

Rheological Properties of Bentonite Suspensions Modified with Polymers

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ABSTRACT

For the application in geotechnics, bentonite suspensions were modified and tested for their rheological behaviour with different devices. Two bentonite types and several polymers with different charge types were used. Whereas anionic polymers worked for both bentonites, cationic polymers influenced only one bentonite.

INTRODUCTION

Bentonite suspensions are commonly used in civil engineering. They are used e.g. for the construction of diaphragm walls or slurry shield tunnelling. Here, bentonite suspensions stabilize the soil during the excavation process and remove the excavated material. The stabilizing effect is dependent on both the soil type and the composition of the suspension. Usually, the suspensions consist of water and approximately 40 kg bentonite per m³ suspension. Bentonite consists mainly of the clay mineral montmorillonite which has a high swelling capacity. The montmorillonite layers form a three-dimensional network. The faces of the layer are negatively charged, whereas the edges carry positive charges. The net layer charge is negative, which is balanced by exchangeable cations, typically Na⁺ or Ca²⁺, in the interlayers.

In general, the above mentioned construction methods are well suited for loose sandy soils with relatively low porosity. However, in the future and already

today, more and more constructions are built in difficult ground. Therefore, nowadays, there is also a demand to use these construction methods in coarse, highly permeable soils. With the commonly used bentonite suspensions, a loss of suspension into the coarse soil is likely and cost-intensive, but what is more, there is a risk of soil collapse. To improve the stabilizing effect, bentonite suspensions can be modified e.g. with polymers. In the studies presented below, bentonite suspensions were modified with different polymers in different concentrations and their rheological behaviour was investigated with various devices.

MATERIALS AND METHODS

Bentonite

Two different types of bentonite were used, in the following named bentonite A and B. Some parameters of the characterisation of the bentonites are summarized in Table 1. Bentonite A is a natural sodium bentonite with Na⁺ ions in the montmorillonite interlayers. Bentonite B is an activated calcium bentonite, which means the Ca²⁺ ions in the interlayers were replaced by Na⁺ ions. The suspensions were made by dispersing bentonite powder in desalted water. Different bentonite concentrations were considered, namely 60 and 70 kg of bentonite A per m³ suspension and 35 and 40 kg/m³ of bentonite B.

Table 1. Selected characteristic parameters of bentonites A and B.

Parameter	Bentonite A	Bentonite B
CaCO ₃ -content	< 5%	12%
Cation exchange capacity (CEC)	98.6 meq/100g	80.2 meq/100g
Particles < 2µm	83.6%	38.8%

Polymers

Polymers are large molecules of repeating units and can adsorb on the clay particles. Table 2 gives an overview of the used polymers.

Mixing procedure

For the production of the suspensions, bentonite and water were mixed with an IKA Ultra-Turrax T50 (Janke and Kunkel GmbH & Co., Germany) for 10 minutes by 3000 rpm, the diameter of the dispersing disk was 42 mm. The swelling time was 24 hours. After the swelling time, a 1 vol. % polymer solution was added in an amount to gain either 0.05 or 0.1 vol. % polymer per m³ suspension. The suspension was then mixed with the Ultra Turrax for 5 min and subsequently with an ordinary mixer of 240 Watt for 60 seconds.

Methods

All tests were carried out under equal conditions in the laboratory to allow for comparison of the results. The samples were prepared and tested at a temperature of about 20°C.

Table 2. Overview of polymers.

Polymer	Type of charge	Charge (meq/g)	Molecular weight (g/mol)
P1 Polyacrylamide	cationic	3.94	250000
P2 PolyDADMAC	cationic	6.06	2000000
P3 Polyethyleniminacetat	cationic	13.43	60000
P4 Polyamin	cationic	7.03	250000
P5 Polyethyleniminacetat	cationic	14.01	500000
P6 CMC low viscosity	anionic	no information	100000
P7 Polyanionic cellulose	anionic	3.80	800000
P8 Polyethylenimin	neutral	-	750000

Rheological measurements were carried out with different devices. A Physica rheometer MCR300 with a plate-plate geometry was used with the upper plate being profiled. In addition, simple devices generally used on construction sites were applied. These are Marsh funnel, “Kasumeter” and “Kugelharfe”. Table 3 shows the rheological measuring devices.

Table 3. Rheological measuring devices (for details see Heinz and Hermanns Stengele³, 2003).

Name of device	Short description
Physica MCR300	rheometer with plate-plate geometry
Marsh funnel	flow cup
Kasumeter	capillary viscosimeter
Kugelharfe	immersion of balls with different weight

Yield point measurements were performed with Kugelharfe, Kasumeter and rheometer. With the rheometer, the cross-over points from amplitude sweep tests were evaluated as “yield points”.

The thixotropy was measured with the rheometer in a three stage oscillatory test. In the first stage, the structure is measured at rest (linear viscoelastic region) and the storage modulus G' is monitored against time. In the second stage, the sample is subjected to high shear load (out of the linear viscoelastic region). The third stage is a repetition of the first stage, but with a longer measuring duration. The values for

G' at time t in the third stage and at the end of the first stage are compared to get information about the structure recovery.

RESULTS AND DISCUSSION

Yield point

The results of the yield point measurements are shown in Tables 4 and 5. It is interesting that for bentonite B, the cationic polymers P1 - P5 do hardly affect the yield point or Marsh flow time when compared to the suspension without polymer. For bentonite A, the yield point or Marsh flow time increases in the order none < P1 < P2 < P5 < P3 < P4. There is no direct correlation with the molecular weight or charge of the polymers.

With the anionic polymer P6, a decrease of the yield point or Marsh flow time is registered for both bentonite A and B, whereas the addition of polymer P7 leads to an increase, compared to the respective suspensions without polymer. The influence of the non-ionic polymer P8 is for bentonite

B insignificant. For bentonite A, the results are comparable to those of P1. In general, all measuring devices give qualitatively the same results, with the Kugelharfe being the least sensitive instrument.

Fig. 1 and 2 show yield points measured with the rheometer for suspensions with polymer P3 and bentonite A or B in different concentrations. The figures are typical examples for the measurements of the suspensions with cationic polymers: For bentonite A, the increase of the yield point with both concentration of bentonite and polymer is clearly visible. This cannot be found for suspensions with bentonite B.

In contrast to the cationic polymers, an increase of the yield point with concentration was found for suspensions with the anionic polymer P7. This applies for both bentonite A and B. The influence of the concentration on the yield point measurements is presented in Fig. 3 and 4.

Table 4. Yield points and Marsh flow time for suspensions with 60 kg/m³ bentonite A and 0.05 vol. % polymer.

Polymer	Yield point (Pa)			Flow time t(1000 ml) (s)
	Rheometer (cross-over point)	Kasumeter	Kugelharfe	
none	6.9	3.8	9.9	45.8
P1	9.8	7.5	18.0	56.4
P2	12.6	10.8	25.0	65.9
P3	17.5	15.7	39.7	81.6
P4	19.0	16.7	39.7	88.7
P5	17.2	15.7	39.7	79.7
P6	2.6	1.1	6.8	44.6
P7	11.7	6.1	13.7	83.9
P8	9.5	7.1	18.0	54.6

Table 5. Yield points and Marsh flow time for suspensions with 35 kg/m³ bentonite B and 0.05 vol. % polymer.

Polymer	Yield point (Pa)			Flow time t(1000 ml) (s)
	Rheometer (cross-over point)	Kasumeter	Kugelharfe	
none	5.1	2.6	13.8	35.1
P1	4.9	2.9	13.8	36.0
P2	4.8	3.0	13.8	36.3
P3	4.6	3.1	13.8	37.0
P4	4.9	3.4	13.8	37.4
P5	5.1	3.6	13.8	37.4
P6	3.6	1.0	10.0	34.6
P7	9.9	3.8	13.8	42.5
P8	4.4	2.3	13.8	34.9

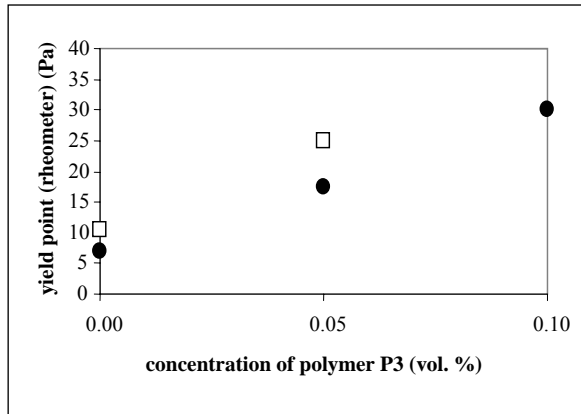


Figure 1. Yield points of suspensions with bentonite A (● 60 kg/m³, □ 70 kg/m³) and polymer P3 in different concentrations.

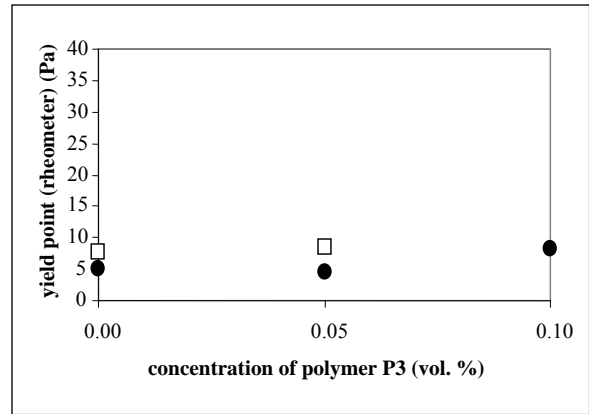


Figure 2. Yield points of suspensions with bentonite B (● 35 kg/m³, □ 40 kg/m³) and polymer P3 in different concentrations.

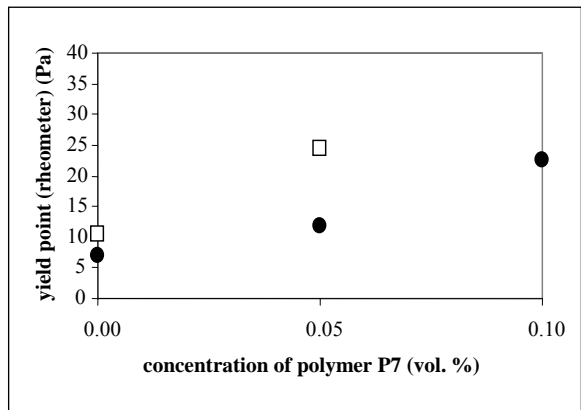


Figure 3. Yield points of suspensions with bentonite A (● 60 kg/m³, □ 70 kg/m³) and polymer P7 in different concentrations.

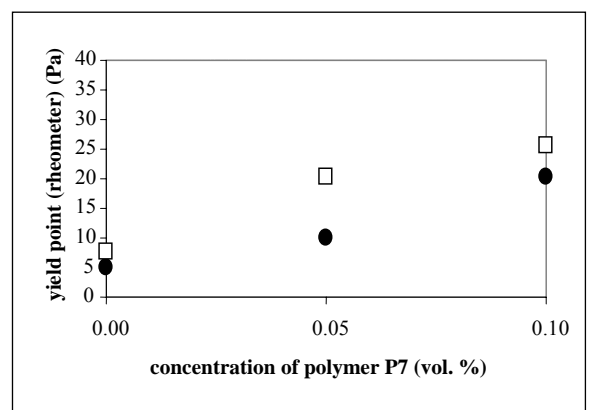


Figure 4. Yield points of suspensions with bentonite A (● 60 kg/m³, □ 70 kg/m³) and polymer P7 in different concentrations.

Cationic polymers adsorb via coulombic interactions between cationic groups on polymer and negatively charged clay surfaces (Breen, 1999)¹. Bentonite B has a lower cation exchange capacity (CEC) than bentonite A, i.e. the surfaces are of lower anionic charge. Thus, fewer contact points for cationic polymers are available. However, the major influencing factors on the rheological behaviour are particle structure and texture of the bentonite type (Brandenburg and Lagaly, 1988, Lagaly, 1989)^{2,5}. Bentonite B is possibly composed of compact stacks of layers (tactoids)

whereas bentonite A has separated layers, offering a greater area for polymer adsorption. The higher CaCO₃-content and the coarser particle sizes (Table 1) indicate that the layers of bentonite B are somehow cemented as a result of the activation process.

Anionic polymers can be adsorbed on the positively charged edges of the clay particles (Jasmund and Lagaly, 1993)⁴. Thus, the influence of tactoids is less important, as the edges are still accessible. The ratio of the clay surfaces to the edges seems to be significant: The more tactoids, the more edges and the fewer surfaces are

available for polymer adsorption. Consequently, the adsorption of anionic polymers is more effective than the adsorption of cationic polymers.

Thixotropy

The results of the thixotropy tests are shown in Tables 6 and 7.

Table 6. Results of thixotropy tests with 60 kg/m³ bentonite A and 0.05 vol. % polymer.

Polymer	Structure Recovery (%)
none	78
P1	70
P2	72
P3	77
P4	75
P5	75
P6	107
P7	98
P8	74

Table 7. Results of thixotropy tests with 35 kg/m³ bentonite B and 0.05 vol. % polymer.

Polymer	Structure Recovery (%)
none	100
P1	95
P2	90
P3	82
P4	82
P5	85
P6	137
P7	126
P8	93

The structure recovery is very high for the suspensions with anionic polymers. A structure recovery of more than 100% means that the structure after the shear load is stronger than before. It seems that during the shearing phase, tactoids were delaminated and in the subsequent phase of rest, further linkings between polymer and clay layers could form.

CONCLUSIONS

The modification of bentonite suspensions with cationic polymers influenced the rheological properties for the natural sodium bentonite, but not for the activated calcium bentonite. Addition of anionic polymers changed the rheological behaviour of both bentonites. With polyanionic cellulose, an increase of the yield point was found. For the application of bentonite suspensions in geotechnics, a modification with polyanionic cellulose is recommendable. Further knowledge about the stabilizing effect of suspensions with polymers or other additives can be gained with penetration tests on permeable soils. These are currently performed at the Clay Mineralogical Laboratory of the Institute of Geotechnical Engineering of ETH.

ACKNOWLEDGMENTS

Many thanks to the staff of the clay mineralogical laboratory of the Institute of Geotechnical Engineering.

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