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INFLUENCE OF ORGANIC POLYMER MODIFICATION ON PHYSICOCHEMICAL PROPERTIES OF BENTONITES

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In the studies we used bentonites hydrophobically transformed through surface modification with organic polymers. They were compared with commercially available bentonites modified with polymers of the Teq gel HD, Swell gel as well as with the pure Fluka bentonite and local bentonites, originating from Zakłady Metalowo-Górnice Zębic. Alterations in physicochemical properties were demonstrated using scanning electron microscopy, dynamic light scattering, elemental analysis and X-ray techniques. Elemental analysis confirmed bentonite processing with polymers in cases of Teq gel and Swell gel samples. Morphological and particle size studies demonstrated a destructive effect of polymer modification on bentonite structure including evidently decreased diameter of particles and agglomerates.

Key words: bentonite, polymer intercalation, nanocomposites

INTRODUCTION

Many scientific centres around the world have recently aimed their studies at the potential for production and application of stratified silicate – polymer nanocomposites (Gemeay, 2002; Kacperski, 2002; Park, 2002). The bentonite exhibits a hydrophilic character and, therefore, its application in hydrophobic systems requires that its surface is modified to increase its affinity to organic radicals (Breakwell, 1995). Offered by us schematic mechanism of the modification is shown in Fig. 1. At the first stage, delamination of bentonite should be followed by ionic exchange.

Ions contained in interpacket spaces (sodium ions are most favourable but also calcium and magnesium ions) are exchanged to monomer particles. Subsequently, the monomer particles in bentonite matrix is subjected to polymerisation. In this way the

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intercalate structure nanocomposite is obtained of an unordered array or in an intermediate form. Bentonite is a mineral of extremely variable composition which varies significantly depending upon the source of origin (Breen, 1988; Benito, 1998, Christidis, 1998; Cara, 2000; Wieczorek, 2001). Principal physicochemical properties of bentonites are shown in Table 1 (Wypych, 1999; Murray, 2000).

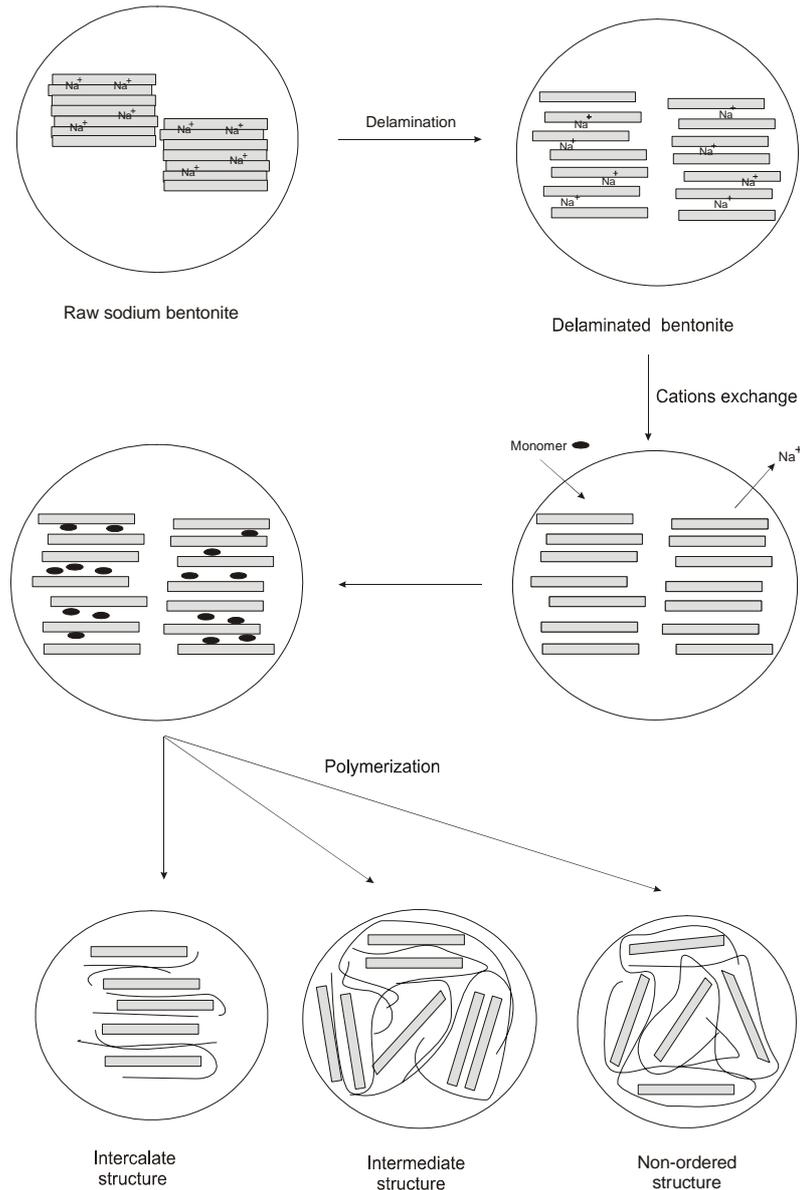


Fig. 1. Schematic of bentonite-nanocomposite generation.

In this paper, the following question was considered: How does intercalation of bentonite with polymer influence its basic properties? The influence of intercalation was examined on shape and size of bentonite molecules, capacity to absorb water, exo- and endothermic transformations in a temperature gradient. Various analytic techniques were used, traditionally applied in studies on nanocomposites.

Table 1. Physicochemical properties of bentonites

Chemical formula	$(\text{Na, Ca})(\text{Al, Mg})_6(\text{Si}_4\text{O}_{10})_3(\text{OH})_6 \cdot n\text{H}_2\text{O}$
Chemical composition, (%)	$\text{SiO}_2 - 56-72$; $\text{Al}_2\text{O}_3 - 13-21$; $\text{Fe}_2\text{O}_3 - 0.9-5.0$ $\text{MgO} - 1.7-2.4$; $\text{CaO} - 0.7-2.2$; $\text{Na}_2\text{O} - 0.3-2.7$; $\text{K}_2\text{O} - 0.2-0.3$
Trace elements	As, Ba, Cd, Pb, Se, Hg
Density, (g/cm^3)	1.6-3.0
Mohs hardness	1-2
Loss on ignition, (%)	8.4-11.9
Moisture content, (%)	2-14
pH of water suspension	7-10.6
Water solubility, (%)	3
Color	white; cream; grey, tan, light green
Particle size, (μm)	0.18-1
Oil absorption, ($\text{g}/100\text{g}$)	36-52
Swelling	high
Specific surface area, (m^2/g)	50-300
Applications	drilling muds, foundry binders, paints, coatings, paper, sealants, adhesives, polymer fillers, pharmaceuticals

EXPERIMENTAL

MATERIALS

The following materials were used for comparative studies: pure montmorillonite MMT (Fluka), Izol and Specjal Extra U activated local bentonites made in Zakłady Metalowo-Górnictwa "Zębiec" and bentonites modified with polymer compounds, Teqgel HD (Heads) and Swell gel (Phrikolat).

METHODS

The identification analysis involved studies using WAXS technique. The results were analysed employing XRAYAN software (Marciniak, 1998). The diffraction patterns were executed employing the horizontal diffractometer TUR-M62. Nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) was used in the measurements. The following measuring conditions were employed: anode voltage - 30 kV, anode current - 25 mA the measurement range of 2θ : $3-60^\circ$, measuring step - 0.04° .

Particle size and particle size distribution, also representing principal properties of bentonites, were measured taking advantage of the dynamic light scattering (DLS)

technique, using optoelectronic systems of ZetaPlus apparatus. Aqueous suspension of the filler was stabilised, placed in a cuvette and particle size distribution of the sample was measured using equipment of Brookhaven Instruments, USA.

Moreover, the zeta potential results were estimated using electrophoretic light scattering (ELS) also on ZetaPlus equipment.

Examinations of particle shape and morphology were conducted using scanning electron microscopy (SEM). The observations were performed with the Phillips SEM 515 microscope.

The bentonite material and functionalised silica samples were characterised by quantitative elemental analysis (C, H and N analysis) using the automatic type EA 1108 instrument (Carlo-Erba). The studies of water wettability of selected bentonites were carried out using K-100 tensiometer (Krüss).

RESULTS AND DISCUSSION

Physicochemical properties of examined bentonites are listed in Table 2. In Teqgel HD bentonite, elemental analysis showed the carbon content of 1.4%. Unmodified bentonites contained, approximately, 0.4% of carbon. The increased amount of carbon in Teqgel HD bentonite was a consequence of bentonite modification process using the polymer.

Table 2. Examined properties of bentonites

Bentonite	Teqgel HD	Swell gel	MMT	Izol	Special extra U
Moisture content, (%)	14.76	12.14	7.00	8.41	8.69
Loss on ignition at 600°C, (%)	5.86	1.24	4.44	3.49	4.65
Mean particle diameter, (nm)	716.1	637.8	773.8	565.0	615.4
Polydispersity	0.218	0.102	0.211	0.005	0.228
Zeta potential*, (mV)	-38.35	-37.19	-21.81	-41.44	-41.35

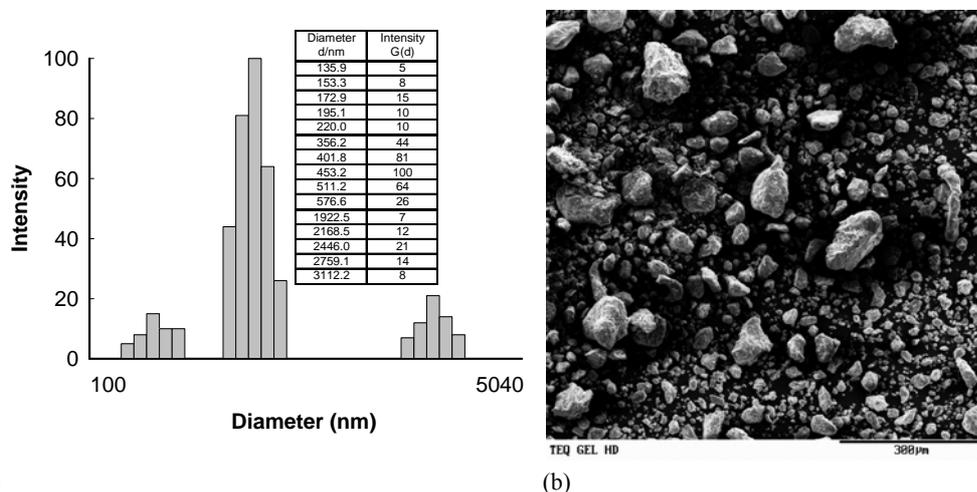
* at pH=6.5

Studies on electrokinetic (zeta) potential provided evidence for high stability of dispersion of tested minerals. The montmorillonite, which is the active component of bentonite, without additional salt contamination, demonstrated the lowest absolute zeta potential value (-21.81 mV). The impurities markedly affected adsorptive character of the studied mineral in a water solution. The occurrence of primary particles in the form of larger clumps, i.e. aggregates or agglomerates was characteristic for all samples of studied bentonites (Fig. 2a-6a). The diameters of bentonite particles were within the range of 560 – 770 nm. Teqgel HD and Swell gel bentonites manifested three ranges of particles size. Monmorillonite, which represent pure chemical form of bentonite also demonstrated three ranges of particles size. In

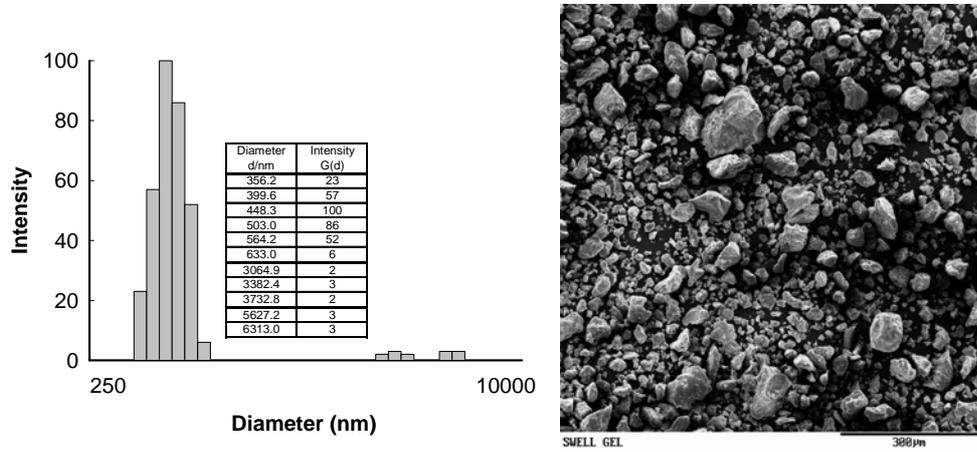
this case, a relatively vast “fraction” of primary particles and of aggregates was present. An almost monodisperse character was shown by particles of Izol bentonite (not activated with polymers) (Fig. 5a). Its range of particle diameters was 561-574 nm. Polydispersity of the bentonite showed the lowest value, 0.005 (Table 2). Particle size distribution of Specjal extra U bentonite, not modified with polymers, is shown in Fig. 6a. An intense band of primary agglomerates was present in the range of 189 – 874 nm. As predicted, MMT, Izol Specjal Extra U bentonites demonstrated a primary packet structure and their particles manifested the form of more or less deformed flakes (Figs. 4b-6b). On the other hand, samples of Teqgel HD and Swell gel bentonites had the shape of irregular blocks. This was probably caused by mechanical processing of the material, mainly during activation by the polymers.

Studies on wettability in water of selected bentonites (Fig.7) showed that, in comparison with bentonites activated by polymers, the sample of Izol had a significantly higher affinity to water. The extent of hydrophobic transformation was the highest in the case of Teqgel HD bentonite.

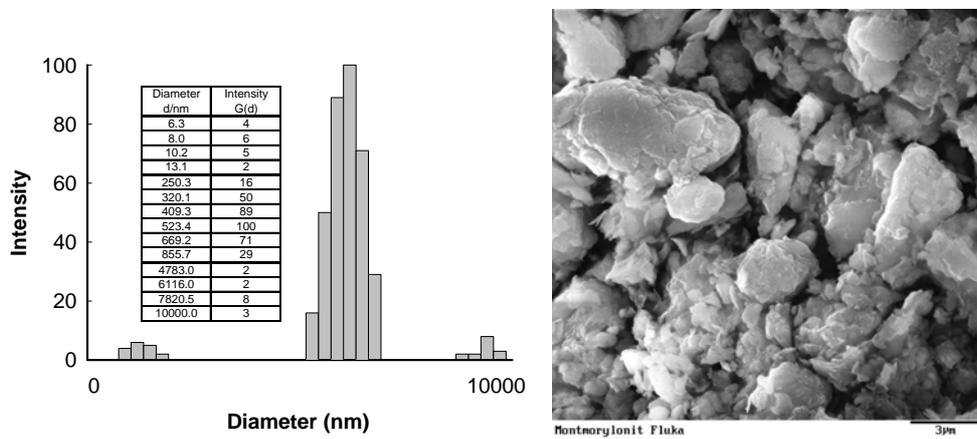
X-ray curves of the Teqgel HD and Swell gel bentonites (Figs. 8 and 9) demonstrated maximum intensities within the ranges typical for smectite group minerals. Analysis of inter-pack distances, determined using Bragg’s equation, proved that no polymer intercalation took place to inter-pack spaces of the clay. The bentonite-polymer interaction was exclusively of the physical adsorption nature.



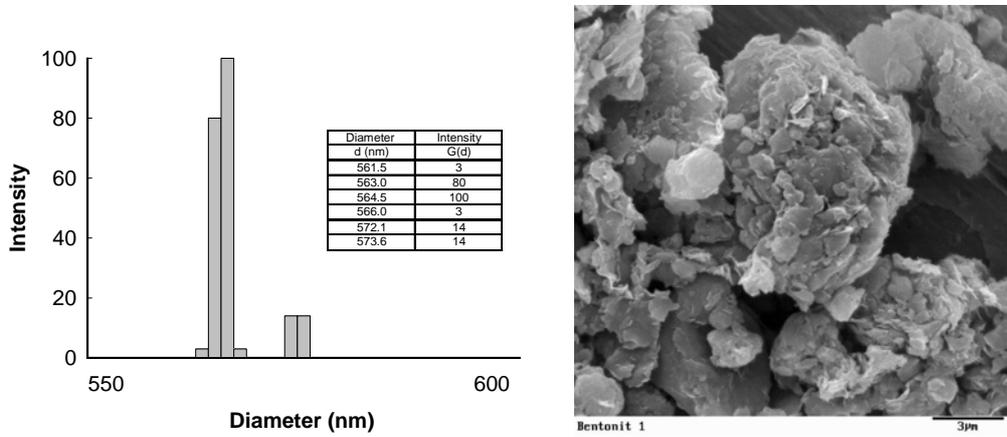
(a) Fig. 2. Teqgel HD bentonite (a) multimodal particle size distribution (b) SEM micrograph.



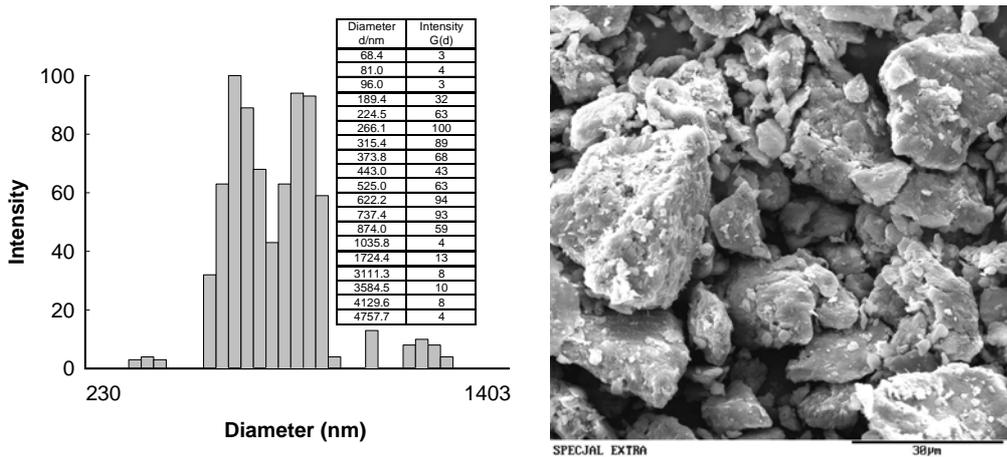
(a) (b)
 Fig. 3. Swell gel bentonite (a) multimodal particle size distribution (b) SEM micrograph



(a) (b)
 Fig. 4. Bentonite MMT (a) multimodal particle size distribution (b) SEM micrograph



(a) (b)
Fig. 5. Izol bentonite (a) multimodal particle size distribution (b) SEM micrograph



(a) (b)
Fig. 6. Specjal Extra U bentonite (a) multimodal particle size distribution (b) SEM micrograph

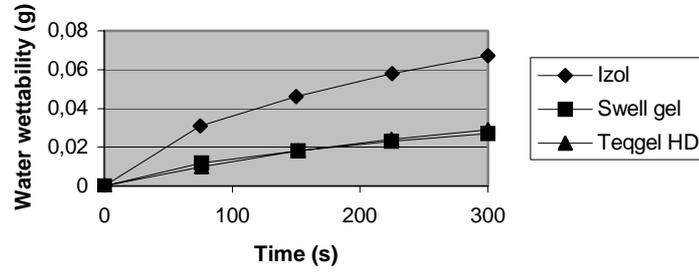


Fig. 7. Dependence of water wettability of bentonites in time

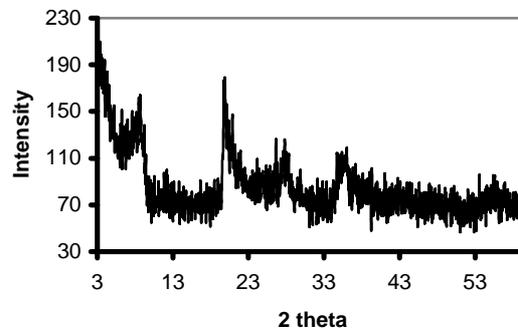


Fig. 8. WAXS pattern of Teqgel HD bentonite.

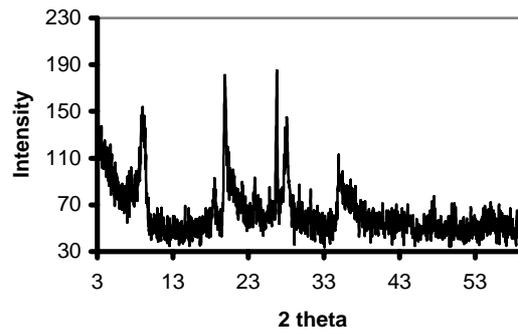


Fig. 9. WAXS pattern of Swell gel bentonite

CONCLUSIONS

The Teqgel HD bentonite contains around 2% of organic modifiers, whereas Swell gel contains approximately 0.5% of organic compounds. The bentonite modifiers contain no nitrogen atoms, thus excluding application of amines and quaternary ammonium salts. The studied bentonites exhibit a surface structure typical for modified bentonites, in which destruction of primary structure takes place. Nevertheless, they partially preserve their stratified microstructural morphology. Activation with organic compounds fails to significantly affect size of particles (aggregates) of studied bentonites (mean particle diameter approximates 700 nm). Also zeta potential acquires almost identical values for unactivated and polymer-activated bentonites (the exception involves MMT). The enclosed X-ray patterns of studied minerals illustrate their crystalline structure, typical for the smectite group. No polymer intercalation takes place to the inter-packet spaces.

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Wieczorek M., Jesionowski T., Krysztafkiewicz A., *Wpływ modyfikacji polimerami organicznymi na właściwości fizykochemiczne bentonitów*, Physicochemical Problems of Mineral Processing, 37 (2003) 131-140 (w jęz. ang.).

W badaniach wykorzystano bentonity hydrofobizowane przez powierzchniową modyfikację polimerami organicznymi. Porównywano komercyjne bentonity modyfikowane polimerami o symbolach Teq gel HD, Swell gel oraz czysty bentonit z Fluki i bentonity krajowe pochodzące z Zakładów Metalowo-Górnictw Zębic. Zmiany w właściwościach fizykochemicznych wykazano wykorzystując następujące techniki: skaningową mikroskopię elektronową, dynamiczne rozpraszanie światła, analizę elementarną oraz technikę rentgenowską. Analiza elementarna potwierdza obróbkę bentonitu polimerami w przypadku próbek Teq gel i Swell gel. Badania morfologiczne i wielkości cząstek wykazały wpływ destrukcyjny modyfikacji polimerami na strukturę bentonitu oraz spowodowały wyraźne zmniejszenie średnic cząstek i aglomeratów.