PREPARATION AND CHARACTERISATION OF UNMODIFIED AND POLY(ETHYLENE GLYCOL) GRAFTED MAGNESIUM HYDROXIDE

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Abstract: The method for the synthesis of either unmodified magnesium hydroxide or functionalised with poly(ethylene glycols) of different molecular weights and physicochemical properties of the products are presented. Magnesium hydroxide was obtained by the precipitation method under well defined conditions from ammonia solution and different magnesium salts. Dispersive properties of the products were characterised by polydispersity index, particle size, as well as SEM images. Crystalline structure of magnesium hydroxide samples were determined by the WAXS method. To confirm the presence of functional groups introduced by appropriate modifiers the samples were subjected to spectroscopic analysis. Electrokinetic stability of the studied samples was determined on the basis of zeta potential dependence vs. pH measurements. The modification has resulted in reduction of particle diameters in some $Mg(OH)_2$ samples.

Introduction

$Mg(OH)_2$ is usually precipitated from solutions of magnesium salts by a precipitating agent which usually is a strong base such as NH_4OH (Fellner 2011, Wang 2007; 2011) or NaOH (Pilarska 2011, Song 2011, Veldurthi 2012). The most often used precursors of magnesium are inorganic salts such as $MgCl_2$, $MgSO_4$ and $Mg(NO_3)_2$. Sometimes organic compounds of magnesium are used, e.g. $Mg(CH_3CO_2)_2$ (Alvarado 2000). Parameters of the process have a considerable influence on the structure and morphological−dispersive properties of the products. For this reason the choice of

optimum conditions of the process that would lead to obtaining products of target properties has been of profound interest to many research groups.

Most often the influences of the rate and direction of reagent dosing, their concentrations, mass and volume contributions, temperature of precipitation and calcination, and methods of drying have been studied (Wang 2005, Wang 2007, Yun 2009).

According to the recent literature data, the final properties of materials, in particular their morphology, are strongly related to the types of precursor and precipitating agents applied (Wang 2011; Pilarska 2012). Recently, besides the main reagents increasingly often the modifying compounds are involved in syntheses of chemical compounds. Modification of the reaction system by introducing an additional organic or inorganic chemical substance, leads to changes in the properties of the products including those in the product surface. The purpose of such modification of the original properties of the reaction products is first of all to increase the activity and selectivity of catalysts based on $Mg(OH)_2$. Modification can also bring improvement in the dispersion and insulating properties of sintered ceramic materials, and sometimes in development of surface area of the material modified (Azhari 2010; Tang 2011). Introduction of organic modifying compounds is particularly important when inorganic compounds such as magnesium hydroxide should be bound to organic compounds such as polymers. The modification results in changing the hydrophilic character of the surface into hydrophobic, which improves the compatibility of the composite components and has beneficial influence on its mechanical properties (Wei 2008; Chen 2009). Organic modifying compounds are also applied to help reduce the magnesium hydroxide particle size and develop their surface area. The majority of the hitherto used modifiers have been relatively expensive. Recently much interest has been paid to the use of PEG type compounds as modifiers PEG (Wang 2007; Wang 2011). Poly(ethylene glycols) are not only cheap but they also have a beneficial effect on the microstructure and surface character of magnesium hydroxide (Pilarska 2012).

One of the parameters characterising functional properties of chemical materials is zeta potential. It is a measure of electrostatic interactions between molecules/partilces and permits estimation of stability of colloidal dispersion of a system that is a tendency to coagulation of particles limited by the repulsive forces between them. This also informs about the magnitude of electric charge in direct vicinity of the solid state surface and has been widely used for quantitative evaluation of the electric charge on the double electric layer (Kosmulski 2001; Jesionowski 2003).

The aim of the study presented is analysis of the influence of the modifiers applied on the dispersive and physicochemical properties of $Mg(OH)_2$ samples obtained in precipitation reaction and discussion of their potential use.

Experimental

The substrates used for the synthesis of magnesium hydroxide were: hydrated magnesium sulphate ($MgSO_4 \cdot 7H_2O$, analytical grade), magnesium chloride ($MgCl_2 \cdot 6H_2O$), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, analytical grade), ammonium hydroxide (NH_4OH, analytical grade) as a precipitating agent (all made by POCh SA.) and non-ionic compounds from the group of poly(ethylene glycols): PEG 200, PEG 8000 and PEG 20000 (purchased from Sigma-Aldrich), as 2% solutions. Magnesium hydroxide was obtained from a 5% solution of a given magnesium salt and ammonia solution prepared with the excess of the stoichiometric amounts of the reactants, where salt/NH_4OH = 1:1.5. Reaction of magnesium hydroxide precipitation was carried out in a reactor of 500 cm^3 in capacity, equipped with a fast rotating stirrer made by Eurostar digital IKA-Werke (1800 rpm.). The reaction system was thermostated in a bath made by MP14 Julabo. The process was conducted at 80 ºC. The reagents were dosed simultaneously into the water system containing PEG. The use of a peristaltic pump (Ismatec ISM833A type) ensured a constant flow rate of the reagents (2.3 cm^3/min). On completion of reagents introduction, the reaction system was stirred for about 30 min. The precipitate of magnesium hydroxide was filtered off, washed out and dried in a dryer (Memmert) at 105ºC for about 6 h. A technological scheme of the process is shown in Fig. 1.
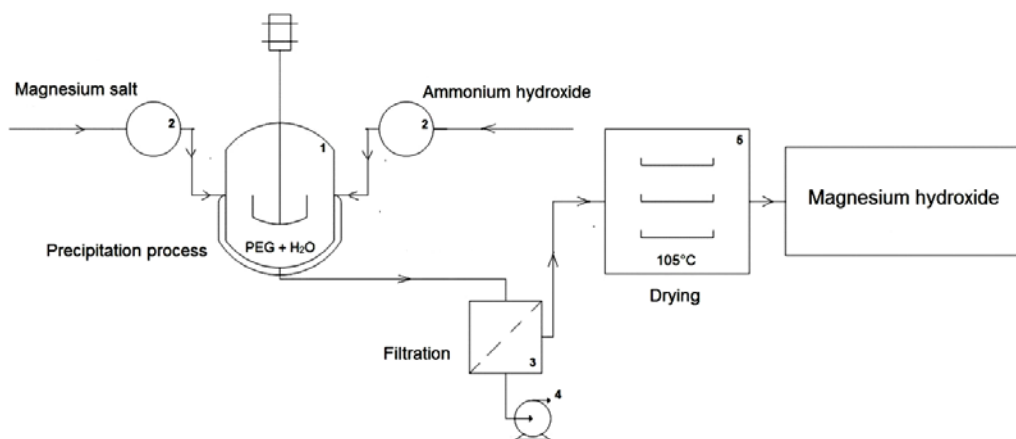

Fig. 1. Preparation of magnesium hydroxides – a technological scheme:
1 – reactor, 2 – peristaltic pomp, 3 – pressure filter, 4 – vacuum pomp, 5 – drier

The magnesium hydroxides obtained were subjected to physicochemical and dispersive-morphological characterisation. The particle size distribution was determined by two instruments Zetasizer Nano ZS (0.6–6000 nm) and Mastersizer 2000 (0.2–2000 μm) employing two measuring methods NIBS and laser diffraction, respectively. Both instruments were made by Malvern Instruments Ltd. The morphology and microstructure of the products were characterised on the basis of

observations by a scanning electron microscope Zeiss EVO 40. The crystalline structure of selected magnesium hydroxide samples was determined by WAXS. The X-ray diffractograms were recorded by a computer-controlled horizontal diffractometer, equipped with a HZG-3 type goniometer. The magnesium hydroxides were also subjected to FT-IR spectral analysis (using an IFS 66v/S made by Bruker). Here the materials were analysed in tablet form, made by pressing a mixture of anhydrous KBr (ca. 0.1 g) and 1 mg of the tested substance in a special steel ring under a pressure of approximately 1000 MPa. The electrokinetic stability of the products was determined on the basis of zeta potential dependence on pH, using a Zetasizer Nano ZS (Malvern Instruments Ltd.) with an autotitrator attached. Measurements were made in a 0.001M NaCl solution in the range of pH from 2 to 12.

Results and discussion

Dispersive and morphological characteristics

Table 1 presents results characterising dispersive properties of magnesium hydroxide samples unmodified and modified by PEG (2% solution) of different molecular mass: PEG 200, 8000, 20000. All magnesium hydroxide samples were obtained using 5% solutions of particular magnesium salt (magnesium sulphate, chloride and nitrate) with an excess of ammonium hydroxide with respect to its stoichiometric amount of 1:1.5 (salt/NH_4OH), at 80 °C. The particle size distribution was determined in two ranges of values by two instruments Zetasizer Nano ZS and Mastersizer 2000.

Pilarska (2012) reported results of dispersion study and other measurements for magnesium hydroxide samples obtained from the same substrates but under different process conditions, that is at the stoichiometric rate of the reagents and at 60°C. For the products obtained in this process the authors have not observed the modification applied to improve the dispersive properties. The smallest particles (59–142 nm) were obtained for the sample precipitated from a solution of magnesium sulphate and modified by PEG 400.

The particle size distributions in the scale extended to 0.2−2000 μm (Mastersizer 2000) of magnesium hydroxide samples obtained in this study evidence the effectiveness of application of ammonium hydroxide in excess amount, in particular in preventing formation of large agglomerates (S-NH_3-unmod., N-NH_3-unmod., Cl-NH_3-unmod, Table 1). Thus the excess of ammonium hydroxide produced a different effect than the excess of sodium hydroxide in the reactions with the same magnesium salts for which a undesirable microstructural changes were observed (Myerson 2002; Pilarska 2010). The best example illustrating the positive effect of the excessive amount of ammonium hydroxide on dispersive properties of the product is the sample S-NH_3-unmod., obtained from a solution of magnesium sulphate and having particles of diameters from the range 160−190 nm and a low polydispersity index of 0.154.

Table 1. Dispersive characteristic of unmodified magnesium hydroxide
and grafted with 2% solution of appropriate PEG

| Sample No. | Precipitation process conditions | | | Dispersive properties | | | |
| | Type of salt | Mean molecular weight of PEG | PdI | Range of particle size from Zetasizer Nano ZS (nm) | Particle size from Masteriszer 2000 (nm) | | |
					d(0.1)	d(0.5)	d(0.9)
S–NH$_3$–unmod.	magnesium sulphate	–	0.154	160–190	3.53	20.58	29.42
1S–NH$_3$–mod.		200	0.641	79–1720	7.78	21.79	39.70
2S–NH$_3$–mod.		8000	0.521	68–531	13.28	20.20	31.00
3S–NH$_3$–mod.		20000	0.437	51–459	3.46	16.84	30.61
N–NH$_3$–unmod.	magnesium nitrate	–	0.496	4800–5560	3.16	7.80	15.97
1N–NH$_3$–mod.		200	0.708	44–5560	5.58	15.46	32.34
2N–NH$_3$–mod.		8000	0.543	51–5560	3.29	8.91	18.27
3N–NH$_3$–mod.		20000	0.582	79–5560	2.81	8.30	17.19
Cl–NH$_3$–unmod.	magnesium chloride	–	0.397	190–615	8.38	14.66	24.57
1Cl–NH$_3$–mod.		200	0.686	59–5560	3.09	6.60	11.76
2Cl–NH$_3$–mod.		8000	0.435	51–1480	4.32	12.24	26.43
3Cl–NH$_3$–mod.		20000	0.205	91–190	7.05	11.67	19.13

Of significant importance is the type of magnesium salt used (Pilarska 2011). It has been shown on the basis of dispersion studies that the salts of higher water solubility, such as magnesium sulphate and magnesium chloride, have beneficial effect on the product dispersion. The results evidencing better properties of samples labelled S and Cl than those obtained for the sample synthesised with the use of magnesium nitrate (sample N) are shown in Table 1. The diameters of particles in sample N often reached values close to 6 μm, and the relatively high values of the polydispersity index determined for this sample, 0.496–0.708, suggest heterogeneous character of this sample. The elevated temperature of precipitation and the use of a salt of good water solubility, like magnesium sulphate, favours formation of particles of smaller sizes.

In general, only in some modified samples the particles had smaller sizes than in their unmodified correspondents. On the basis of measurements by Zetasizer Nano ZS, a considerable improvement in the dispersive properties was noted for sample 3Cl–NH$_3$-mod (Fig. 2). The particle size distribution (Fig. 2a) confirms that the modified sample has particles of significantly smaller diameters, reduced from 459 to 142 nm. The SEM images presented in Figs. 2b, c, clearly reveal the differences in dispersive properties between the unmodified and modified samples. The sample of magnesium hydroxide obtained with the use of PEG 20000 is homogeneous (PdI = 0.205) and small particle sizes, while in the unmodified sample the particles form smaller and

larger agglomerations. Restricted tendency towards formation of secondary agglomerates was also noted for the sample 1Cl–NH$_3$-mod. (PEG 200). For the other samples no significant improvement in the dispersive properties was observed upon modification.
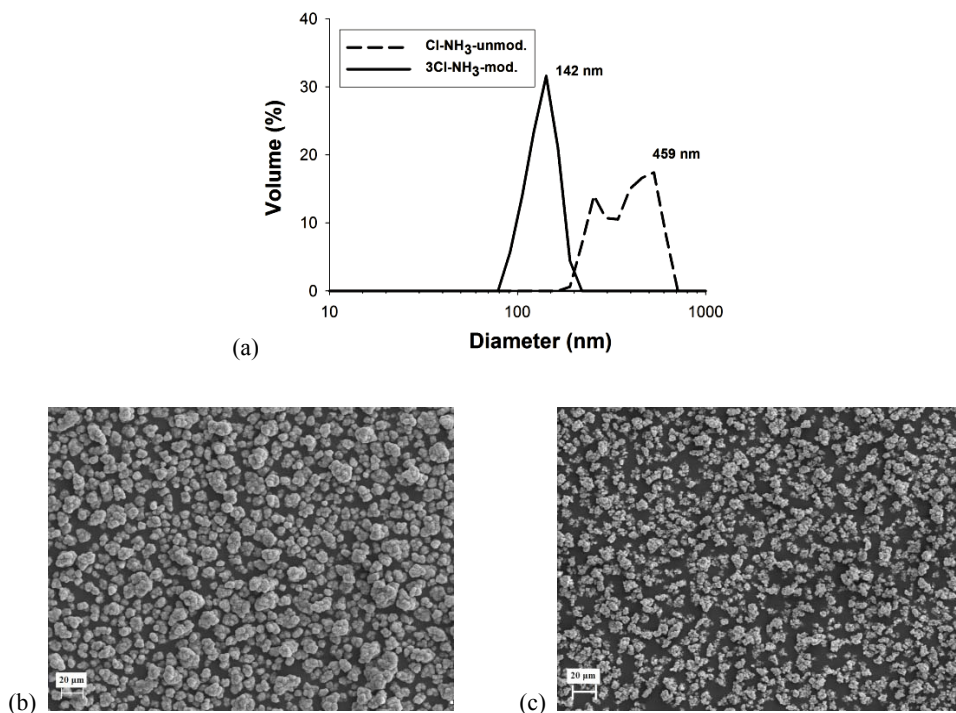

(a)

(b)

(c)

Fig. 2. (a) Particle size distributions (Zetasizer Nano ZS) and (b), (c) SEM images
of magnesium hydroxides Cl-NH$_3$-unmod., 3Cl-NH$_3$-mod.

WAXS analysis

Physicochemical characterisation of the magnesium hydroxide samples obtained was supplemented with X-ray studies. Exemplary X-ray patterns are presented in Fig. 3 and show the maxima characteristic of the crystalline structure of Mg(OH)$_2$ brucite. Figure 3a shows the X-ray patterns of unmodified samples precipitated with the use of three different magnesium salts. In the samples Cl–NH$_3$-unmod. and N–NH$_3$-unmod., the crystalline structure was much better developed than in S–NH$_3$-unmod., as follows from the shape and intensity of peaks. These observations confirm that the type of magnesium salt used as magnesium precursor affects the development of crystalline structure. For instance when magnesium sulphate is used, the crystallites of magnesium hydroxide are poorer developed and irregular, which is reflected in the properties (e.g. adsorptive or catalytic) of magnesium hydroxide produced (Climent 2007; Pilarska 2012).
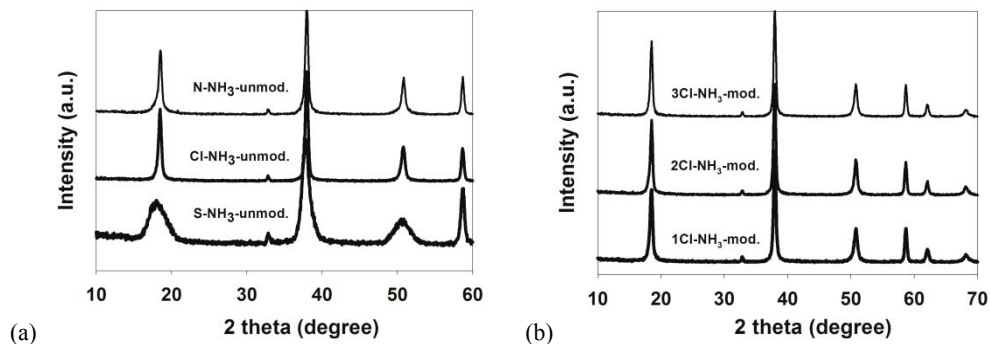
Fig. 3. X-ray diffraction patterns of magnesium hydroxides obtained with the use of
(a) magnesium sulphate, chloride and nitrate (unmodified); (b) magnesium chloride
and modifiers of different molecular weights of poly(ethylene glycols)

According to literature (Lv 2004) the crystalline structure characteristic of brucite does not change, despite the differences in the particles morphology. According to literature, the parameters of the method of synthesis of magnesium hydroxide e.g. temperature, time of reaction, time of maturation of the post-reaction mixture (Alvarado 2000; Meshani 2009), also have no effect on the crystalline structure. As follows from the X-ray patterns of the modified samples precipitated with the excess of ammonia solution and magnesium chloride, Fig. 3b, also the type and amount of the modifier have no effect on the crystalline structure.

FT-IR analysis

In order to confirm the presence of functional groups introduced by the modifiers (poly(ethylene glycols)), the samples of magnesium hydroxide precipitated in solutions of different salts were subjected to FT-IR analysis. The studies were performed for
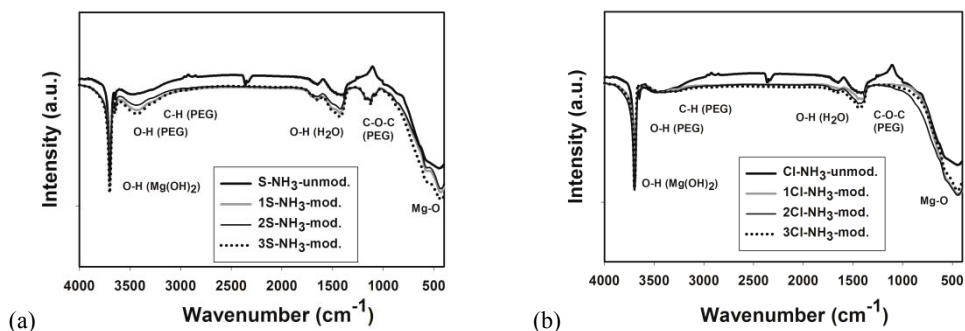

Fig. 4. FT-IR spectra of magnesium hydroxide samples precipitated (a) without and with modifiers of PEGs and magnesium sulphate (b) without and with modifiers of PEGs and magnesium chloride

both unmodified samples and those modified with PEG 200, 8000, 20000. The FT-IR spectra presented in fig. 4 prove the presence of functional groups introduced from PEG grafted to $Mg(OH)_2$. In the spectra of the samples obtained with the use of magnesium sulphate as a precursor of magnesium the bands assigned to the functional groups O–H (PEG) and C–H (PEG) have significantly higher intensities. Small and rather insignificant changes in the character of the FT-IR spectra of all modified samples imply incorporation of similar amounts of the modifiers in the samples.

The first absorption maximum, of pointed shape and high intensity at 3700 cm^{-1} is assigned to the asymmetric stretching vibrations of –OH groups from $Mg(OH)_2$. The band at 1650 cm^{-1} is assigned to the stretching vibrations of –OH groups from water. The broad peak at 3430 cm^{-1} corresponds to the adsorbed –OH PEG groups, while the low-intensity bands at 2930 cm^{-1} and 2860 cm^{-1} are assigned to the methylene groups –CH_2 (stretching vibrations of PEG). The broad peak at 1400 cm^{-1} is also assigned to –CH_2 groups from PEG (bending−scissoring vibrations). The band at 1115 cm^{-1} corresponds to the asymmetric stretching vibrations of ether groups C−O−C PEG. The last intense and broad maximum at 440 cm^{-1} corresponds to the stretching vibrations of Mg–O. The assignment is in agreement with literature data (Hsu 2005; Wang 2011).

Electrokinetic characterisation

Figure 5 presents zeta potential versus pH for unmodified magnesium hydroxide samples obtained with the use of magnesium sulphate (S-NH_3-unmod., Fig. 5a) and magnesium nitrate (N−NH_3-unmod., Fig. 5b) and for these samples modified with PEG 200, 8000, 20000. In the analysed pH range, the electrokinetic curves reach zeta potential values from the range −5÷62 mV. The unmodified samples S−NH_3-unmod., N-NH_3-unmod. show electrokinetic stability in a relatively wide range from pH 2 to 9, while their modified correspondents are stable in a narrower range of pH, from 1 to 6.5.
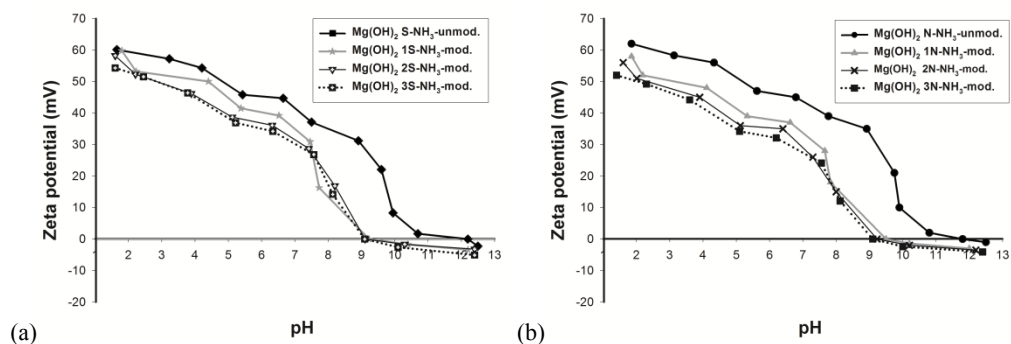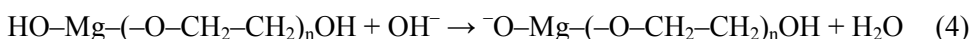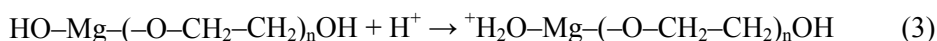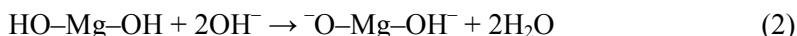

(a)   (b)

Fig. 5. Zeta potential vs. pH for $Mg(OH)_2$ samples unmodified and modified with PEGs
and precipitated with the use of (a) magnesium sulphate, (b) magnesium nitrate solutions

According to the DLVO (Deriaguin, Landau, Verwey, Overbeek) theory, stability of colloidal systems at particular values of zeta potential is determined by overlapping of double electric layers that protect two approaching each other molecules from colliding. In other words, the sample is stable until the electrostatic (repulsive) forces overcome the attractive van der Waals forces (Kosmulski 2009).

The proposed method for the synthesis of magnesium hydroxide in the presence of poly(ethylene glycol) has slightly reduced the pH range of electrokinetic stability of the analysed samples. The small changes in stability of magnesium hydroxide samples after introduction of PEGs are arguments for the use of such modifiers. According to literature data (Saravanan 2005) poly(ethylene glycol) shows electrokinetic stability in two pH ranges, from 2 to 6.5 and from 10 to 12. Probably, if PEGs were applied in higher concentrations, the electrokinetic curves measured for the modified samples would be shifted towards much smaller potential values (below –30 mV). Because of a number of attractive properties of PEG, such as nontoxicity or biocompatibility, this compound has been often used as an adhesive in the ceramic industry, as a plasticiser, as a stabiliser of oxide ions (*PEG protects iron oxide nanoparticles, PEG-PIONs*) or as a modifier of a layered double hydroxides, LDHs of multifunctional use, e.g. in polymer coatings (Ujii 2011; Li 2011). The isoelectric points of unmodified hydroxides (S-NH$_3$-unmod., N-NH$_3$-unmod., Figs. 5a, b) occur at pH of about 11, which fully correlates with literature data (Schott 1981). Zeta potential of a colloidal system is a parameter directly related to its pH. The reactions of dissociation of unmodified and modified products in acidic environment (HCl) and alkaline environment (NaOH) (1–4), were proposed to occur according to the scheme:

$$HO–Mg–OH + 2H^+ \rightarrow {}^+H_2O–Mg–OH_2^+ \tag{1}$$

$$HO–Mg–OH + 2OH^- \rightarrow {}^-O–Mg–OH^- + 2H_2O \tag{2}$$

$$HO–Mg–(–O–CH_2–CH_2)_nOH + H^+ \rightarrow {}^+H_2O–Mg–(–O–CH_2–CH_2)_nOH \tag{3}$$

$$HO–Mg–(–O–CH_2–CH_2)_nOH + OH^- \rightarrow {}^-O–Mg–(–O–CH_2–CH_2)_nOH + H_2O \tag{4}$$

In the acidic environment (HCl) in which zeta potential takes the most beneficial values, proton is attached to the –OH group and generates charge thanks to which the surface of the products becomes more reactive (1, 3) and their colloids much more stable. It should be noted that thanks to the electrostatic interactions in acidic media, a reaction between MgOH$_2^+$ and ethoxyoxgen from PEG of small negative electric charge, which makes the modification with these reagents even more effective. The negative charge appearing upon the reaction of the products in an alkaline medium (NaOH) causes a decrease in zeta potential, leading to total destabilisation of the system at certain pH values (reactions 2, 4). For modified samples of Mg(OH)$_2$, reactions with the –OH groups from PEG are also possible both in acidic and alkaline media.

The knowledge of zeta potential of a given substance permits a selective use of its properties, so the interest in its determination has substantially increased, also in industry. On the basis of the known zeta potential it is possible to indentify the mechanisms and conditions of adsorption or separation (flotation) of dispersed solids for which isoelectric point determination is essential (Fuerstenau 2005; Kosmulski 2001). The same is true for $Mg(OH)_2$ both that obtained from minerals and by synthesis.

Conclusions

No particularly beneficial changes in the dispersive properties have been noted as a result of functionalisation of precipitated magnesium hydroxide samples with PEG compounds. Only for a few samples modified with PEG 20000 (3S-NH$_3$-mod., 3N-NH$_3$-mod., 3Cl–NH$_3$-mod), the formation of particles of smaller size was evidenced. As confirmed by the WAXS study, modification with PEGs had no effect on the crystalline structure that remained to be typical of brucite. However, differences in the degree of development of this structure were observed, depending on the magnesium salt used as magnesium precursor. In the samples obtained with the use of magnesium sulphate the structure was irregular and poorly developed. The results of FT-IR analysis confirmed the presence of functional groups coming from PEG in the modified samples. The zeta potential measurements proved that the samples obtained were electrokinetically stable in a wide range of pH, from 2 to 9. The isoelectric points detected corresponded to the pH values being in full agreement with the literature data. Modification with PEG compounds only slightly reduced the pH of electrokinetic stability of the samples studied (to 1−6.5).

Acknowledgements

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