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Research paper

The water effect on instrumental hardness and adhesiveness of clay mixtures for pelotherapy

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ABSTRACT

This study was designed to assess several clay-water mixtures in terms of their instrumental texture to identify candidates for use as peloids in pelotherapy. Eight commercially available clays (including three from Spanish quarries) were characterized in terms of their mineralogical composition (X-ray diffraction). Using each clay, series of mixtures containing different proportions of distilled water were prepared and hardness and adhesiveness measurements made using a Brookfield® texture analyzer. The data obtained were then used to derive exponential equations describing the hardness and adhesiveness of the mixtures depending on their water content. Four new parameters were also defined: reference water content for adequate hardness and adhesiveness and water content required to reduce hardness or adhesiveness by half. The bentonites composed of Mg-smectite with interlayer Na, need the higher water contents to obtain hardness/adhesiveness values in the range of Spanish peloids, follow the bentonites composed of Mg-smectite with divalent interlayer cations and dioctahedral smectites (Al-smectite). Sepiolite and palygorskite samples also need high water contents. Kerolite-stevensite and kaolins showed the lower water contents. According to the equations and parameters defined, peloids similar to those currently used in spas could be tailored for pelotherapy.

1. Introduction

According to Gomes et al. (2013), a peloid is "a maturated mud or muddy dispersion with healing and/or cosmetic properties, composed of a complex mixture of fine-grained natural materials of geologic and/or biologic origin, mineral water or sea water, and commonly organic compounds from biological metabolic activity". The topical use of peloids for therapeutic or cosmetic purposes is known as pelotherapy.

Especially interesting for pelotherapy are those peloids composed of different types of clays mixed with mineral waters (Pozo et al., 2013; Carretero et al., 2014).

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 own perception. Investigators should be able to count on a set of empirical instrumental tests to quantify these properties. Texture analysis is widely used in the field of materials science to determine the physical properties of materials and behavior of solids and semi-solid dispersions when subjected to compression. Over more than 50 years, texture analysis has also been used in the food industry (Szczesniak, 1963; Breene, 1975; Bourne, 1982; Szczesniak, 1987; Borwankar, 1992; Roudot, 2001; Rahman and Al-Farsi, 2005; Sahin and Sumnu, 2006).

Szczesniak (1963) defined texture in terms of three main characteristics: i) mechanical, referring to material response to an applied force, ii) geometric, indicating the size, shape and organization of particles comprising the material, and iii) other factors related to a material's temperature response, water content and cooling speed. Texture analysis assesses mechanical properties by subjecting a material to a controlled force. This procedure generates a plot of the strain produced over time as the response to deformation. A technique known as texture profile analysis (TPA) was developed in the early 1960's by the US Company General Foods. The method measures a series of texture variables that relate the force applied to the deformation produced. These variables were subsequently described by Bourne (1978).

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In this study, the TPA procedure was used to assess peloids with the idea that it could be a useful tool to optimize and control peloid quality. From both theoretical and practical perspectives, several different clay preparations were characterized in terms of their hardness or adhesiveness for varying water contents. Once this relationship was established, we determined the range of water retention capacity for each clay for the hardness and adhesiveness values determined by Pozo et al. (2013) in peloids used in Spanish spas.

2. Materials and methods

Five commercially available clays and three clays quarried in Spain previously tested for their use in pelotherapy by Carretero et al. (2014) were used (Table 1).

The mineralogical study of the samples was performed by X-ray diffraction analysis with a Bruker instrument modelo D8 ADVANCE. The bulk samples were X-rayed from 2° to 65° 2θ using disoriented powder and CuKα radiation with a scanning speed of 1° 2θ/min. The identification of clay fraction minerals was carried out on three oriented samples sedimented onto glass sample holders, including air-dried sample, solvated with ethylene glycol and heat-treated at 550 °C during 2 h. The diagrams were obtained between 2 and 35° 2θ. Semi-quantitative estimation of the mineral content was carried out using the intensity factors calculated by Schultz (1964) and Van der Marel (1966). The smectites crystallinity was studied through measurement of the full width at half maximum peak intensity (FWHM) of the d(001) peak after treatment with ethylene glycol (approximately at 17 Å). The software used was Xpowder (http://www.xpowder.com). The procedure is based on the direct relationship existing between crystallinity and crystallite size, the latter being calculated through the Scherrer equation. Crystallite size is inversely proportional to the FWHM value, crystallinity thus decreasing as the FWHM value increases.

The measure of the d(060) reflection in random polycrystalline powder of the clay fraction has been used to establish the dioctahedral (1.40–1.50 Å) or trioctahedral (1.52–1.53 Å) character of clay minerals.

Hardness and adhesiveness (texture profile analysis) were determined in a Brookfield Texture Analyzer model LRFA 1000. The procedure involves compressing a solid or semisolid twice until the sample approaches 80% of its original height to give two positive and two negative curves. Force peaks and areas under the curve are used to calculate several variables including hardness and adhesiveness (Fig. 1). Hardness, defined here 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, defined as the work needed to extract the probe from the sample, is given by the area under the negative portion of the force peak in the first TPA cycle (Fig. 1), and is measured in grams per second (g·s) (Bourne, 1978; Armijo, 2007; Armijo et al., 2012; Pozo et al., 2013; Fernández-Torán, 2014).

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 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 are placed in a polymer recipient shaped like an inverted conical trunk, eliminating air bubbles (Armijo, 2007; Pozo et al., 2013; Fernández-Torán, 2014). The instrument provides numerical and graphical data for each product analyzed. Samples were tested in triplicate and the means recorded for each sample.

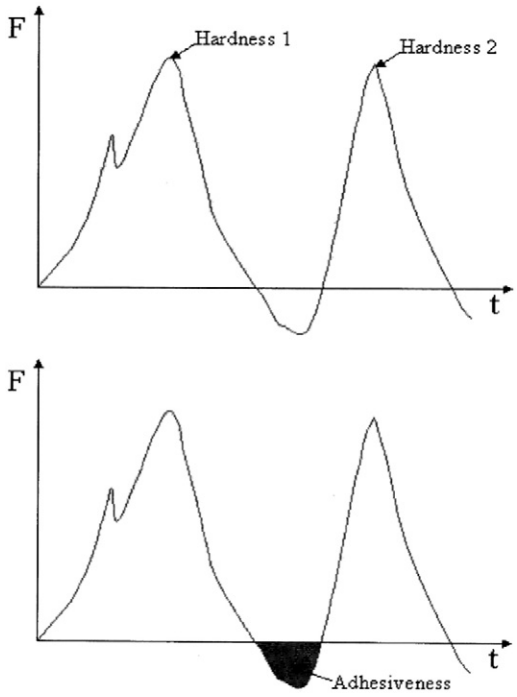

Fig. 1. Textural profile analysis (TPA) graphs illustrating the procedure to obtain the hardness and adhesiveness. F: strength (g), t: time (s).

Distilled water, 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 homogenizing the mixture. After preparing a paste with very little water, further water was added to obtain a more moist 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.

The 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).

Table 1
Studied clay materials and their source.

Sample	Trade name	Company
M1	Volcangel	Benesa
M2	Atox	Tolsa
M3	Palygel SMV	Tolsa
M4	SPLF ELITE	Tolsa
M5	Clay1*	Süd Chemie España
M6	Clay2*	Süd Chemie España
M7	Clay3*	Süd Chemie España
M8	Caolin G-40/77M	Avisa

* Clays studied in Carretero et al., 2014.

3. Results and discussion

3.1. Mineralogical composition of the clays

The mineral contents of the eight clays analyzed are described in Table 2. M1 shows a predominance of mainly trioctahedral clay minerals (88%) although a small reflection indicating subordinated dioctahedral minerals was also observed (d(060) = 1.52 − 1.49 Å). Quartz, feldspar (K and Ca–Na) and calcite were detected in proportions lower than 5%. The clay fraction (<2 μm) shows smectite as the main component at 85%, with minor amounts of illite (15%). The full width at half maximum peak intensity (FWHM) of smectite was 1.04 2θ and its crystallite size was 9 nm. The 001 reflection of smectite appeared