Applied Clay Science 165 (2018) 40–51

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Texture profile analysis (TPA) of clay/seawater mixtures useful for peloid preparation: Effects of clay concentration, pH and salinity

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ARTICLE INFO

Keywords:
Instrumental texture
Hardness
Adhesiveness
Bentonite
Sepiolite
Seawater

ABSTRACT

The liquid phase of a peloid can be mineral-medicinal, marine or salt lake water. This study was designed to experimentally determine the interaction between two bentonites and one sepiolite, and seawater as well as dilutions thereof to verify the effect of salinity on instrumental texture measurements in clay-water mixtures prepared with these components. In all the clay-water mixtures tested, instrumental hardness and adhesiveness decreased with water content. For a given instrumental hardness or adhesiveness, bentonite retained more water in the mixture with distilled water than with seawater. In contrast, sepiolite retained more water in the mixture with seawater than with distilled water. These differences affected the thermal behaviour of the clay-water mixtures. Instrumental hardness and adhesiveness curves may be a suitable tool to tailor concentrated dispersions and after maturation could be used in thalassos and medical spas as peloids.

1. Introduction

Some spas and thalassos use peloids composed of various clays mixed with mineral water that are subjected to a maturation process of variable duration (Gomes et al., 2013). This ageing needed for a peloid to form is a complex process involving physical, chemical, physical-chemical and biological phenomena. Besides depending on the nature and initial composition of the mineral water and clayey material used, ageing is also conditioned by the characteristics of the clay/water mixture both before and after maturation. The main factors controlling the physical and chemical characteristics of the resulting peloid are the composition and grain-size distribution of the initial clay, the composition of the mineral water used in the mixture and the maturation process including the mixing mode (Veniale et al., 2004; Carretero et al., 2007; Tateo et al., 2010; Pozo et al., 2013; Carretero et al., 2013; Carretero et al., 2014; Morer et al., 2017). Peloids are a special kind of semisolid system consisting of a solid phase commonly rich in clay minerals dispersed in mineral medicinal water or seawater (Aguzzi et al., 2013; Glavas et al., 2017).

In the field of pelotherapy, much emphasis is placed on sensory perception, though the impressions of users are subjective and thus difficult to measure. Instrumental procedures are usually more sensitive and reproducible than subjective sensory tests in which variations in measures are generally attributed to heterogeneity among samples and to individual perception (Fernández-Torán, 2014). Researchers should be able to count on a set of empirical instrumental tests to quantify these properties. For a clay paste or peloid to be suitable for pelotherapeutic use, it should have certain properties such as a low cooling rate, high absorption capacity and CEC, and also good adhesiveness, ease of handling, and low hardness offering a pleasant feeling when applied to the skin (see reviews of Gomes et al., 2013, Carretero et al., 2013, Gomes, 2017).

Texture analysis is widely used in the field of materials science to determine the physical properties of materials and behaviour of solids and semisolid dispersions when subjected to compression. Instrumental tests, also known as mechanical texture tests, simulate the sensory effect. Texture profile analysis (TPA) provides quantifiable, repeatable and accurate data on the physical properties of food, cosmetics, pharmaceuticals and chemical products, but also of peloids and clay/water mixtures for pelotherapy (Pozo et al., 2013; Armijo et al., 2015). Force peaks and areas under the curve are used to calculate several variables including hardness and adhesiveness (Szczesniak, 1963; Bourne, 1978). Hardness (popular nomenclature: soft, firm, hard) –here defined as the compression force needed to produce a given deformation– is measured as the compression force peak in the first TPA cycle (which can be a real peak or a plateaux) in grams (g). Adhesiveness (popular nomenclature: sticky, tacky, gooey) is the work required to pull a material away from a surface; it is measured in grams per second (g.s), and the instrumental

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https://doi.org/10.1016/j.clay.2018.08.001
Received 6 May 2018; Received in revised form 29 July 2018; Accepted 1 August 2018

definition is the negative area for the first compression. Variations in these parameters seem to be related to the rheological behaviour of clay/water mixtures. Moreover, in the case of instrumental hardness, positive correlation with abrasiveness has been described (Pozo et al., 2013).

In a previous paper, variations were reported in the instrumental hardness and adhesiveness of mixtures of distilled water plus several clay materials (Armijo et al., 2015). The present study was designed to assess the influence of salinity (actually dry solid matter) and pH on instrumental hardness and adhesiveness variability in mixtures of different waters with three clays composed of absorbent clay minerals (raw Al-smectite and Mg-smectite, and a commercial sepiolite). The reference values for instrumental hardness and adhesiveness were those determined by Pozo et al. (2013) in peloids used in Spanish spas.

Our main objective was to compare the behaviour of semisolid water/clay mixtures to improve the preparation of pastes for pelotherapy purposes, ensuring their suitable hardness and adhesiveness but also a water content favouring their application in thermotherapy. Casás et al. (2013) described the influence of salinity and ion content on the thermal behaviour of absorbent clays (bentonite). Clay composition is important because ab/adsorption capacity is related to thermal properties, especially the retention of a large volume of water. Clays (e.g. bentonites) and sepiolite give rise to systems showing better thermal performance in comparison with common clays (Legido et al., 2007). On the other hand, the therapeutic activity of peloids is also related to the ion composition of the liquid phase and thus the hydrochemistry of the water mixed with the clay is also important (Carretero et al., 2007; Carretero et al., 2010; Maraver et al., 2015; Carbajo and Maraver, 2018).

2. Materials and methods

2.1. Studied materials

The absorbent clay samples examined, two bentonites and one sepiolite, were supplied by the companies Clariant and Tolsa, and obtained from the Spanish deposits of Cabo de Gata (dioctahedral bentonite, hereafter BD), and of Madrid Basin (trioctahedral bentonite and sepiolite, hereafter BT and SE respectively). Bentonites are raw materials but sepiolite is a refined and beneficiated product with the commercial name of sepiolite SPLF ELITE (Tolsa) which is used as a rheological additive with a high emulsifying and dispersion-forming capacity.

The seawater was supplied by Quinton Labs (Quinton Hypertonic). Its chemical composition and physical properties are described in Casás et al. (2011). This seawater has a salinity (expressed as dry solid matter) of 39 g/L (39‰) and a pH of 8.2. After its dilution in distilled water, solutions of salinities of 19.5 g/L (pH = 8.2), 13 g/L (pH = 7.9), 5.5 g/L (pH = 7.4) and 1.65 g/L (pH = 7.1) were prepared. The isotonic water (Quinton isotonic) is composed of mixed seawater (29%) and spring water (71%) to give a salinity of 11 g/L and a pH of 7.7.

2.2. Analytical methodology

The mineralogical characterization of the clay samples was performed by X-ray diffraction in a Bruker instrument model D8 ADVANCE. The bulk samples were X-rayed from 2° to 65° 2θ using disoriented powder and CuKα radiation at a scanning speed of 1° 2θ/min. The identification of clay minerals fraction was carried out on three oriented samples sedimented onto glass sample holders, including an air-dried sample, solvated with ethylene glycol and heat-treated at 550 °C for 2 h. Diffractograms were obtained between 2 and 35° 2θ. The mineral intensity factors (MIF) method was applied to XRD reflection intensity ratios normalized to 100% with calibration constants for the quantitative estimation of mineral contents (Chung, 1974). The measure of the d(060) reflection in random polycrystalline powder of the clay fraction was used to establish the dioctahedral (1.49–1.50 Å) or trioctahedral (1.52–1.53 Å) character of the clay minerals.

Grain-size distribution was determined in the 0.01–1000 μm range using a laser diffraction particle size analyzer (Malvern Mastersizer 3000). The statistical parameters considered were the mode, median (Dv50), volume mean diameter (D[4,3] and Dv10 and Dv90 percentiles (Planz, 1984).

Nitrogen adsorption–desorption isotherms of the samples were measured at 77 K using a Micromeritic ASAP2020 (static volumetric technique). Total specific surface area (SBET) was determined through the BET equation (Brunauer et al., 1938).

The cation exchange capacity (CEC) was determined following the Tucker method (Tucker, 1974), wherein the clay sample is saturated with 1 N ammonium chloride at pH 8.2. After which the presence of ammonium is measured using a Kjeldahl distillation apparatus and exchangeable Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} cations determined by atomic absorption spectrophotometry using a PerkinElmer AAnalist-100 spectrophotometer.

Hardness and adhesiveness (texture profile analysis) were determined with a Brookfield Texture Analyzer, model LRFA 1000. The working parameters of this instrument are: load 0 to 1000 g, resolution 0.10 g, precision ± 0.5% Full Scale Range, probe speed 0.1 to 10 mm/s in 0.1 mm/s steps, or 1 to 10 mm/s in 1 mm/s steps with an accuracy of ± 0.1% of set point. Probe position can be adjusted from 0 to 75 mm with a resolution of 0.1 mm and precision of 0.1 mm. The probe used here was a stainless steel, spherical 10 mm diameter probe (reference TA 38), manufactured with a tolerance better than 0.1%. Samples were placed in a polymer recipient shaped like an inverted conical trunk, eliminating air bubbles (Pozo et al., 2013). The instrument provides numerical and graphical data for each product analyzed. Samples were tested in triplicate and the mean value recorded for each sample.

Distilled water (pH around 6.9), obtained using a Fistreen Cyclon distiller, Water Pro PS system Labconco and Synergy UV Millipore, was used to prepare several mixtures of each clay. Samples were prepared by adding water to the solids, leaving the water to soak in and then manually homogenising the mixture. After preparing a paste with very little water, further water was added to obtain a more moistened and easier to manipulate product as the first of the dilution series. The series was continued until the hardness of the sample was such that the instrument did not detect it as a sample. The water contents of the different preparations were determined by desiccation at 105 °C in an oven until constant weight and were expressed as percentages relative to the whole mixture.

Equations best describing hardness and adhesiveness variations according to water content of each clay-water mixture were obtained using the statistics software package Origin Pro 8 (Origin Lab Corporation, Northampton, MA, USA).

Given the composition of the seawater provided by Quinton Labs (both the hypertonic and isotonic water) without dispersed particles and with a very low concentration of carbonates and bicarbonates, the total dissolved solids (TDS) obtained by evaporation to 180 °C was taken as equivalent to salinity.

3. Results

3.1. Compositional and textural characterization of the clay samples

Bulk sample mineralogy and clay fraction mineralogy, grain-size distributions and BET specific surface areas of the three analyzed clays are shown in Table 1. In the case of bentonites the cation exchange capacity values and percentage of exchangeable cations are also shown.

Sample BT shows a predominance (95%) of trioctahedral clay minerals ($d_{(060)}$ = 1.529 Å). Quartz and feldspar (K and Ca—Na) were detected in proportions lower than 5%. The clay fraction (< 2 μm) shows Mg-smectite as the main component reaching 92%, with minor amounts of illite (8%) and traces of kaolinite and sepiolite (Fig. 1). The