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TRIBOCHEMICALLY ACTIVATED NATURAL CHALK AS A FILLER FOR PLASTO- AND ELASTOMERS

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Physicochemical evaluation of chalk limestone subjected to tribochemical activation with or without a promoter of adhesion and strengthening is given. The powder materials processed in an electro-magneto-mechano-chemical reactor have undergone evident transformations, which increased their capacity to react and which involved:

- creation of additional network effects,
- formation of new surfaces which, due to deformations, are particularly reactive,
- development of additional network deformations due to the increased surface to volume ratio.

Dispersion and particle morphology were studied by scanning electron microscopy (SEM) and dynamic light scattering (DLS), moreover tap and bulk density, capacities to absorb water and dioctyl phthalate were evaluated. The chalk samples ground in the electro-magneto-mechano-chemical reactor demonstrated highly uniform granule size, usually smaller than 1 μm , measured by SEM and DLS.

Key words: chalk, chemical and mechanical modification of surface, microstructure

INTRODUCTION

In cases of plastics, ground natural chalks, limestone and various types of precipitated calcium carbonate can be used as fillers (Wypych, 1999). The precipitated calcium carbonates in particular exceed other CaCO_3 - based fillers in respect to whiteness and, first of all, in respect to the extent of disintegration. The application of

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modified chalk and carbonate fillers clearly improves physicomachanical properties of plasto- and elastomers (Wypych, 1999; Gächter and Müller, 1987). The modifiers can be fatty acids or their derivatives (Tabtiang and Venables, 2000; Domka et al., 1999), surfactants (Domka et al., 2002), coupling agents (Demjén et al., 1997; Plueddemann, 1991; Mittal, 1992; Domka, 1993, Domka, 1994) and, in particular, titanate proadhesive compounds (Domka, 1996). Recently, the surface modification with a combination of action of modifying agent and the mechano-chemical effect of ultrafine grinding was studied in surface modification of calcium carbonate particles by polymer grafting (Wua and Lu , 2003).

In processing of plastics, chalks are most frequently used as fillers. Due to the relatively low adsorption of plasticisers and stabilisers on the chalk surface, the latter may be introduced to plastics in relatively high amounts. The amount of the introduced filler may vary from 5 to 100 weight parts per 100 weight parts of polymers, depending upon the required physical properties of the product (Domka, 1979). Chalks used in polymer processing should be fully neutral towards the plastic and the applied supplements, should be thermostable, capable of rapid and easy formation of a dispersion in the plastic, should exhibit low adsorption of softeners, should not exert negative effects on mechanical properties of the plastic, should be white in colour, possibly homogeneous and relatively inexpensive (Wypych, 1999; Ishida, 1988; Katz and Milewski, 1987). Also the particle size distribution of filler is one of the most important parameters in the reactivity of such materials. Therefore, development of new grinding methods such as Hicom mill (Braun et al., 2002; Hoyer and Morgan, 1996; Hoyer, 1999) or electro-magneto-mechanical mill (Binczyk et al., 2001) is highly relevant.

EXPERIMENTAL

The studies were performed on the chalk limestone from the Sobków deposits, near Kielce (Poland). The limestone was subjected to processing by liquid classification, by removal of particles of the larger size. For the studies the chalk was dried and passed through the 6.3 μm sieve. The applied chalk consisted of:

- CaCO_3 - 96.8%,
 - MgCO_3 - 2.3%
 - insoluble residue (IR) - 0.70%,
 - Fe - 0.03%,
 - Mn - 0.02%,
 - Cu, Pb - traces,
 - H_2O - 0.15%,
- and showed:
- specific gravity - 2.59 g/cm^3 ,
 - specific area - 8.6 m^2/g ,

- bulk weight - 0.74 g/cm³,
- dominating crystal structure - calcite type.

The Sobków chalk was modified with fatty acids (maleic acid and stearic acid) and acrylic acid. The natural chalk was modified in two ways: in the electro-magneto-mechano-chemical reactor (Domka et al., 1999; Polechonski et al., 1996) and by depositing of the adhesion promoter from the solution (Domka et al., 2002; Domka, 1993; 1994; 1996). Each time, the modifier (adhesion promoter) was deposited on the chalk in the below described way (1 weight part of the modifier was used per 100 weight parts of the chalk). The carboxylic acids were dissolved in the mixture of methanol or isopropanol and water (at the ratio of 1:1 or 3:2). The final acids concentration in modification solution was 1% (w/v). The modification was performed in a spherical flask of 500 cm³ capacity, in a vacuum evaporator, in 1 h at room temperature. Subsequently, the samples of the chalk with the solution were left for 24 h. Then, the solvent was evaporated in an evaporator, at an increased pressure, at approx. 80 °C and the modified chalk was dried in a stream of hot air, at 100 °C. If needed, the chalk aggregates were disintegrated in a mortar and passed through a sieve of a mesh diameter 6.3 µm. The modification was performed also in an electro-magneto-mechano-chemical reactor (Binczyk et al., 2001; Polechonski et al., 1996). The reactor used the energy field generated in the reactive chamber by a rotating electromagnetic field and a ferromagnetic dipole movement. The reactor permits intensification of a number of technological processes due to a simultaneous and complex action on the processed media of several varying physical energy fields, including the electric, magnetic, acoustic, temperature fields, high pressures and friction. The media processed, contained in the reactive chamber, i.e. in the zone of moving ferromagnetic dipoles, are subjected to intense mixing and dispersion due to strong ultrasonic fields, high pressures and friction. In parallel, the media are affected by the heat field, variable electric and magnetic fields of pronounced gradients and intensities which evoke a number of complex electrochemical and magnetochemical phenomena. This causes that in several technological processes application of the reactor is of a unique significance and practically cannot find an equivalent in the other equipment known and applied till now (Binczyk et al., 2001).

The size distribution of the chalk particle agglomerates and aggregates was estimated using a lab-made system by dynamic light scattering (DLS) method with a laser light source of 635 nm.

Morphology of the filler was observed by scanning electron microscopy. SEM micrographs were taken using Philips SEM 515 field emission scanning electron microscope. The beam voltage used was 12 - 15 kV. The powdered sample, intended for the studies, was dispersed in t-butanol and, following sedimentation on a microscope holder, it was coated with gold in an ionisation chamber.

Surface areas of the chalk powders were determined by nitrogen adsorption (the BET method) using an ASAP 2010 instrument (Micrometrics Instrument

Corporation). The sizes of the pores of the fillers were also examined. All samples prior to the measurements were heated at 120 °C for 2 hours.

RESULTS AND DISCUSSION

Some physicochemical properties of the chalk samples after their modification are listed in Table 1.

Table 1. Principal physicochemical properties of the tested chalk samples

Parameter	Natural chalk	Chalk ground for 30 s	Chalk ground for 60 s
Bulk density (g/dm ³)	740	540	500
Tap density (g/dm ³)	1480	624	630
Whiteness (%)	90.0	90.8	91
Specific area (m ² /g)	8.6	10.5	11.1

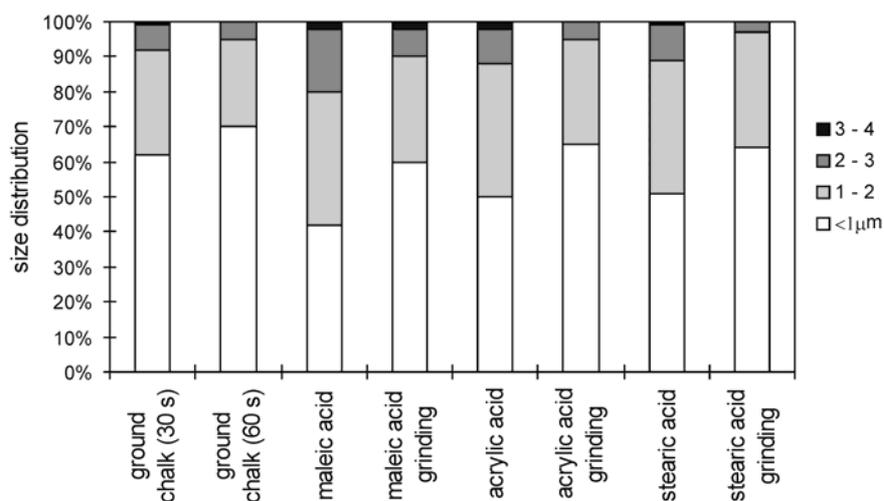


Fig. 1. Chalk granule size distribution determined using electron microscope photograms

As indicated by the Table 1 data, tribochemical modification promoted alteration of the surface character (evident increase in specific area and decrease in size of CaCO₃ particles - lowered tap density). The chalks modified with various acids contain also particle aggregates of significant size, linked to the preparation of the granule surface. However, the aggregates did not have much significance and disintegrated in the equipment used to homogenise the filler with the polymer.

The size distributions of chalk granules, determined using electron microscopy photograms, are shown in Figures 1 and 2.

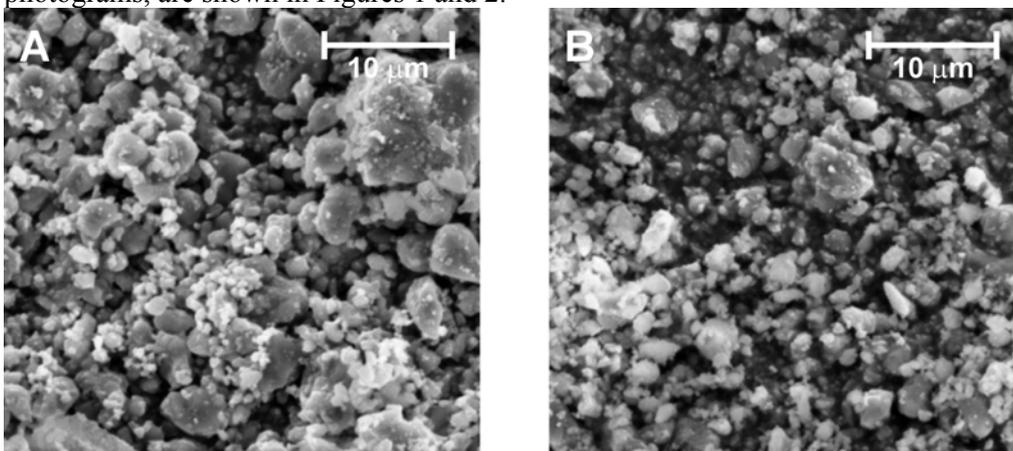


Fig. 2. SEM micrographs of natural chalk (A) and after grinding (60 s) in the electro-magneto-mechanico-chemical reactor (B)

The size distributions of the chalk particles before and after tribochemical activation with and without a coupling agent, determined by DLS, are presented in Table 2 and Figure 3. In the natural chalk, the small (primary) particles form a strong band (particle diameter range 780 – 1150 nm). The maximum intensity (100) corresponds to a particle diameter of 1010 nm. Also, as demonstrated in Figure 2, the electron micrograph shows some primary agglomerates of particles (aggregates). The mean diameter of the particles of unmodified chalk was 910 nm and the polydispersity was 0.112. Between 2110 and 3200 nm there was a band (maximum intensity of 21 at 2330 nm) which could be ascribed to secondary agglomerates in the chalk.

In the particle size distribution of the tribochemically modified chalk (after grinding for 30 s), the strongest band was present within the range of 720 to 1064 nm (a maximum intensity of 100 corresponded to a particle diameter of 905 nm). The second band was observed between 1890 and 2810 nm (with maximum intensity of 17 at 2205 nm). The mean diameter of the particles of tribochemically modified chalk was 892 nm and the polydispersity was 0.099.

The chalk after 60 s grinding was characterised by two other bands: 641 to 1020 nm (maximum at particle diameter 822 nm) and 1905 to 2688 nm (maximum intensity of 9 at 2109 nm). The mean diameter of the chalk particles was 835 nm and the polydispersity was 0.092. The detailed analysis of the change in the mean particle diameter and polydispersity of the chalk modified with various proadhesive compounds (Table 2) clearly shows that these values decreased significantly on modification in the electro-magneto-mechano-chemical reactor.

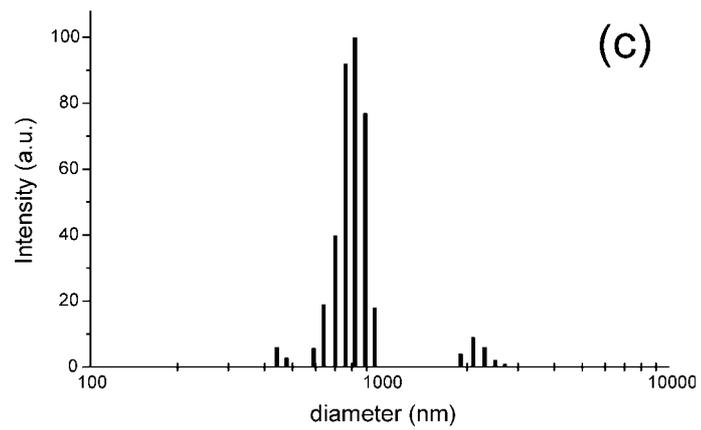
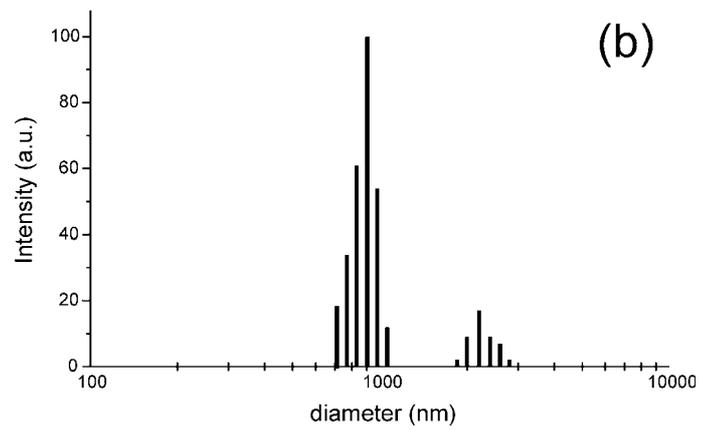
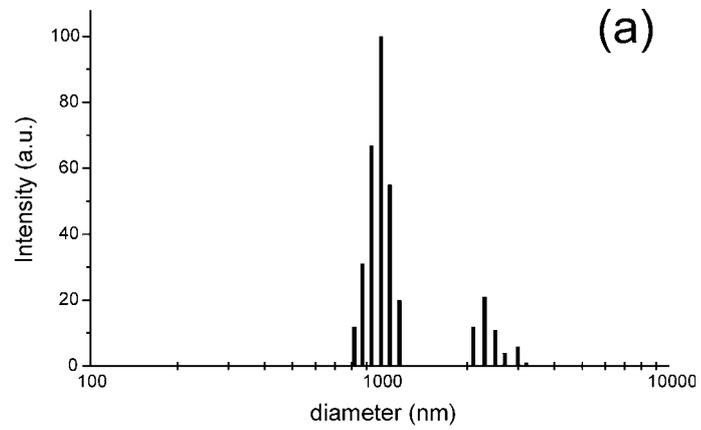


Fig. 3. The particle size distribution of the chalk: (a) natural chalk, (b) chalk ground for 30s, (c) chalk ground for 60 s

Table 2. Mean particle size and polydispersity of the examined unmodified and modified chinks.

Sample	Mean diameter (nm)	Polydispersity
Natural chalk	910	0.112
Chalk ground (30 s)	892	0.099
Chalk ground (60 s)	835	0.092
Maleic acid	1220	0.182
Maleic acid/ grinding	1092	0.167
Acrylic acid	1784	0.211
Acrylic acid/ grinding	1433	0.190
Stearic acid	1447	0.201
Stearic acid/ grinding	1187	0.192

The chinks ground in the electro-magneto-mechano-chemical reactor demonstrated highly uniform granule size usually smaller than 1 μm , which is more uniform than that of the chalk ground in Hicom mill (Braun et al., 2002). Despite a similar granule size distribution, the chinks modified with proadhesive compounds contained in their samples a few granules of the size exceeding even 5 μm , which was not encountered in the ground chalk. In the latter the typical granule size was 1-2 μm . The ASAP2010 sorptometer (Micrometrics) study of adsorption isotherm demonstrated changes in the specific area of the chalk (Figure 4), depending upon the adhesion promoter and the way of modification.

Tribochemical activation, either with or without an adhesion promoter, increased specific area of the chalk. Only difference was observed for tribochemical activation with addition of acrylic acid. In this case, the decrease in the surface area was probably associated with acrylic acid polymerisation in the course of tribochemical processing and agglomeration of particles of the modified chalk. Mean pore size decreased by almost 40% on average, which was linked with filling the pores with the surface modifying substance. One of the methods of testing surface modification was estimation of capacities to absorb water and the plasticiser. Water absorption capacity permitted an evaluation of the extent of surface hydrophobic transformation. Natural chalk is strongly hydrophilic, easily absorbs water, which is unfavourable when it is used as a filler since plasto- and elastomers remain strongly hydrophobic. For this reason the natural chalk has to be modified.

As shown by the water absorption capacity data in Figure 5, the chalk tribochemically modified with acids demonstrated better parameters than that obtained after traditional modification (using deposition of the modifier from the solution). The results obtained in testing the ground chalk without adhesion promoter indicated that tribochemical activation was associated with alteration in the chalk particle

morphology, with the transformation of aragonite into calcite (accompanied by a decrease in hydrophilicity).

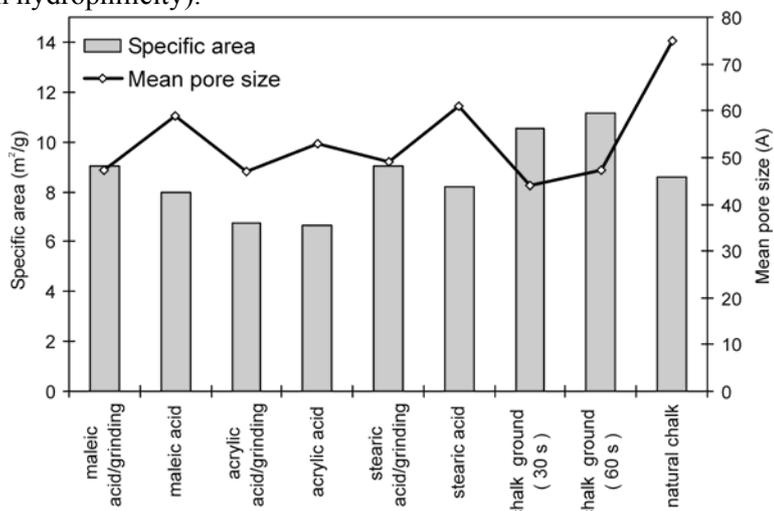


Fig. 4. Distribution of the full isotherm of adsorption

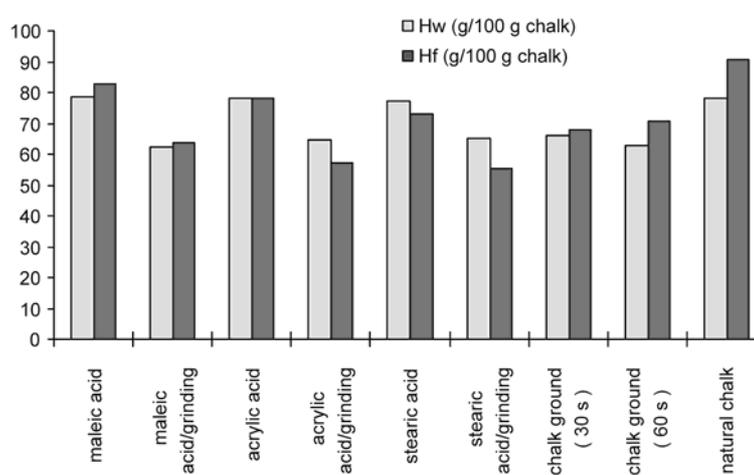


Fig. 5. Water (H_w) and dioctyl phtalate (H_f) absorption capacity

The transformation resulted from shearing and local forces and extensive compressive stresses which acted on various granules. The prolonged mixing might

be accompanied by the appearance of a significant aragonite fraction, in a composition or otherwise, the aragonite might be partly transformed into calcite (Domka, 1979).

Examination of the plastifier absorption capacity involved another way of appraising the surface modification effects. Dioctyl phthalate, the plasticiser used for absorption evaluation, is a hydrophobic substance. The deposited fatty acids accumulating in the chalk micropores, blocked them and changed the surface of the chalk, leading to decreasing plasticiser absorption capacity. The results of the tests clearly indicated a decreased absorption capacity in the samples of the chalks ground with a promoter of adhesion or without it. Tribochemical modification with stearic acid decreased the phthalate absorptive capacity up to 50%. One-minute tribochemical modification with stearic acid markedly increased the hydrophobic character of chalk and increased the phthalate absorption capacity as compared to the samples subjected to 30 s tribochemical activation. Electron microscopy demonstrated that the small fraction of the aragonite form was transformed into the calcite form on the mechanical modification, which resulted in a decreased hydrophilic character.

The presented results have permitted a conclusion that tribochemical activation with the addition of an adhesion promoter is most effective in modification of the natural chalk surface, decreasing the chalk capacity of the water and the plasticiser absorption.

CONCLUSIONS

Chalk, after tribochemical modification in the electro-magneto-mechano-chemical reactor, demonstrated highly uniform granule size, usually smaller than 1 μm . Tribochemical activation, either with or without an adhesion promoter, increased specific area of chalk. Chalk, tribochemically modified with acids, demonstrated better water and plasticizer absorption capacity than that obtained after traditional modification (by deposition of the modifier from the solution).

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Domka L., Kozak M., *Aktywowana trybochemicznie naturalna kreda jako napelniazcz dla plasto- i elastomerów*, Physicochemical Problems of Mineral Processing, 38, (2004) 187-196 (w jęz. ang.).

W prezentowanej pracy przedstawione zostały wyniki analizy fizyko-chemicznej kredy naturalnej poddanej aktywacji trybochemicznej w obecności i bez związków powierzchniowo czynnych z grupy kwasów tłuszczowych (kwas stearynowy, maleinowy i akrylowy). Napelniazcz był modyfikowany przy użyciu reaktora elektro-magneto-mechano-chemicznego. Modyfikacja ta powodowała ewidentne przemiany obejmujące m.in. powstawanie dodatkowych defektów sieciowych, tworzenie nowych, reaktywnych powierzchni oraz wzrost powierzchni właściwej. Efekty modyfikacji mikrostruktury analizowane były z wykorzystaniem techniki skaningowej mikroskopii elektronowej (SEM) oraz dynamicznego rozpraszania światła (DLS). Ponadto zbadano zdolność zmodyfikowanego napelniazcza do absorpcji wody i plastyfikatora – ftalanu dioktylu oraz gęstość nasypową. Analiza SEM wykazała, że cząstki napelniazcza po modyfikacji cechuje jednolity kształt oraz wąski zakres rozmiarów (zwykle zbliżony do 1 µm). Wyniki SEM potwierdzają badania DLS wskazujące na zmniejszenie średnich rozmiarów cząstek po modyfikacji trybochemicznej z 910 nm charakteryzujących kredę niemodyfikowaną do 835 nm po modyfikacji. Widoczne jest także zmniejszenie średnich rozmiarów porów oraz wyraźne zwiększenie powierzchni właściwej.