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ORIGINAL CONTRIBUTION

Untypical rheological behaviour of the lignite–carboxymethylcellulose–water dispersion system

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Abstract Suspensions of lignite in a solution of a high molecular weight carboxymethylcellulose show peculiar rheological behaviour. Unless the lignite concentration is sufficiently high, apparent viscosity and viscoelastic moduli of the suspension are lower than those of the pure solution. This effect is not suppressed by changing pH and seems to be common for low-concentrated suspensions in solutions of high molecular weight (bio)polymer. It is explained by specific structuring of the suspensions. Lignite particles at lower concentration separate long cellulose chains and facilitate their movement under shear flow. The particles loosen inter-chain contacts, disturb and release elastic gel-like structure formed by the long cellulose chains, which results in the low strain oscillatory deformation, the decrease in the moduli and the increase in the loss angle. If the amount of lignite particles is sufficiently high, suspension stiffening occurs as usual. No such effect was observed for suspensions prepared from the low molecular weight derivative.

Keywords Carboxymethylcellulose · Dispersion · Lignite suspension · Viscoelasticity · Viscosity

Introduction

We have already reported on rheological problems in processing lignite pastes to form extrudates for alternative lignite applications outside the power generation industry [1, 2]. We have also shown recently how these problems can be overcome using cellulose derivative as a rheological aid [3]. Because of the high concentration of solids, flow properties of lignite dispersions could not be studied using rotational rheometer, and Höppler consistometer should be used. This is more of a technological apparatus than a scientific device, with no precisely defined flow conditions and parameters. In this study, suspension concentrations were lowered so that the resulting dispersions were amenable to measurement in a rotational rheometer, and rheological behaviour of the system lignite–carboxymethylcellulose (CMC)–water could be investigated.

Rheological properties of CMC solutions are well documented. Ghannam and Esmail [4] investigated the concentration range 1–5% and found a nearly Newtonian behaviour at the lower concentration and pseudoplastic, thixotropic and viscoelastic responses at the higher end of the concentrations. They did not report the molecular weight of used biopolymer. Yet higher concentrations (5–8%) were studied by Edali et al. [5] who further confirmed non-Newtonian and viscoelastic behaviour. Kulicke et al. [6] established relationships between CMC molecular structure and rheological behaviour of its solutions (concentration range ca. 0.5–3%). They found that molar mass and concentration are governing parameters, whereas the degree of substitution has little influence and affected primarily the solubility. Clasen and Kulicke [7] reviewed the determination of viscoelastic and rheo-optical properties of various water-soluble cellulose derivatives. They summarised attempts to correlate viscosity data with the molecular structure parameters as well as studies on

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pseudoplastic flow behaviour of the solutions. Cellulose derivatives are known as rheological additives in various industry branches. For instance, Chandramalar et al. [8] examined hydroxyethylcellulose influence on the flow behaviour of titanium dioxide dispersion and found its shear-thinning effect depending on its molecular weight.

This work reports on the rheological behaviour of lignite suspensions prepared by dispersing the lignite in a solution of CMC of a given concentration, depending on the lignite loading. Two cellulosics of different molecular weight (high and low) were used.

Experimental

South Moravian (Czech Republic) lignite from the locality of Mikulèice [9] was used in our experiments. It was received in the pre-dried and milled state from the power plant. First, it was dried at 105 °C for 24 h and then sieved. Fraction captured between 0.1- and 0.2-mm sieves was used for subsequent experiments after moisture equilibration at ambient conditions. Moisture contents of lignite material used for preparation of pastes were thus within the range 5–7%. Because lignite particles are highly sticky, particles smaller than 0.1 mm were also presented in the used lignite fraction [3].

CMC (in the form of sodium salt) was supplied by Aldrich. Two preparations were used with the following producer's specifications: high molecular weight, M_w= 700,000 g/mol, degree of substitution, 0.9; low molecular weight, M_w=90,000 g/mol, degree of substitution, 0.7. Moisture contents were determined as 8.2 and 9.4%, respectively.

Suspensions were initially prepared by two procedures. In the one-step procedure, weighted amounts of lignite and CMC were suspended in corresponding amount of warm (70 °C) deionised water. Mixture was stirred for 1 h; temperature was maintained during the first 30 min only. In the two-step procedure, CMC solution was prepared at first using the same way as described above. After stirring for 1 h, weighted amount of lignite was added, and the mixture was stirred for another hour. Because preliminary tests revealed no significant differences in rheological behaviour, the one-step method was then used as the standard procedure.

Composition of samples is given in Table 1.

Table 1 Composition of samples prepared with 1% (w) of the high (HMW)- or 8% (w) of the low-molecular-weight (LMW) sodium carboxymethylcellulose

Sample	Water		Lignite
	HMW (wt%)	LMW (wt%)	
0	99	92	0
5	94	87	5
10	89	82	10
15	84	77	15
20	79	72	20
25	74	67	25
30	69	–	30

CMC also significantly facilitated preparation of suspensions and improved their stability. The lignite is of hydrophobic nature and poorly wettable by water. It was very difficult to prepare suspensions of lignite in water only because of the repulsive interactions between the particles and water, and to measure any properties because of rapid phase separation—part of lignite settled down at the bottom and part of it floated at the water level. No such effects were observed when the suspensions were prepared from CMC solutions, and these suspensions gave no noticeable stability problems. These observations indicate that lignite particles are really incorporated into the structure formed by the polymeric chains.

Measurements of the flow properties were carried out at 25 °C in the Haake RS100 rheometer equipped with the double cylinder sensor Z20 DIN both in the constant rate and constant stress modes. From the time flow curves, it was found that the longest time to achieve the steady state was about 150 s. However, shear stress–shear rate curves measured in the ramp regime and in the stationary regime (with the waiting time not greater than 300 s) showed no differences. Thus, the ramp regime with at least 50 data points in both measuring modes was used regularly. Preliminary tests on the time evolution of flow properties of the studied suspensions were made first. It was found that suspensions slowly matured during hours after preparation, and the numerical values of their rheological properties slightly changed (evolved). Two-day maturing was sufficient to obtain suspensions with stabilised rheological properties. Therefore, measurements were made both immediately after the suspension preparation (fresh suspension) and also after 48 h of maturing under laboratory temperature in a closed vessel to prevent water evaporation. All reported data points are averages from the three replicates. Relative deviation between two replicates never exceeded 5%.

Results and discussion

Flow curves

Lignite is of a physically and chemically heterogeneous nature. It was found that suspensions with high lignite loadings sometimes did not give quantitatively the same flow curves when prepared repeatedly, although retaining their qualitative features. Nevertheless, data reported in this work were obtained within the same lignite and suspension batch and showed real and reproducible trends in the rheological behaviour.

Figure 1 shows flow curves measured immediately after preparation of suspensions based on the high molecular weight cellulose derivative, with the increasing lignite contents (for the exact sample composition, see Table 1). The same trends were obtained after 48 h of sample maturing. Higher lignite loadings (15% and more) shifted the flow curves "up" to the higher shear-stress values, and on increasing lignite contents, also the apparent viscosity rose. On the contrary, flow curves for the low lignite loadings (5 and 10%) were situated below the curve of the blank CMC solution, and the suspensions had also lower apparent viscosities. The same trends were observed for the analogical samples prepared by the two-step procedure, which effectively means adding lignite to the same initial solution of CMC (concentration, 1%). Thus, adding lignite to the CMC solution does not increase its (apparent) viscosity as expected, unless the lignite concentration is sufficiently high.

Suspensions prepared from the low molecular weight cellulose derivative did not show this untypical behaviour. Increasing lignite concentration resulted in the increase in the shear stress under the same shear rate (cf. Fig. 2) and in the increase in the (apparent) viscosity as usual.

Measured flow curves clearly demonstrate differences in rheological behaviour of suspensions prepared from the low and high molecular weight CMC. These polymers differ in the rheological behaviour of their pure (i.e. not containing lignite) aqueous solutions (see Fig. 3). The low molecular weight preparation shows curves close to the Newtonian flow, whereas the high molecular weight material is clearly shear thinning. The figure also shows that it was not possible to obtain the solution of the high molecular weight derivative giving flow curves comparable to that of the solution of the low molecular weight preparation. Suspensions prepared from the solution of the high molecular weight derivative of higher concentration (1.2%), i.e. with higher apparent viscosity, did not show so strong viscosity-decrease effect—flow curve of the pure cellulosic solution was almost identical with the flow curve of the suspension containing 5% of lignite. Thus, unusual flow behaviour of lignite suspension in the aqueous solution of CMC is also contingent on the solution concentration.

Viscoelastic behaviour

Oscillatory measurements gave a little bit more complicated results. When measured immediately after preparation, suspensions prepared from the high molecular weight derivative (1% solution) showed an increase in both moduli with increasing lignite concentration. Measurements made after 48 h of maturing under laboratory temperature revealed the same effect as in the shear experiments—especially under lower frequencies, both moduli of pure cellulosic solution were higher than the moduli of the suspensions with 5 and 10% of lignite (see Fig. 4). In the case of suspensions

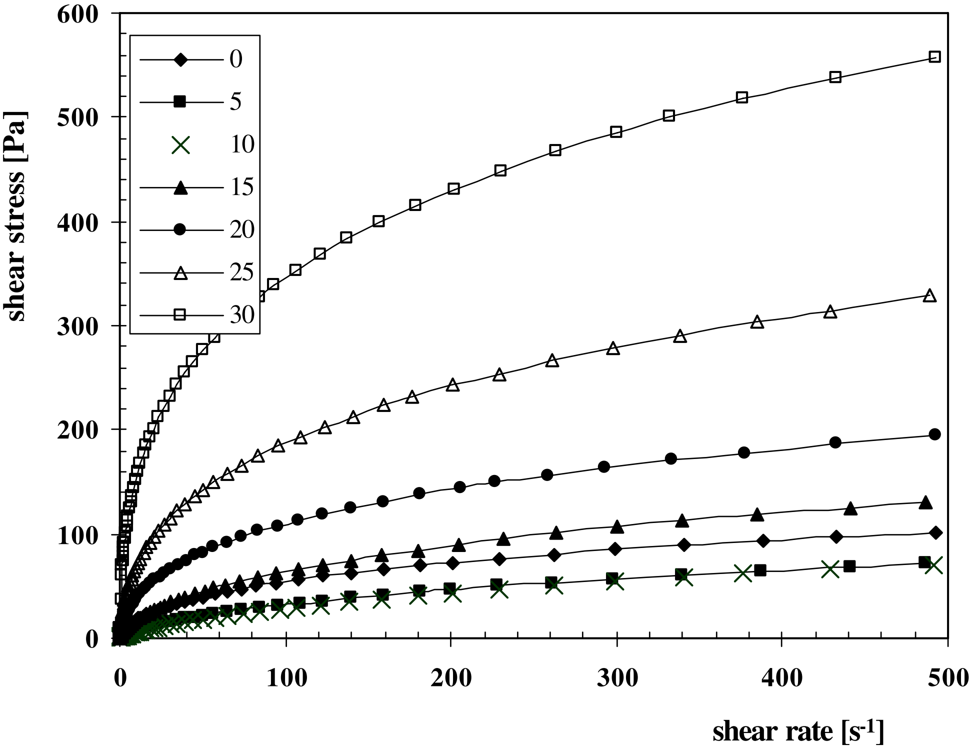


Fig. 1 Flow curves of dispersions prepared from the high molecular weight sodium carboxymethylcellulose and with various lignite contents (see Table 1)

Fig. 2 Flow curves of dispersions prepared from the low molecular weight sodium carboxymethylcellulose and with various lignite contents (see Table 1)

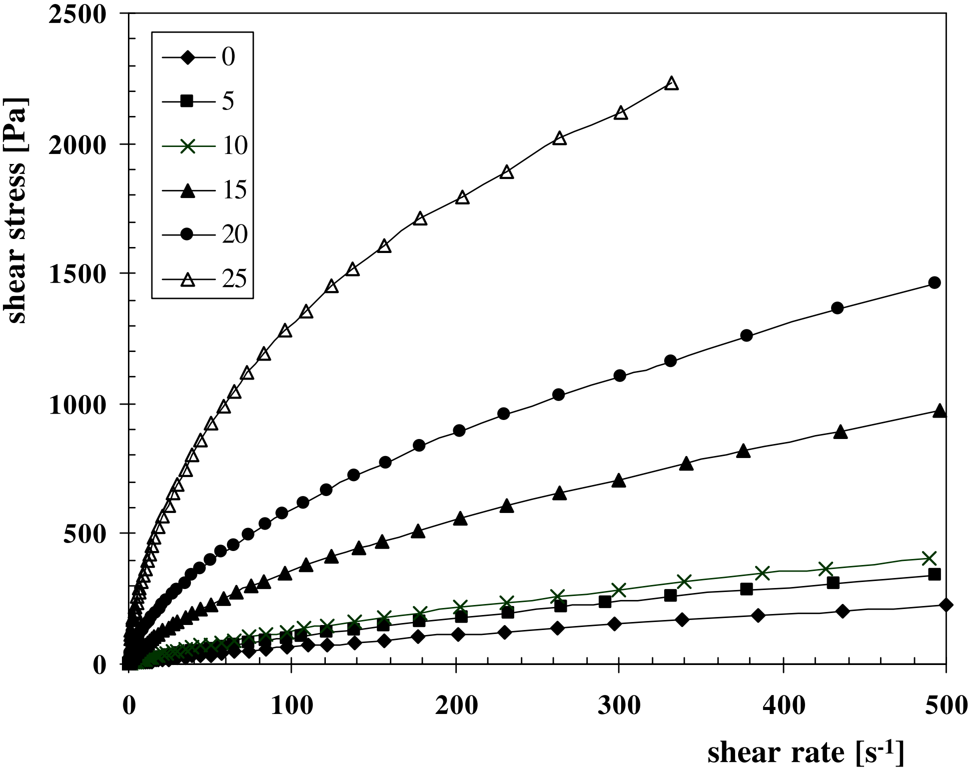
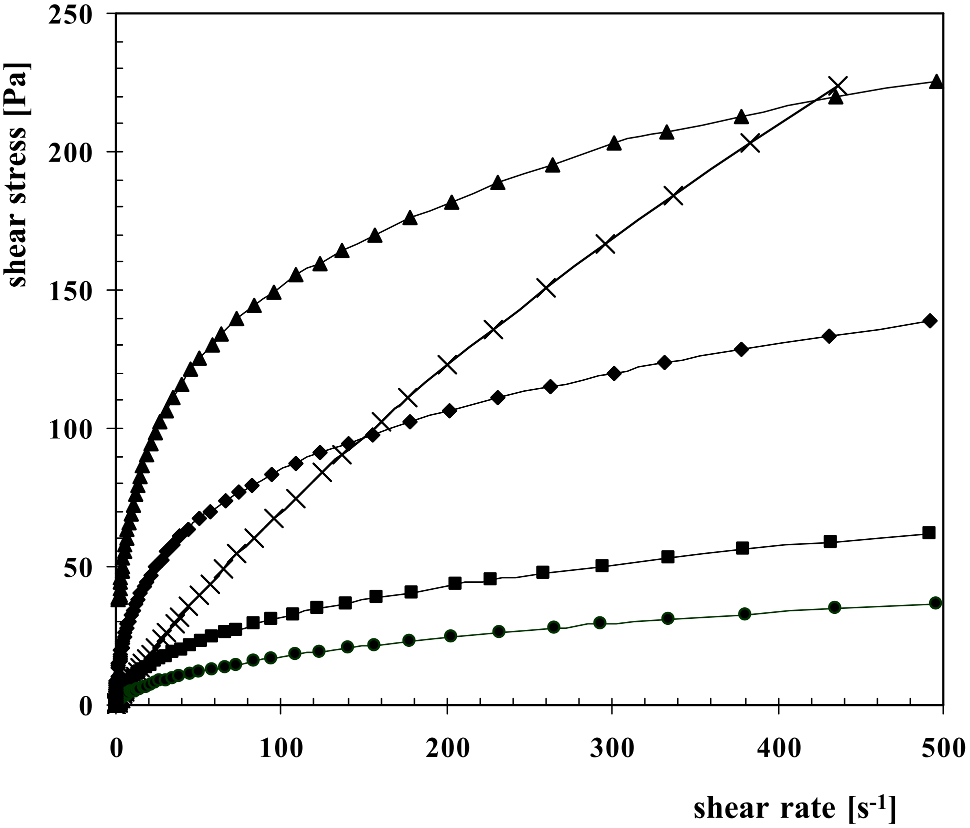


Fig. 3 Flow curves of solutions of the low molecular weight sodium carboxymethylcellulose (8%; *cross*) and of the high molecular weight sodium carboxymethylcellulose at various concentrations: 0.5% (*circle*), 0.8% (*box*), 1.2% (*diamond*) and 1.4% (*triangle*)



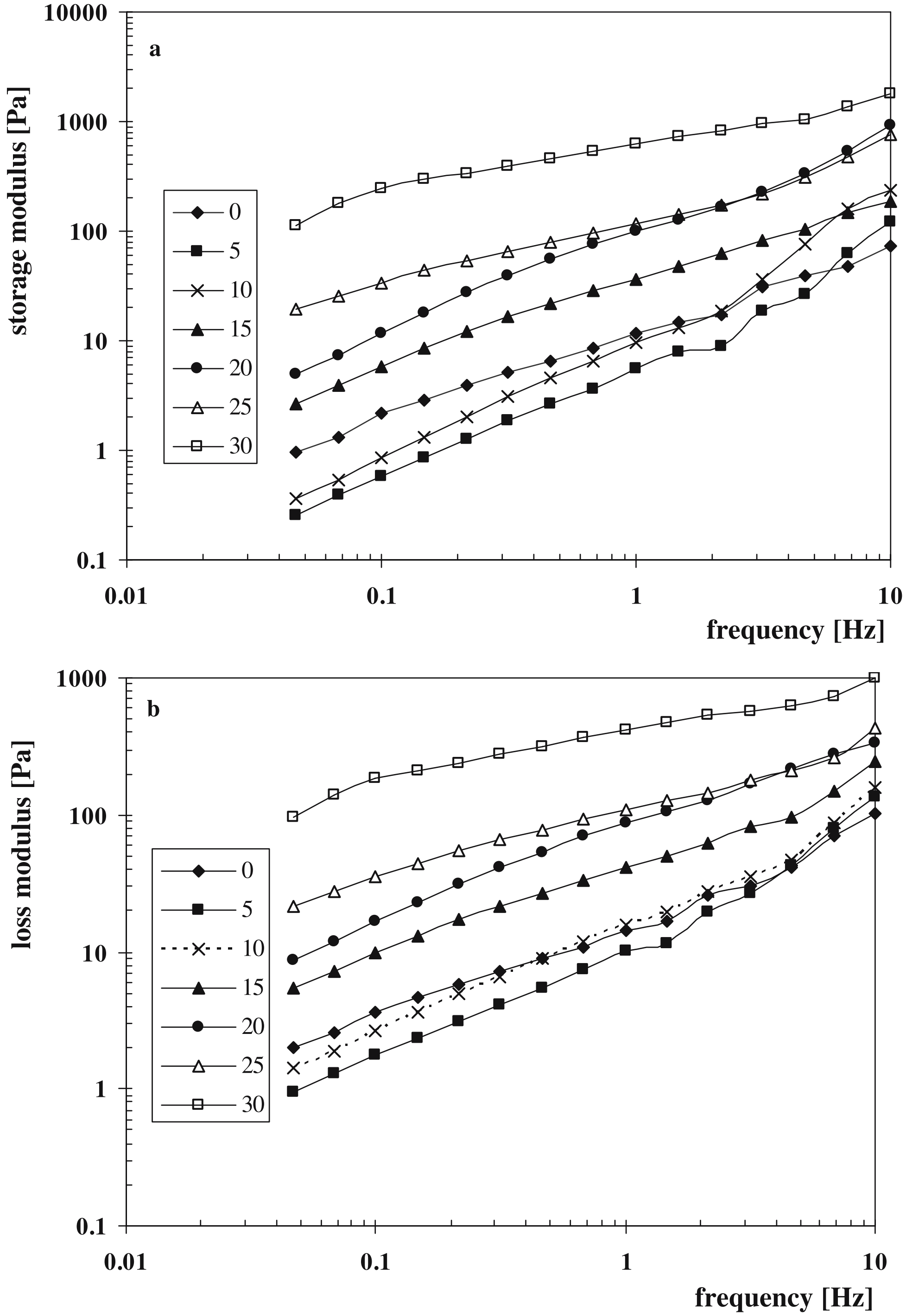


Fig. 4 Storage (**a**) and loss (**b**) moduli of dispersions prepared from the high molecular weight sodium carboxymethylcellulose and with various lignite contents (see Table 1) after 48 h of maturing

prepared from the low molecular weight derivative, both moduli of the pure solution were always lower than those of the suspensions of any tested concentration.

Relative values of the two moduli are represented by the loss angle in Fig. 5. Frequency dependence of the loss-angle tangent well illustrates the lignite effect on dispersion structuring. Lower lignite dose enhances loss-angle sensitivity to the frequency of deformation, especially under low values of the frequency. This indicates creation of slowly relaxing, long chain-like structures supporting liquid-like (viscous) behaviour of the dispersion. High lignite dose solidifies the dispersion and conduces to only slight dependence of the loss angle on the frequency. Curves for the 20 and 25% dispersions clearly show transition from the liquid-like to the solid-like behaviour at and above this concentration region. Concentrated dispersions evidently contain well-developed elastically active junctions between lignite particles and CMC chains. Some scatter of the loss-

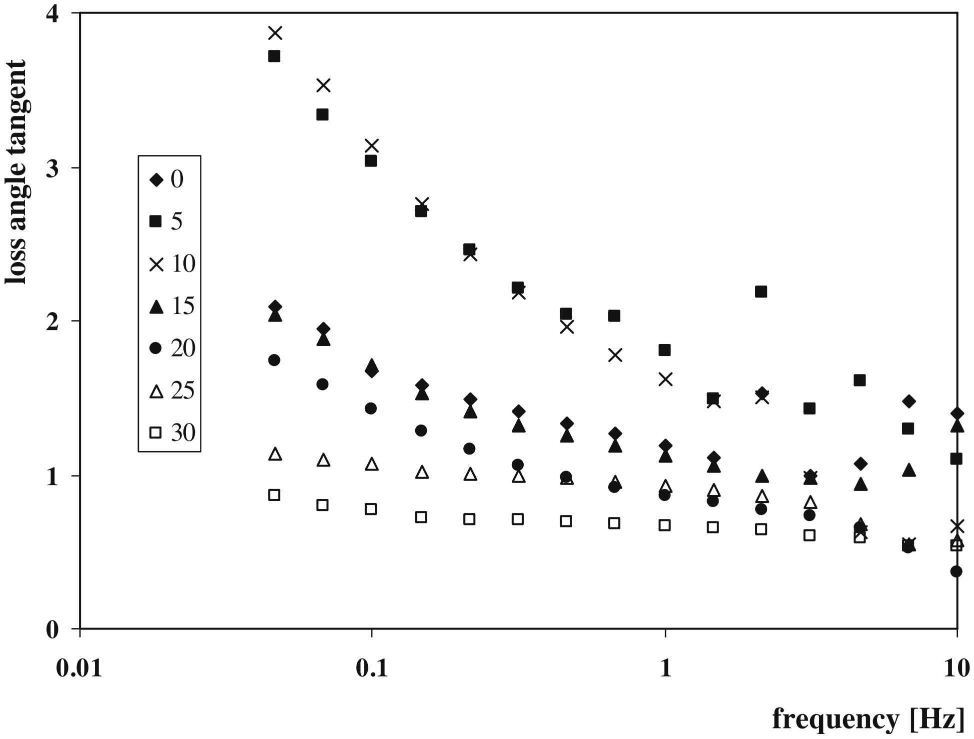


Fig. 5 Frequency dependence of loss angle tangent of dispersions prepared from the high molecular weight sodium carboxymethylcellulose and with various lignite contents (see Table 1) after 48 h of maturing

angle data for the low-concentrated dispersions at high frequencies indicates breaking the structures formed in the dispersions and, consequently, mechanical weakness of the structure-forming forces.

Data modelling

Measured flow curves can be adequately fitted by the Ostwald–de Waele model

$$\tau = K\dot{\gamma}^n$$

(τ is the shear stress and $\dot{\gamma}$ is the shear rate) which was also used, for instance, in [4]. The model parameters K and n reflected the influence of lignite on the suspension-flow behaviour. Figure 6a shows dependence of the model parameters on the lignite contents for suspensions prepared from the high molecular weight CMC. The flow coefficient K is minimum, whereas the flow index n is maximum corresponding to the position of the flow curves in Fig. 1. On the contrary, the model parameters obtained for the suspensions prepared from the low molecular weight derivative have only simple trends, i.e. the flow coefficient increases and the flow index decreases with the increasing lignite contents (Fig. 6b). For all samples, the flow index is lower than one, which corresponds to the observed shear thinning behaviour. If we consider the difference between the one and the particular value of the flow index as a measure of the shear thinning, then the addition of lignite to the aqueous solution of the low molecular weight CMC (at a given concentration) intensifies its shear-thinning properties. In the solution of the high molecular weight CMC, lower amounts of lignite “suppress” the shear thinning, i.e. shift the flow curves closer to Newtonian and only then start to support shear thinning. This probably indicates differences between properties of structures formed in solutions of low and high molecular weight derivatives and in solutions of the high molecular weight derivative with different concentrations of lignite. In the dispersion containing the low molecular weight derivative, some rigid structures are formed from lignite particles, cellulose macromolecules and water molecules as is common in suspensions. By the action of shear stress, the structure is broken, and shear-thinning behaviour is observed. The higher the lignite concentration is, the tougher the structure because lignite particles are its main constituents. In the dispersion prepared from the high molecular weight derivative, similar structures should be expected. However, at low lignite concentration, when the structure is broken by the stress action, lignite particles facilitate movement of long cellulose chains resulting in the decrease in apparent viscosity compared with the pure solution. A low number of lignite particles probably produce some “ball-bearing” effects [3], which enables easier flow of the long macromolecular chains compared with the state in the pure solution where they are in closer contact. Increasing concentration of lignite or cellulose derivative suppresses this effect because of the increasing number of interacting particles, i.e. increasing number of inter-particle contacts, and because of the decreasing free volume available to movement of lignite particles and slip of macromolecular chains.

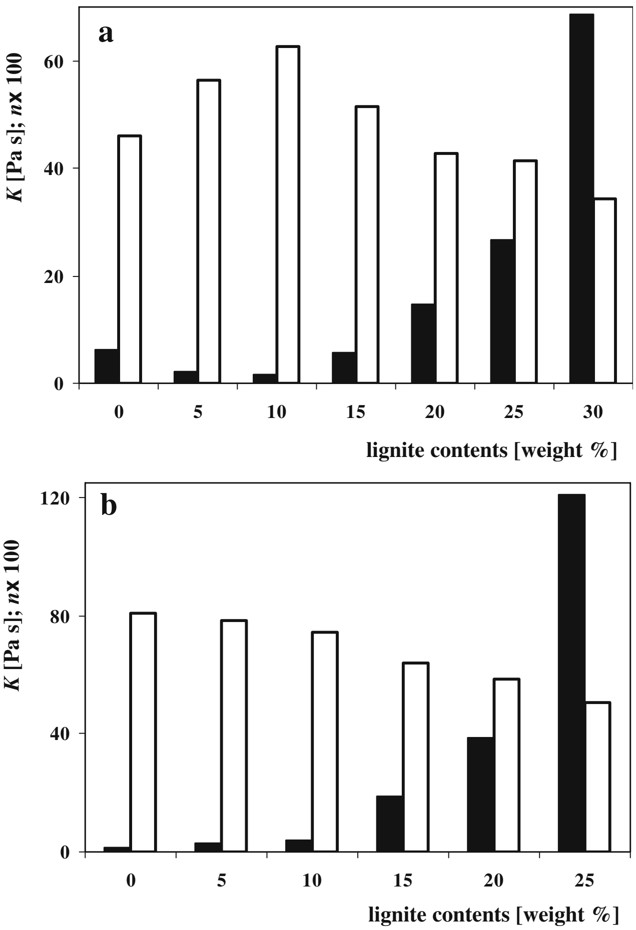


Fig. 6 Dependence of values of the flow coefficient K (■) and the flow index n (□) from the Ostwald–de Waele model on the lignite contents for dispersions prepared from the high (**a**) and low molecular weight (**b**) sodium carboxymethylcellulose

Dependence of the Ostwald–de Waele model parameters on the lignite content can be well fitted either by second-order polynomial or exponential, especially in the case of suspensions prepared from the low molecular weight CMC. The flow coefficient changes as follows: $K=1.13\exp(0.179w)$; the flow index, $n=-2.30\times10^{-04}w^2-6.81\times10^{-03}w+0.816$. w is the lignite percent contents. The dependences for suspensions made from the high molecular weight CMC could not be successfully fitted over all concentration regions but only from the 10% lignite contents, i.e. starting at the minimum K and maximum n. Resulting fitting equations are as follows: $K=0.297\exp(0.184w)$ and $n=4.63\times10^{-04}w^2-3.19\times10^{-02}w+0.895$. It can be seen that sensitivity of the flow coefficient to the lignite contents, expressed by the numeric factor in the exponential, is similar for both suspension types, and that dependence of the flow index on the lignite concentration is concave for the low molecular weight CMC-based suspensions, whereas that for the high molecular weight CMC-based suspensions is convex (cf. different signs of numerical factors at w^2).

Oscillatory experiments are done under much smaller deformations when the chain slip plays no substantial role. Lower moduli observed for suspensions with low lignite contents under low frequencies after 48 h should be the result of some weakening of the gel-like structure formed in suspensions immediately after the preparation. Lignite particles may perhaps absorb water molecules, which participate in the formed cellulose gel structure by hydrogen bonding during suspension maturing and thus release some junctions of the gel network. Lignite particles may slowly change the hydration shells of cellulose chains, change their conformation and disturb strength of structure formed from them.

Modulus-frequency curves were fitted by simple power models. Detailed results are given in the electronic supplementary material (Tables 1s and 2s). In this study, we only point out that both moduli are in the logarithmic coordinates virtually linearly dependent on the frequency (see Fig. 4). The slope of these straight lines is determined by the power parameter in the model. The slopes depend on the lignite concentration analogous to the flow index in Fig. 6—they decrease for the suspensions prepared with the low molecular weight CMC and have a maximum at 5–10% lignite contents for the suspensions prepared with the high molecular weight one. Effect of lignite on the suspension structuring and flow properties is thus matched both in shear and oscillatory regimes.

Study of effect of pH

We have also investigated the effect of pH on flow curves of dispersions prepared from the high molecular weight cellulose derivative. Because of the acidic nature of lignite, it is not easy to control the dispersion pH especially in the

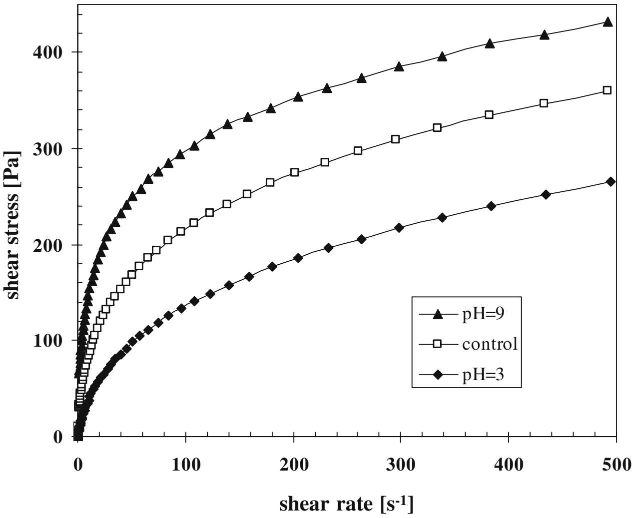


Fig. 7 Flow curves of dispersions prepared at various initial pH from the high molecular weight sodium carboxymethylcellulose and with 25% of lignite after 48 h of maturing

alkaline region. Acidic conditions (pH about 3) were set using concentrated solution of HCl, alkaline (pH about 9), with saturated solution of NaOH. Added volume of acid or hydroxide never exceeded 0.6%; therefore, no concentration correction to dilution was made. Generally, pH affected particularly the flow curves of concentrated suspensions, and its effect was more evident after 48 h of suspension maturing. The increase in pH shifted the flow curves “up,” i.e. to the higher values of shear stress for the same values of the shear rate. The decrease in pH manifested just the opposite effect. An example is shown in Fig. 7 for 25% suspension after 48 h of maturing. Whereas pH of acidic suspension almost did not change during maturing (from 2.9 to 3.1), pH of alkaline suspension decreased from 9.4 to 6.0.

It should be stressed that change of pH did not change succession of the flow curves—that of pure CMC solution was still above those of low-concentrated suspensions. The decrease in pH is supposed to protonize acidic functional groups (their dissociation degree is reduced) and suppress electrostatic interactions. On the contrary, the increase in pH can ionise (weak) acidic groups and also neutralise them by the sodium ions. Because the effect of pH is evidently dependent on lignite concentration, protonization relates to lignite particles. Electrostatic interactions thus contribute to the flow properties of studied dispersions but most probably are not the cause of observed untypical flow behaviour of low-concentrated lignite suspensions and have very little effect on it.

On the role of humic acids

We have also speculated on the potential role of humic acids on the rheological behaviour of studied dispersions. Lignite is well known for relatively high contents of humic acids [9], which could perhaps be leached out during suspension preparation. Humic acids are used as rheologically active agents, e.g. in drilling mud. Suspensions prepared with the solid humic acids isolated from lignite at concentration 0.5% showed the same peculiar behaviour on their flow curves. On the other hand, tests on CMC solutions prepared from the sols of water-soluble humates did not display any such rheological effect of the humates. These experiments confirmed the principal role of mechanical causes and solid particles in observed rheological behaviour of lignite–CMC–water suspensions. Further confirmation comes from experiments done with suspensions of sand or glass particles in CMC solutions where the same peculiar rheological behaviour was observed under low concentrations [10]. These particles also represent much better defined material systems than lignite that is a complex mixture with a non-homogenous structure and properties (and was used here because of our interest in technologies of its non-fuel utilization). Consequently, the decrease in apparent viscosity with the increase in suspension concentration is not a lignite-specific phenomenon.

Conclusions

Lignite suspensions prepared from the (liquid-like) aqueous solution of high molecular weight sodium CMC show untypical flow behaviour under both shear and oscillatory deformation. Apparent viscosity or loss and storage moduli of the suspensions are lower than those of the pure CMC solution, unless the lignite concentration is sufficiently high (above about 10% by weight). These effects are not observed in the suspensions prepared from the solution of the low molecular weight cellulosics and are not suppressed by changing suspension pH. Lignite particles at lower concentration separate long cellulose chains and facilitate their movement under shear flow. The particles loosen inter-chain contacts or entanglements, disturb and release elastic gel-like structure formed by the long cellulose chains, which in the low strain oscillatory deformation results in the decrease in moduli and the increase in the loss angle. If the amount of lignite particles is sufficiently high, the usual suspension stiffening occurs and the apparent viscosity and the moduli increase, whereas the loss angle decreases. The observed effects seem not to be specific for lignite but common for low concentrated suspensions in solutions of high molecular weight (bio)polymers.

Our previous work [3] reported on the specific rheological effect of cellulose derivatives in lignite pastes. Thus, rheological specialities can be observed on both concentration limits of the lignite–CMC–water dispersions.

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