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SHORT COMMUNICATION

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# Study of the rheological properties of dispersed lignite suspensions

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**Abstract** The aim of this study was to determine the basic rheological parameters of dispersed highly concentrated lignite aqueous suspensions. Typical dilatant behavior was observed, where critical parameters of dilatancy were determined for different size fractions and concentrations. To modify the non-Newtonian behavior of the lignite highly concentrated suspensions, the effect of surfactant addition on the flow parameters of the suspensions was determined.

**Key words** Lignite · Flow behavior · Rheology · Dilatancy

## Introduction

In general, according to the mechanical properties of materials it is possible to distinguish between three basic states of matter: gaseous, liquid and solid states. Nonviscous ideal gas, noncompressible viscous liquid and isotropic flexible material (so-called Hookes body) correspond to the simplest mathematical models of the mechanical properties of the three states of matter. From the point of view of mechanical behavior, it is possible to deduce the rheological properties and simultaneously to predict the behavior at limiting shear conditions. Dilatant flow behavior occurs in many technologically important processes [1–3].

Lignite, as defined from the point of view of chemistry, is an organic substrate with mineral inclusions situated on the transformation route from phytomass to a dehydrated, dehydrogenated and deoxidized carbon-type complex and water [4, 5]. From the point of view of physical chemistry, lignite represents a solid colloidal system with a different surface morphology depending on the degree of coalification, the properties of which are determined by the composition of the parental phytomass and the pressure and the thermal conditions at the time of its transformation. For simplicity, we consider lignite particles of spherical shape [6]. The relative molar mass of lignite varies over a wide interval, ranging from 700 to $2 \times 10^6$ Da.

In this study we measured the rheological properties of highly concentrated aqueous lignite suspensions at concentrations of 1.0 and 1.25 g/g for three different fractions ranging from 0.063 to 0.2 mm, with the aim to determine the basic flow parameters of original and surfactant-modified lignite suspensions.

## Materials and methods

### Materials

The South Moravian lignite studied was obtained from the Mikulčice mine. Each sample was dried at 120 °C for 24 h prior to vibrational sieving (Fritsch). The basic physicochemical characteristics of the three lignite fractions prepared are given in Table 1. A commercially available surfactant, Pur (Henkel), was used.

### Determination of the size distribution functions

A gravitation sedimentograph SG4 (Regea, Brno) was used. Measurements were performed at the ambient temperature of 20 °C.

### Measurement of the flow curves

Measurements were performed using Höppler consistometer (MLW Medingen, Germany).

### Calculation of the sedimentation rate

The sedimentation rate of the spherical particles in the laminar flow regime is described by the Stokes equation:

$$v_s = \frac{d^2(\rho_2 - \rho_0)g}{18\eta_0} \ , \quad (1)$$

where $d$ is the particle diameter, $\rho_2$ is the specific weight of the particles, $\rho_0$ is the specific weight of the dispersion medium, $\eta_0$ is the dynamic viscosity of the dispersion medium and $g$ is the gravitational acceleration. As a criterion of the sedimentation velocity, the sedimentation coefficient, $S$, was defined:

$$S = \frac{m}{f}\left(1 - \frac{\rho_0}{\rho_2}\right) \ , \quad (2)$$

where $m$ is the weight of the lignite particle, $f$ is the friction coefficient, which for a spherical particle is defined by Eq. (3):

$$f = 6\pi\eta_0 r \ , \quad (3)$$

where $r$ is the particle radius.

### Calculation of the viscosity

The calculation of the viscosity was based on the measured quantities (trajectory, time and loading) according to Eq. (4):

$$\eta = \frac{G}{v}K = \frac{Gt}{s}K \ , \quad (4)$$

where $\eta$ is the apparent dynamic viscosity, $G$ is the loading, $s$ is the trajectory, $t$ is the time, $v$ is the flow rate and $K$ is the instrument constant. $K = 570$ mPa cm/g for a sphere of diameter 1.27 cm [8]. Equation (4) is valid for the case where the movement of the sensor sphere has a steady character and contrary to this movement the dispersion is extruded through the slit between the sphere and the wall of the measuring tube.

## Results and discussion

Typical patterns observed for the consistometer measurements of 1.0 g/g concentration lignite aqueous suspension ($d > 0.2$ mm) are shown in Fig. 1. Similar data were also observed for lignite suspensions at different concentrations (1.25 and 2.0 g/g). The dependencies were characteristic with the increase of the passed trajectory (by the test sphere pushed through the lignite paste) reaching the limiting value, where the system was so compressed that the sphere movement was stopped. The values of the initial flow rate were calculated based on the first derivative of the time dependence of the sphere trajectory (Table 2). A typical situation is shown in Fig. 2. The sphere flow rates determined $b(1)$ and the intercepts [$b(0)$] of the linear regression for untreated (without surfactant addition) lignite suspensions are given in Table 2. It was found that at concentrations higher than 2.0 g/g the paste is not able to flow because of its dilatant behavior. To modify such technologically inconvenient rheological behavior, a commercially available surfactant was added to the suspension in 0.3 vol% concentration. Then the same experiments were performed with surfactant-treated lignite suspensions. The results of these experiments are summarized in Table 3. From the data in Tables 2 and 3 the apparent dynamic viscosities of the suspensions were calculated according to Eq. (4). A typical dependence is shown in Fig. 3 for a surfactant-modified suspension. Similar dependencies

**Table 1** Lignite fractions and their sedimentation characteristics

| Lignite fraction ($10^{-3} \times$ m) | Sedimentation coefficient[a] ($s$) |
|---|---|
| <0.063 | $4.1 \times 10^{-11}$ |
| >0.100 | $6.2 \times 10^{-7}$ |
| >0.200 | $2.1 \times 10^{-6}$ |

[a] A lignite density of 1350.0 kg/m$^3$ was used in the calculation [7]

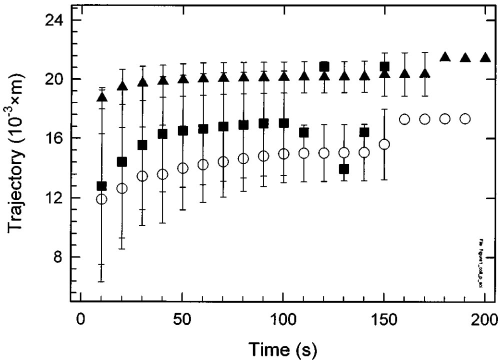

**Fig. 1** Time dependence of the sensor sphere trajectory of the lignite aqueous suspensions (mean particle diameter $d > 0.2$ mm) at 1.0 g/g concentration: 250 g loading (○), 500 g loading (■), 750 g loading (▲)

**Table 2** Determination of the initial flow rate [parameter $b(1)$] of the sensing measuring sphere (in the lignite suspensions under study) by the tangent method [the intercept at zero time is the parameter $b(0)$]

| Conc. (g/g) | Applied loading | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 250 (g) | | 500 (g) | | 750 (g) | | 1000 (g) | |
| | $b(1)$ ($10^{-5} \times$ m/s) | $b(0)$ ($10^{-2} \times$ m) | $b(1)$ ($10^{-5} \times$ m/s) | $b(0)$ ($10^{-2} \times$ m) | $b(1)$ ($10^{-5} \times$ m/s) | $b(0)$ ($10^{-2} \times$ m) | $b(1)$ ($10^{-5} \times$ m/s) | b(0) ($10^{-2} \times$ m) |
| 1.00 | 5.9 | 1.1 | 12 | 1.2 | 3.8 | 1.8 | – | – |
| 1.25 | 4.2 | 0.9 | 4.3 | 1.2 | 2.9 | 1.6 | 2.8 | 1.6 |
| 2.00 | – | – | 14 | 9.2 | 3.5 | 19.1 | 4.0 | 20.2 |

were observed for non-modified lignite suspensions and for all concentration ranges under study. To compare the particular measurements, the calculated apparent initial viscosity was determined by a linear regression fit of the viscosity data to zero time. These data are summarized in Figs. 4 and 5 as a function of the initial flow rate of the sphere. Both dependencies have typical dilatant behavior, i.e. with increasing sphere flow rate the viscosity also increases. It is well known that the dilatancy is caused by the structural changes of the suspensions, and in some cases it is due to the changes in the particle arrangement in the course of the flow process [9, 10]. Such an ordered arrangement is changed to a disordered structure [1]. The critical dilatancy parameters are given in Table 4. The theoretical mechanisms of dilatancy flow are mostly based on the effect of the Brownian movement of particles in the flow, and in part also on the influence of the hydrodynamic forces affecting particles in the dispersed phase induced by suspension flow [2]. It is clear from Table 4 that the values of the critical sphere flow rates for the surfactant-treated suspensions are approximately 50 times higher than for the untreated ones (e.g. for a concentration of 1.0 g/g of the surfactant-free system the value of the critical sphere flow rate was $3.8 \times 10^{-5}$ m/s and for the surfactant modified system it was $160.0 \times 10^{-5}$ m/s). This phenomenon is very favorable from several technological aspects for the technologies used in forming of the lignite-based products by pressing techniques. Even if an increase in the values of the critical sphere flow rate was observed for the surfactant-treated suspensions the characteristic shape for the dilatant rheological behavior of the measured dependencies was not changed.

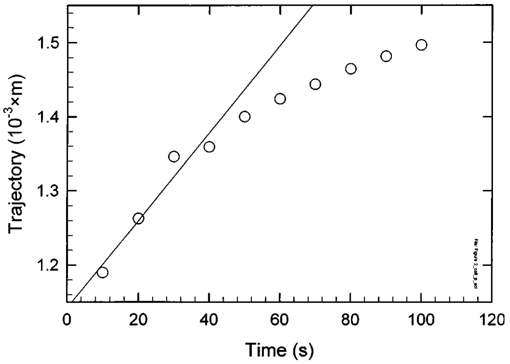

**Fig. 2** Time dependence of the sensor sphere trajectory of the lignite suspension (mean particle diameter $d > 0.2$ mm) at 1.0 g/g concentration and 250 g loading (connected with high particle pressing and aqueous media extrusion)

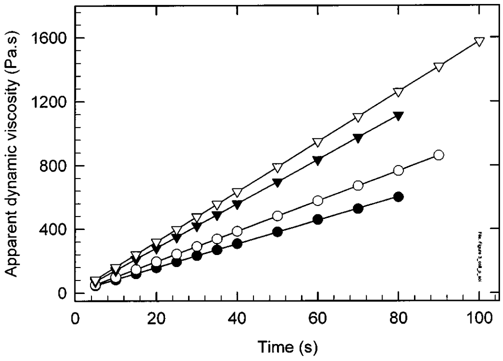

**Fig. 3** Time dependence of the apparent dynamic viscosity of the surfactant-modified lignite suspension (lignite concentration 1.0 g/g): 250 g loading (●), 340 g loading (○), 500 g loading (▼), 590 g loading (▽)

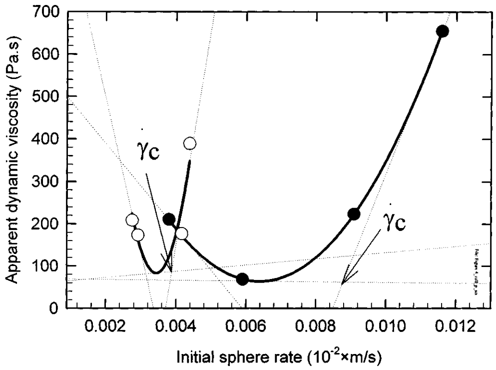

**Fig. 4** Sphere flow rate dependence of the initial apparent dynamic viscosity of the lignite suspension ($d > 0.2$ mm): 1.0 g/g concentration (○), 1.25 g/g concentration (●)

**Table 3** Determination of the initial flow rate [parameter $b(1)$] of the sensing measuring sphere (in surfactant-treated lignite suspensions) by the tangent method [the intercept at zero time is the parameter $b(0)$]

| Conc. (g/g) | Applied loading | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 250 (g) | | 340 (g) | | 500 (g) | | 590 (g) | |
| | $b(1)$ ($10^{-5}$ × m/s) | $b(0)$ ($10^{-2}$ × m) | $b(1)$ ($10^{-5}$ × m/s) | $b(0)$ ($10^{-2}$ × m) | $b(1)$ ($10^{-5}$ × m/s) | $b(0)$ ($10^{-2}$ × m) | $b(1)$ ($10^{-5}$ × m/s) | $b(0)$ ($10^{-2}$ × m) |
| 1.00 | 236.0 | 14.5 | 180.0 | 17.9 | 49.0 | 19.6 | 92.0 | 19.8 |
| 1.25 | – | – | 0.7 | 7.7 | 171.0 | 14.0 | 280.0 | 17.6 |

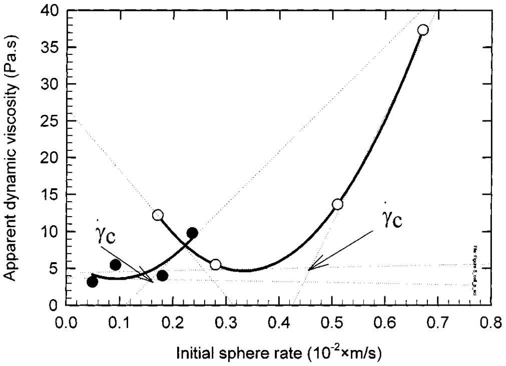

**Fig. 5** Sphere flow rate dependence of the initial apparent dynamic viscosity of the surfactant-treated lignite suspension (*d* > 0.2 mm): 1.25 g/g concentration (○), 1.0 g/g concentration (●)

**Table 4** Critical parameters of dilatancy of the lignite suspensions (*d* > 0.2 mm) at 25 °C

| No. | Lignite conc. (g/g) | Critical sphere flow rate (m/s) |
|---|---|---|
| 1[a] | 1.0 | $3.8 \times 10^{-5}$ |
| 2[a] | 1.25 | $9.0 \times 10^{-5}$ |
| 3[b] | 1.0 | $161.2 \times 10^{-5}$ |
| 4[b] | 1.25 | $459.8 \times 10^{-5}$ |

[a] Surfactant-free suspensions
[b] Surfactant-treated suspensions

## Conclusions

The aim of these measurements was to determine the rheological parameters of the flow curves of lignite suspensions. These systems had the characteristic of an increase in viscosity with increasing shear rate. The critical parameters of dilatant flow were determined for the lignite fraction (*d* > 0.2 mm) dispersed in an aqueous highly concentrated (pastelike character) dispersion. For original lignite suspensions these parameters were $4.0 \times 10^{-5}$ m/s for 1.0 g/g concentration and $9.0 \times 10^{-5}$ m/s for 1.25 g/g concentration. In an attempt to influence the non-Newtonian behavior of the lignite suspensions they were modified by surfactant addition. This triggered an increase in the values of the critical parameters of dilatancy by 2 orders of magnitude, i.e. to $160.0 \times 10^{-5}$ and $460.0 \times 10^{-5}$ m/s for 1.0 g/g and 1.25 g/g concentrations. It was interesting that the typical dilatant shape of the measured dependencies was not changed by surfactant addition.

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## References

1. Laun HM, Bung R, Hess S, Loose W, Hess O, Hahn K, Hadickek F, Hingmenn R, Schmidt F, Lindner P (1992) J Rheol 36:743–787
2. Frith WJ, Lips A (1995) Adv Colloid Interface Sci 61:161–189
3. Kulicke W-M, Arendt O, Berger M (1998) Colloid Polym Sci 276:617–626
4. Mikulášková B, Lapčík L'Jr, Lapčík L, Mašek I, Salyk O (1996) In: Palmer KR, Marx DT, Wright MA (eds) Carbon and carbonaceous composite materials. World Scientific Publishing, Singapore, pp 76–89
5. Mikulášková B, Lapčík L' Jr, Mašek I (1997) Chem Listy 91:160–168
6. Filgasová G (1997) Thesis. Technical University of Brno
7. Lide DR (1994) In: Table 15–39. In: Lide DR (ed) CRC handbook of chemistry and physics. CRC Press. Boca Raton, Table 15–39, p 15–39
8. Medinger MLW (1981) Höppler-Konsistometer Gebrauchsanleitung. Catalogue no. JeG 007 81 III 9 177. VEB Kombinat Medizin-und Labortechnik, Leipzig
9. Reynolds O (1985) Philos Mag 20:469
10. Hoffman RL (1972) Trans Soc Rheol 16:155