Effect of low temperature air plasma treatment on physico-chemical properties of kaolinite

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Abstract

It was found in this study that air plasma treatment of particular kaolinite has led to the change of its wettability. This was reflected in the decreased values of water contact angles of wetting. There were determined yield locus and flow function dependencies at different stress levels for virgin and different time plasma treated samples (flow index - *ffc*, effective angle of internal friction - phi*e*, unconfined yield strength - *sigmac*). It was found that by plasma treatment the character of the flow was shifting from region of very cohesive (*ffc* = 2.39) to the cohesive (*ffc* = 3.19). For untreated samples effective angle of internal friction was decreased with increasing applied consolidation stress, while for plasma treated kaolinite it was increased.

Introduction

Granular materials occupy a prominent place in our culture, the worldwide annual production of grains and aggregates of various kinds reaching approximately ten billion metric tons [1]. They are used in many different applications and industries, such as basic construction materials, agriculture, synthetic polymers fillers, cosmetic, pharmaceutical, processing and food industry. Many practical engineering applications involve handling, flow and storage of bulk solids (e.g. pelletizing, particle size reduction, tableting, mixing, packaging etc.) require knowledge and understanding of the particular solids flow properties and surface energy

distribution. For example, the compaction of particular solids may be defined as a reduction in the total volume of an assembly of solid particles by the application of stress. The formation of a coherent body from such an assembly can be then described in terms of the stresses required to overcome cohesion, internal friction and the yield criterion of particular material. The strength of a bulk solid is used to determine the ability of the material to form cohesive arches, as well as to correlate process behaviour to material properties.

Methods

Air plasma treatment of studied powder was performed in Diener Femto (Diener Electronic, Germany) capacitively coupled plasma reactor operating at 13.56 MHz frequency for 10, 20 and 30 minutes. Kaolinite powder was placed into the rotating rectangular parallel piped glass reactor chamber (borosilicate glass cylinder of 320 mm length and 150 mm diameter), which was placed inside the plasma reactor. The processing reactor conditions were as follows: generator power 100 W, air flow rate 5 cm^3/min, processing pressure 35 Pa. The latter construction configuration enables high uniformity of the surface modification of treated powder samples.

Shear cell tester measurements were performed on untreated and air plasma treated kaolinite powder samples using a ring shear cell tester (RST-XS, Dr. Dietmar Schulze, Germany) at laboratory ambient temperature 24°C. Tested powders were of 0.27 w.% moisture content and were kept for 48 hours prior to the measurement at constant humidity conditions in desiccators. Powders were distributed into the shear cell under gentle vibration in order to achieve a similar packing state for each sample under study. The samples were tested using different pre-loads of 8.6; 13; 22; 33 and 43.5 kPa. Calculated experimental error was less than 1 %.

Kaolinite particles ζ-potential and effective diameter were determined on ZetaPlus instrument (Brookhaven Instruments Corporation, USA) in 0.001 M KCl at 24°C. Prior to each measurement the vial was kept in ultrasonic bath for 5 minutes to destroy all possible conglomerates.

Contact angle measurements of wetting of studied kaolinite powders were performed on Krüss K12 Tensiometer apparatus (Krüss, Germany) by means of Washburn method [8], where the porous solid was treated as a bundle of cylindrical capillaries with mean or equivalent radius. Each measurement was repeated for 5 ×. Measurements were performed at ambient laboratory temperature of 24°C. Re-distilled water, ethylene glycol, ethyl alcohol,

dimethyl sulfoxide and diiodomethane were used as testing liquids (ACS grade, Sigma-Aldrich, USA).

Inverse gas chromatography was conducted using a Surface Energy Analyser (SEA) (Surface Measurement Systems, UK). Samples were placed in 4 mm (internal diameter) columns, to give a total surface area of approximately 0.5 m^2. Specific surface area measurements were made using a Micromeritics TriStar 3000 surface area and porosity analyser (USA), using the nitrogen BET technique. All reagents were obtained from Fisher Scientific (USA), and were of analytical grade. The following eluent vapours were passed through the column: Nonane, Octane, Hexane, Heptane. The injection of vapours was controlled to pass a set volume of eluent through the column to give pre-determined fractional coverage of the sample in the column. The retention time of the vapours by the particles gives an indication of the surface properties of the material, including the surface energy. By gradually increasing the amount of vapour injected, it is possible to build up a surface heterogeneity plot [9,18-20].

FT-IR spectra were recorded on FTIR- 8601PC spectrometer (Shimadzu, Japan) by means of KBr disk method. The resolution of the instrument was set to ± 2 cm^{-1}. A mixture of the studied kaolinite and dried KBr (1.3 mg kaolinite/160 mg KBr) was grand and pressed using a pellet die under pressure to obtain transparent disk. During dressing, the press was connected to the vacuum pump to remove water moisture. Analytical grade potassium bromide (Aldrich, USA) was used for disk preparation.

Conclusions

It was found in this study that the air plasma treatment of particular kaolinite has led to the increased wettability, which was reflected in the observed decreasing values of contact angles of wetting. Due to the fact, that contact angle measurements are best suited mainly for low surface energy solids, there were used the inverse gas chromatography measurements for determination of both the dispersive surface energy distributions as well as dispersive surface energy profiles for virgin and plasma treated samples. Results of these measurements confirmed our assumption, that air plasma treatment activates surface energy of the crystal planes of the kaolinite as reflected in the broadened dispersive surface energy distribution after 10 minutes treatment time. However with prolonged 30 min treatment time the dispersive surface energy distribution profile was decreased. We assume, that the latter decrease reflects the distorsion of the crystal lattice of the kaolinite. Calculated dispersive surface free energy for 24 % surface coverage was increased from original 35 mJ/m^2 to 40.3 and 40.8 mJ/m^2 for 10 and 30 minutes treatment times. Plasma treated samples show higher

average surface energies in the wide range of coverage regimes in comparison to the virgin samples. Observed changes of the surface properties of studied kaolinite samples were reflected also in decrease of the negative values of electrokinetic ζ-potential in 0.001 M KCl aqueous solutions from -8.0 mV to -11.0 mV. By means of FT-IR analysis there was confirmed the fact, that air plasma treatment is changing internal structure of the kaolinite crystal lattice most probably due to the ongoing initial stages of the internal disintegration process as reflected in changes of Si-O-Si and Al_2O-H infra red characteristic spectral regions. With respect to the characterization of macroscopic powder flow behaviour, yield locus and flow function dependencies at different stress levels for virgin and different time plasma treated samples were determined. It was found that by plasma treatment the character of the flow was shifting from region of very cohesive (ff_c = 2.39) to the cohesive (ff_c = 3.19). For untreated samples effective angle of internal friction was decreased with increasing applied consolidation stress, while for plasma treated kaolinite it was increased. However, the latter mentioned changes of the φ_e values for materials under study were not changed significantly.

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References

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