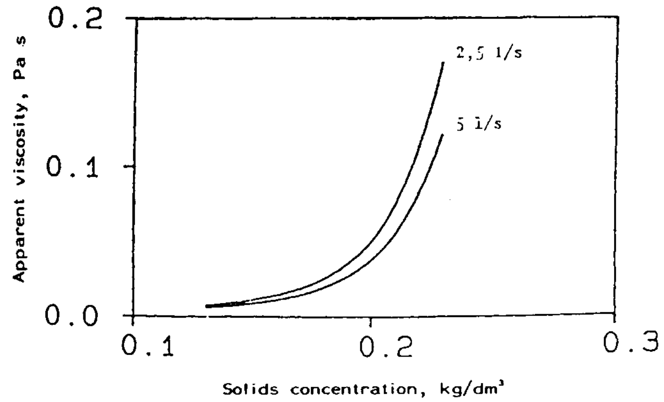

Fig. 4. Apparent viscosity of polyethylene suspension as a function of solid material concentration. Agitator speed is a parameter. Temperature = 30°C, average particle diameter is 0.605 mm. Bulk density of dry solid polymer powder = 220 g/dm^3.

suspensions were found to be pseudoplastic ($n' < 1$) at the studied temperatures.

In Figure 4 is presented the apparent viscosity of polyethylene suspension as function of solid material concentration, calculated by quadratic model. Figure 4 shows that the apparent viscosity of a polyethylene suspension increases sharply as a function of solid material concentration, when solid material concentration exceeds 0.20 kg/dm^3. At high solid material concentrations, the apparent viscosity is strongly dependent on agitator speed. At process scale, agitation becomes problematic when $\mu_a > 0.1 \ldots 0.3$ Pa s.

Apparent viscosity of a suspension decreases with increasing temperature, if there are no changes of particle size or shape, and if solid material concentration is small. The decrease of apparent viscosity in these cases is caused by the decrease of viscosity of liquid when the temperature increases. Figures 5 and 6 show the rheological parameters of polyethylene and poly-1-butene suspensions as a function of temperature.

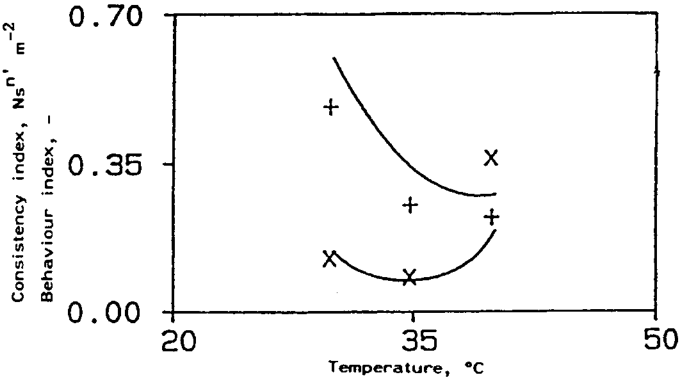

Fig. 5. Consistency index and behavior index of polyethylene suspension as a function of temperature. Average particle diameter 0.605 mm, solid material concentration 0.1935 kg/dm^3. + = Behavior index; × = Consistency index; – = Calculated.

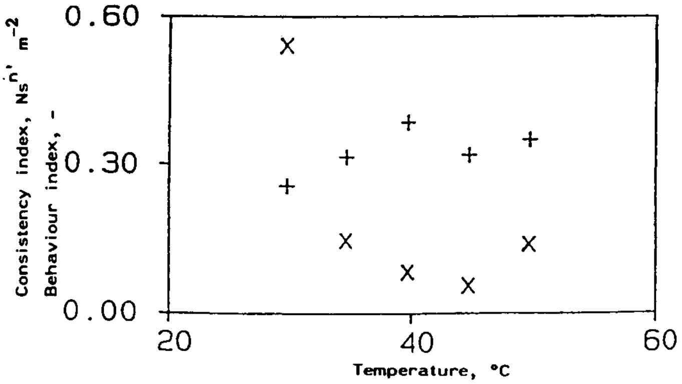

Fig. 6. Consistency index and behavior index of poly-1-butene suspension as a function of temperature. Average particle diameter 0.602 mm and solid material concentration 0.171 kg/dm^3. + = Behavior index; × = Consistency index.

Figure 5 shows that the consistency index of polyethylene suspension decreases with temperature increase up to 35°C. Behavior index decreases as well. The decrease in consistency index is caused by the viscosity change of the liquid, because consistency index happens to be the rheological parameter having the greatest influence on the level of viscosity. When the temperature rises above 35°C, consistency index increases steeply as a function of temperature. The rise in the consistency index is caused in this case by the changes of size, shape, and surface structure of the particles. The consistency index of poly-1-butene suspension increases as a function of temperature above 45°C (Fig 6). The effect of particle size on rheological parameters was studied using polyolefin suspensions with different average particle sizes, at temperature of 35°C and solid mass concentrations of 0.1935 kg/dm^3.

Figure 7 shows that the consistency index increases and behavior index decreases as the particle size increases. Thus, the apparent viscosity increases with particle size. However, the dependence of apparent viscosity on particle

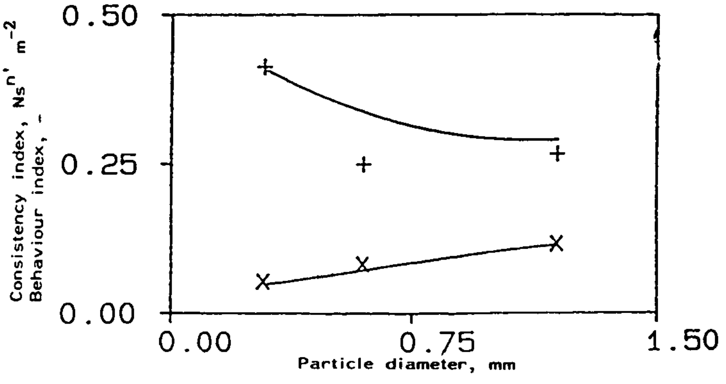

Fig. 7. Consistency index and behavior index of polyethylene suspension as a function of average particle diameter. Temperature 35°C and solid material concentration 0.1935 kg/dm^3. + = Behavior index; × = Consistency index; — = Calculated.

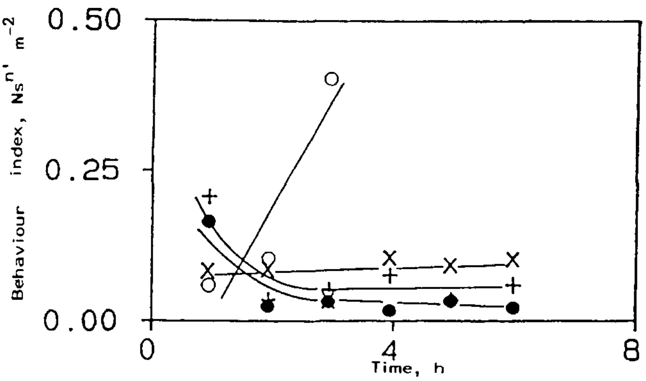

Fig. 8. Behavior index of polyethylene suspension as a function of time. Temperature is a parameter, average particle diameter 0.60 mm and solid material concentration 0.1935 kg/dm^3. + = 30°C; × = 35°C; ● = 40°C; ○ = 42.5°C.

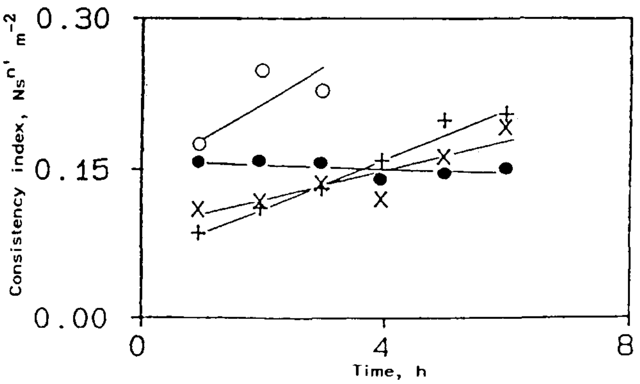

Fig. 9. Consistency index of polyethylene suspension as a function of time. Temperature is a parameter, average particle diameter 0.60 mm, and solid material concentration 0.1935 kg/dm^3. + = 30°C; × = 35°C; ● = 40°C; ○ = 42.5°C.

size is not very strong, so the effect of particle size distribution was not studied in this paper.

Time dependencies of polyethylene suspension viscosity was studied by measuring the rheological parameters as a function of time at different temperatures. Particle diameters ranged between 0.25 and 1.41 mm. The bulk density of the particles was 0.30 kg/dm^3 and Sauter diameter was 0.60 mm.

Figures 8 and 9 do not show a significant dependence on time at temperatures below 42.5°C. At temperature 42.5°C the consistency index and behavior index increase sharply as a function of time, thus the slurry has also slight time variant properties.

CONCLUSIONS

In this article some rheological parameters of polyolefin suspensions have been studied as a function of solids concentration, temperature, and particle size. The experimental results have been fitted into a quadratic equation. Slurries showed pseudoplastic properties, however, having also slight time variant character at higher temperatures. Particle diameter had a minor effect on the rheology. The quadratic model equation can be used to predict rheological properties of a polymer slurry.

SYMBOLS

B	constant
C_s	solid concentration, kg/dm^3
d	diameter of tube, m
d_p	diameter of particle, mm
k	constant, $Ns^{n'}/m^2$
K	consistency index, $Ns^{n'}/m^2$
n'	behavior index
Re	Reynolds number
S	ratio of vessel diameter to impeller diameter
w	flow speed, m/s
y	distance, m
θ	temperature, °C
μ_a	apparent dynamic viscosity, $Pa\ s$
ρ	density, $kg\ m^{-3}$
τ	shear stress, Pa cursivated

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