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Polymer modification of bentonite: impact of molar mass

Modification du polymère de la bentonite: impact de la longueur de la chaîne polymère

W. Lieske
Ruhr-University, Bochum, Germany

R. Verst
University of Wuppertal, Wuppertal, Germany

G. Di Emidio
UGent, Ghent, Belgium

W. Baille
Ruhr-University, Bochum, Germany

ABSTRACT: The potential of polymers to improve the structural stability and hydro-mechanical behaviour of clays with respect to engineering application was demonstrated in several studies. However, only few studies set focus on the impact of the basic polymer composition on the soil mechanical behaviour of the modified clay, rather than exclusively focusing on the properties of the modified clay. The current study addresses the importance of the polymer chain length on the plasticity, the compression behaviour and the micro fabric of a modified bentonite. Cationic polymers of varying molar mass were used to produce a modified bentonite by wet-mixing. Mixtures were directly tested without prior drying. Another series of tests was performed on a material which was dried and grinded after wet mixing. The results indicate a significant impact of the chain length on the liquid limit and a moderately pronounced impact on the compression behaviour. Drying and grinding yields a significant deviation of the material performance in terms of plasticiy and compression behaviour.

RÉSUMÉ: Le potentiel des polymères pour améliorer la stabilité structurelle et le comportement hydromécanique des bentonites par rapport à une application donnée a été démontré dans plusieurs études. Cependant, peu d'études ont mis l'accent sur l'impact de la constitution du polymère de base sur le comportement mécanique du sol de l'argile modifiée. La présente étude aborde l'importance de la longueur de la chaîne polymère sur les propriétés plastiques et le comportement mécanique d'une bentonite modifiée. Des polymères cationiques de différentes longueurs de chaîne sont utilisés pour produire une bentonite modifiée par mélange humide. Les mélanges ont été directement testés sans séchage préalable. Une autre série d'essais a été réalisée sur un matériau qui a été séché et broyé après mélange humide. Les résultats indiquent un impact significatif de la longueur de la chaîne sur la limite de liquidité, ce qui était moins remarquable pour le comportement en compression. Le séchage et le broyage donnent lieu à des écarts importants du comportement du matériau en termes de comportement plastique et de compression.

Keywords: Polymer modification, cationic polymer, bentonite, mechanical behaviour, polymer bridging

1   BACKGROUND

Polymers are utilised in several geotechnical and geo-environmental applications to modify soil-water-interaction, soil structure and strength properties. In particular fine grained soils such as clays are modified by the addition of polymers to enhance strength properties in tunneling (Zumsteg et al., 2013), to inhibit swelling during tunneling (Alexanderson, 2001) and drilling processes (Anderson et al., 2010), and to improve the structural and chemical stability in clay liners (Ashmawy et al., 2002; De Camillis et al., 2016; Razakamantsoa et al., 2014) or natural clay barriers (Daniels et al., 2003), to name a few.

In this context, polymer is used as a general term for long-chained macromolecules composed of several repeating units, namely monomers. Polymers can be categorised regarding ionic charge (positive, negative, neutral), polarity (polar, non-polar), structure (linear, branched, cross-linked) and molar mass, which equate to the length of the particular polymer chains for a linear polymer (Theng, 2012, Ward, 1981). Unlike ordinary molecules or oligomers, polymers in a solvent may change their conformation depending on the boundary conditions, e.g. pH-value, concentration, temperature (Fleer et al., 1988, Roiter & Minko, 2005). In solution, flexible non-ionic linear polymers adopt a coiled form while charged polymers exhibit a more stretched conformation (Theng, 2012).

When polymers enter into contact with clay, the functional groups of the polymer can interact with clay faces (basal planes and edges), exchangeable cations and water molecules, which in turn leads to altered surface properties and water interaction of the modified clay (Theng, 2012). The thermo-dynamical behaviour of polymers in solution and the interaction with charged and uncharged solids highly depends on the polymer characteristics, the nature of the solids and the quality of the solvent (Theng, 2012; Fleer et al., 1988). The adsorption of polymers to clay surfaces is considered to be irreversible due to the high number of binding sites (Theng, 2012). When conditions during mixing allow particular chains to attach themselves to more than one clay particle, polymer bridging takes place (Bergaya, 2006). On the macroscopic scale, polymer bridges might induce an irregular behaviour (Chenu & Guerif, 1991).

The impact of fundamental charge properties of the polymer and the mineralogy of the clay on the engineering properties of the modified product has been outlined in literature (Haase & Schanz, 2016). Some studies emphasise the importance of the polymer conformation on the engineering behaviour of modified clays (Inyang & Bae, 2004; Halder et al., 2018). However, molar mass as a fundamental parameter for the characterisation of polymers has not been studied in detail with regard to the engineering properties of a modified clay.

In the framework of the present research, a systematic study on bentonite modified with cationic polymers was conducted with special emphasis on the importance of polymer characteristics. Cationic polymers (polycations) are polymers containing positively charged monomers. The number of charged monomers in the polymer chain, called ionicity, has a major influence on the interaction between the polymer and the clay surface (Breen, 1999). When adsorbed to negatively charged surfaces, polycations lead to charge neutralization and compression of the diffuse double layer (Theng, 2012; Haase & Schanz., 2016). Cationic polymers absorb in 'patches' rather than covering the whole surface in a homogeneous way. This effect yields 'patch flocculation' since positively charged patches are attracted by the unaltered negatively charged clay surfaces (Szilagyi et al., 2014). In addition, polymer bridging is an important factor in cationic modification, since the stretched geometry of a cationic polymer chain and the strong bonding of the cationic parts to the negatively charged surface of a clay give perfect boundary conditions for a linking of different clay particles. On the macroscopic

scale, effects that arise from a modified physico-chemical behaviour and bridging effects are superimposing (Theng, 2012).

In geotechnical applications, polycations are used for structural stabilisation through aggregation (Inyang & Bae, 2005) and increase of mechanical strength due to the addition of an additional attractive force (Chenu & Guerif, 1991). Due to aggregation and charge neutralisation in clays, polycations lead to an increase in permeability (Di Emidio et al., 2017; Inyang & Bae, 2005).

In the current study different clay–polymer mixtures are studied, which were obtained by wet-mixing. The raw materials are a natural Wyoming bentonite (MX80) and cationic polyacrylamide copolymers, flexible chain polymers of linear structure, with varying molar mass. The macroscopic behaviour was studied with regard to compression behaviour, determination of engineering index properties (plasticity) and micro fabric. Subsequently, the impact of reconstitution (drying and grinding) was analysed.

2 EXPERIMENTAL PROGRAM

The experimental programme of this study is designed to characterise the impact of the polymer chain length on the mechanical and index properties of a modified bentonite. Microstructural investigations were carried out to link observations made on the macroscopic scale to microscopic properties.

2.1 Material

Three commercially available unbranched co-polymers containing polyacrylamide are used in
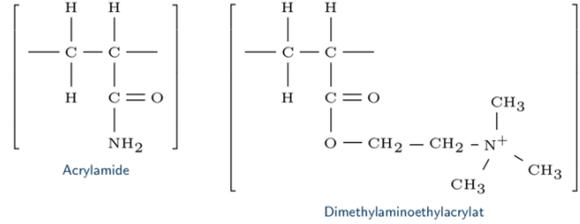

Figure 1. Molecular configuration of the monomers

the present work, which differ according to man-ufacturer specification in their average molar mass. An exact specification of the method used to determine molar mass is not given. The poly-mer chains are composed of a polyacrylamide backbone and cationic functional groups. The chemical formula is given in Figure 1, while rel-evant information about molar mass and ionicity are given in Table 1. The bentonite used is a nat-ural bentonite (MX80) which is frequently stud-ied in literature. Exchangeable cations are domi-nantly sodium with minor amounts of calcium (Tripathy et al., 2004).

The bentonite is suspended by stirring bentonite powder (initially smaller than 1 mm) in deinonized water for 12 hours using an agitator with a paddle blade. The water content is chosen to obtain a final water content of $10 \cdot w_L$ (liquid

Table 1: Properties of the bentonite, polymer, and modified bentonite

	Bentonite	**PAA$^+_{short}$**	**PAA$^+_{medium}$**	**PAA$^+_{long}$**	**PAA$^+_{short,dried}$**
Ionicity [%]	-	40			
Molar Mass [g/mol $\cdot 10^6$]	-	3.5-4.5	7.0-9.5	9.5-12	3.4-4.5
Ratio Polymer/bentonite [-]	-	0.236	0.185	0.191	0.236
Liquid limit w_L [%]	588*	461.4	543.4	633.3	167.7
Plastic limit w_P [%]	37*	98.7	108.6	122.9	80.8
Shrinkage limit w_S [%]	14*	9.99	9.14	9.95	-
C_c [-]	6.46*	1.1-1.9	-	1.24-1.90	0.42
C_s [-]	1.95*	0.22	-	0.31	0.10

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*(Haase & Schanz, 2016)

limit). Therefore, approximately 41 g of dry bentonite are suspended in one liter of deionised water. The polymer is dissolved in water in accordance with the polymer/clay ratios given in Table 1 (adsorption maximum) and then admixed with the bentonite suspension. The procedure to determine the maximum absorbability of polymer is described in detail in Haase & Schanz (2016). Large flocs form during the mixing process of the polymer suspension with the bentonite suspension. After stirring for 12 hours, the material is centrifuged off in a laboratory centrifuge. The target water content for the compression tests is achieved by adding distilled water to the centrifuge residues.

Another series of tests is carried out on short-chain modified material which is first dried to constant mass at 40 °C and then milled to obtain a powder < 1mm. The characteristics of the bentonite and the polymers used and the plasticity properties as well as the shrinkage limit of the modified bentonite are given in Table 1. Figure 2 shows the effect of polymer modification in the plasticity chart.

Plasticity is determined using the Casagrande method according to DIN 18122-1. The shrinkage limit was determined according to DIN, whereas the volume of the shrunken sample was determined by the wax method in accordance with DIN EN ISO 17892-2.

2.2 Compression-decompression behaviour

The mechanical behaviour of the polymer-modified bentonites is investigated in a high pressure oedometer. The material is gradually loaded to 1600 kPa and then unloaded. A detailed description of the equipment is given in Baille et al. (2010). The previously dried material is tested in a conventional oedometer up to 800 kPa and then unloaded.

The polymer modified bentonites were tested from slurry condition (1.1 w_L). A first loading step of approximately 5 kPa is applied to prevent
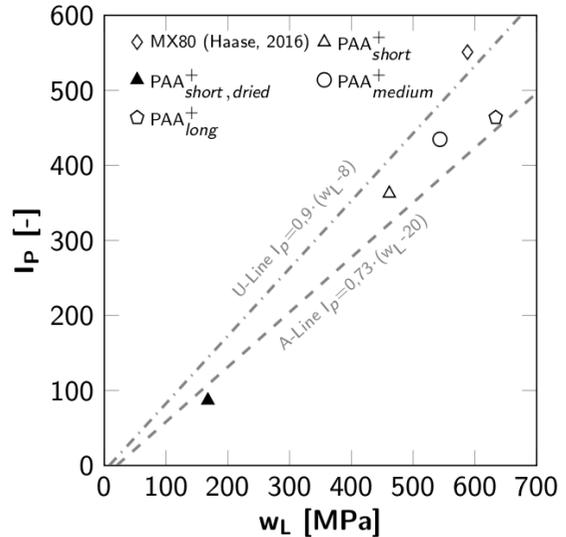

Figure 2. Classification of the materials in the plasticity chart

material to be sqeezed out of the oedometer due to high excess pore water pressure.

2.3 Microstructural investigations

The material obtained from the mixing of bentonite modified with the polymer of medium chain length was studied using a scanning electron microscope. The material was directly taken from the residues in the centrifuge and afterwards frozen in liquid nitrogen be able to inspect the sample in an hydrated configuration. The sample was cut using a diamond saw and afterwards polished using a broad ion beam. Sublimation of the upper water layer was conducted before starting the imaging.

3 RESULTS AND DISCUSSION

3.1 Index properties

The liquid limit values of the modified material decrease with decreasing average chain length of the polymer. However, in particular the experimental determination of the liquid limit for the PAA^+_{long} shows a certain scattering during the

test, which might be due to gradual destructuration or polymer bridge break off during mixing. However, the results of the modified material do not show a clear trend in comparison to the unmodified material. While the long-chained polymer reaches values above the unmodified material, the short chain is attributed to a significant decrease of the liquid limit. This comparison shows that opposite effects arising from polymer-clay-interaction are superposing on the macroscopic scale. Bridging stabilizes a porous structure since it limits the level of freedom to deform of the clay matrix, whereas the positive parts of the polymer adsorbed on the smectite surface neutralize the negative charge of the smectite and therefore reduces the amount of physico-chemically bond water.

The same order found for the liquid limit was found for the plastic limit, starting with the highest value for the bentonite mixed with long-chained polymer to the lowest value for the bentonite mixed with short chained polymer. However, all values of the modified material are higher than the results of the unmodified material.

The results of the shrinkage limit tests for the modified material are equal and smaller than the unmodified material. Since the results do not correlate with the average chain length, it can be concluded that polymer bridges are to weak to hinder shrinkage, irrespective of chain length of the polymer.

Similarity of the values obtained for the shrinkage limit indicates a drying induced alteration of material properties. This might caused by flocculation which is made possible by the reduction of the distances between the clay surfaces during the shrinkage process.

Similar observations are made for the material which was dried after centrifugation and milled to a powder. A significant reduction of liquid and plastic limit was oberserved, resulting in a drop of the material below the A-Line in the Casagrande chart. According to the plasticity properties obtained, the modified product is no longer classified as an inorganic clay of high plasticity but rather as an organic clay.
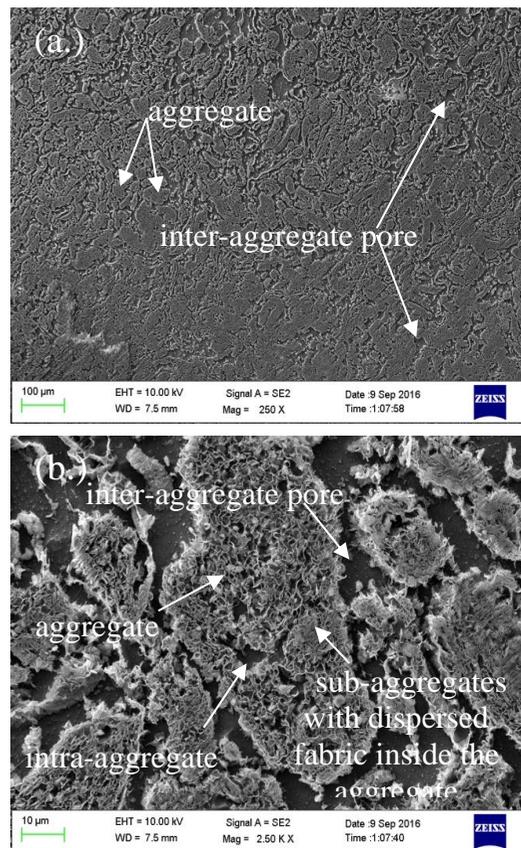

Figure 3. Cryo-BIB-SEM photographs of bentonite modified with medium molar mass poly-acrylamide

3.2 Microstructure

After mixing the bentonite suspension and the polymer solution, large aggregates could be seen with the blank eye. The shape of the aggregates is strongly influenced by the mixing method. The viscosity of the mixture and the applied mixing energy (here in the form of a paddle) lead to an elongated shape of the aggregates. Shear energy introduced during mixing influences the shape and size of the aggregates and polymer bridges may crack during stirring (Yu et al., 1979).

Figure 3 shows photographs of the microstructure in different magnifications. The images show an open-pored structure with a complex inter-aggregate and intra-aggregate pore distribution. When looking at larger areas, it can be seen that the dimensions of the aggregates are more than 100 micrometers.

Polymerbridging may stabilize the open-porous structure and prevent surfaces getting close enough to attract each other and thus form large floccs.

3.3 Compression-decompression behaviour

The compression behaviour of PAA^+_{short}, PAA^+_{long}, $PAA^+_{short,dried}$, and natural MX80 (Haase & Schanz, 2016) is compared in Figure 4. During virgin compression both modified materials show a comparable compression index which is much stiffer than the unmodified material. At this point, it should be taken into account that the void ratio of the modified bentonite was calculated based on the mass of the bentonite including polymer. The void ratio of the clay matrix in the mixture can therefore only be compared qualitatively with the pure bentonite.
This difference is even more pronounced for the modified material after drying and milling. The compression coefficient of the material is even below the swell coefficient of the natural bentonite. During unloading, all modified materials show a significantly lower volume increase due to swelling compared to the natural material which exhibits pronounced swelling.

Taking into account the obervations made on the microstructure and the plasticity behaviour, different effects arising from the polymer modification may dictate the engineering behaviour of modified bentonite.

Cationic polymer adsorbed on the smectite surface reduces repulsive forces due to compensation of the negative charge of the clay. Patch charges might induce an additional attractive force when positively charged polymer patches are attracted by free negatively charged clay surfaces. Polymer bridges induce an additional stabilizing force by connecting the clay components and thus, reducing the degree of freedom to rearrange in a denser state during compression. This is also supported by findings on the microstructure (Figure 3). However, the behaviour induced by the polymer bridges can cause a mechanical behaviour which cannot be captured by common soil mechanical concepts. When polymer bridges become mechanically overloaded, they irreversibly tear off (Yu et al., 1979). In contrast, coagulation by patch flocculation is considered reversible because the
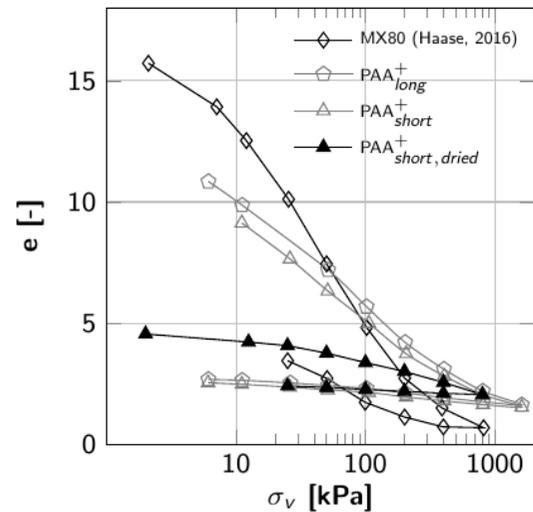

Figure 4 Volumetric behaviour of the tested materials in the oedometer compression device

attraction between the particles is very weak.

4 CONCLUSIONS

Polymers are of growing interest for the modification of fine-grained soils in engineering applications. In particular the modification of bentonite gained frequent attention in the field of geotechnical research and applications. It has been demonstrated in literature that both: polymer composition and conformation are crucial for the polymer-clay interaction.

However, the attribution of fundamental polymer properties to the engineering behaviour of modified bentonite is lacking.

The focus of the present study is set on the importance of moalr mass on the engineering properties of bentonite modified with polycations. The investigations show that the consideration of individual effects resulting from the change in surface properties or bridging alone is not sufficient to explain the macroscopic behavior of the bentonite-polymer mixtures. The influence of the polymers is based on a complex overlay on different levels. As fundamental mechanisms of the polymer-clay interaction on the microscale, the compensation of the negative charge of the smectite surface, patch flucculation, and polymer bridges were discussed. Some conclusions can be drawn as follows:

1. Molar mass is a crucial polymer property with a pronounced impact on the index properties of modified bentonite.
2. Polymers might induce properties which are beyond common soil mechanical behaviour.
3. High stresses and treatment (drying and grinding) cause an irreversible change of material behaviour which can be linked to a change in the dominating effect on the microscale.

5 ACKNOWLEDGEMENTS

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