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Research Paper

# Rheological and thermal characterization of peloids made of selected Portuguese geological materials

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ABSTRACT

Tailored peloids are prepared by the maturation of selected clay minerals mixed with thermo-mineral waters. These dispersions are topically applied to the skin to treat different ailments because of their unique rheological and thermal properties. Colloidal dimensions of the dispersed clay mineral particles yielded stable and viscous dispersions capable of flowing when spread and stand in the area to be treated without flowing away. To be easily handled and cause a pleasant sensation during application, the clay mineral dispersions must have good consistency and cause no abrasion. As thermotherapeutic agents, these systems are heated before application being important to ensure that the clay paste has heat retention capacity and adequate cooling kinetics.

On the basis of a previous detailed characterization of Portuguese clayey materials for medical hydrology applications, six clay raw materials were selected as candidates to be used in the preparation of tailored peloids. This study aims to obtain tailored peloids with suitable technical, rheological and thermal properties. Samples from "Serra de Dentro" and "Barracão Clays" formations exhibited adequate abrasivity and consistency. Regarding sedimentation volume and apparent viscosity, the majority of samples showed some difficulties as they were coagulated in the absence of a dispersing agent. Specific heat and cooling rate were adequate in samples from "Serra de Dentro" and "Luz Clays" formations.

## 1. Introduction

Peloids or thermal muds are dispersions of clay-rich solid fractions in mineral-medicinal water (Viseras et al., 2006, 2007). They appear in the nature but can also be prepared by maturation (mixing during a long period) of selected clayey materials with salty thermo-mineral waters (Veniale et al., 2004, 2007). These systems are topically applied in different parts of the body or the whole body for therapeutic and cosmetic purposes (Carretero et al., 2010; Veniale et al., 2007).

As disperse systems, rheological and thermal behaviors are of great concern in the study and characterization of peloids (Viseras et al., 1999; Viseras et al., 2006; Cerezo et al., 2006). Besides predicting the properties which are directly related with the peloid application (e.g. spreading qualities, adhesion to skin and removal), the rheological properties of the dispersion (viscosity and sediment volume) are also responsible for the settling of dispersed particles and the formation of a sediment at the bottom of containers. Furthermore, in the manufacture of a dispersion, the aggregation state of solid particles is important as it determines the quality of the dispersion (De Bernardi and Pedrinazzi, 1996; Minguzzi et al., 1999; Veniale, 1999). Together with the rheological properties, a set of other important technical qualities are considered in the materials suitable to produce peloids with therapeutic validity (Barbieri, 1996). Among them, the thermal properties (good cooling kinetics and high heat capacity) play an important role. In most of the cases, the heat application is directly responsible for the therapeutic effect as the peloids are applied hot or involved in preserving the heat (Cara et al., 2000; Ferrand and Yvon, 1991; Legido et al., 2007; Yvon and Ferrand, 1996). Another category of important technical properties, scarcely explored in previous studies, are consistency and abrasivity (or mechanical properties) of the materials when applied topically. These mechanical properties determine the molding capacity to the peloid before its use. In addition, they provide easiness of handling and a pleasant sensation when the peloid is applied.

On the basis of a previous detailed characterization of Portuguese clayey materials for medical hydrology applications, six clay raw materials were selected due to their good compositional and flow properties (Rebelo et al., 2010b). This study aims to determine the rheological, technical and thermal properties and their capacity to produce qualified tailored peloids.

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## 2. Materials and methods

The six clayey materials were collected from well known geological formations, previously described in terms of their composition and micromorphology for healing purposes (Rebelo et al., 2005; Rebelo et al., 2010a,b). They comprised clay-rich levels of Jurassic to Pliocene age formations collected from Freixial (J-F1), Aveiro (C-F2), Luz (C-F3), Xabregas (M-F4), Serra de Dentro (M-F5) and Barracão (P-F6) formations. Samples J-F1, C-F2 and P-F6 are sediments collected in the Lusitanian basin, along the Western-Central Border. Sample C-F3 was collected in the Algarve Basin (Southern Border) at Lagos region. Sample M-F4 is a sediment collected from the Sado Tertiary Basin, located in the Setúbal Peninsula. Finally, sample M-F5 is a bentonitic alteration product, collected at Serra de Dentro, at the Madeira Archipelago (Fig.1).

### 2.1. Description of the materials

On the previous work by Rebelo et al. (2010b) the mineralogical composition (<63 μm) and bulk granulometry were determined (Table 1).

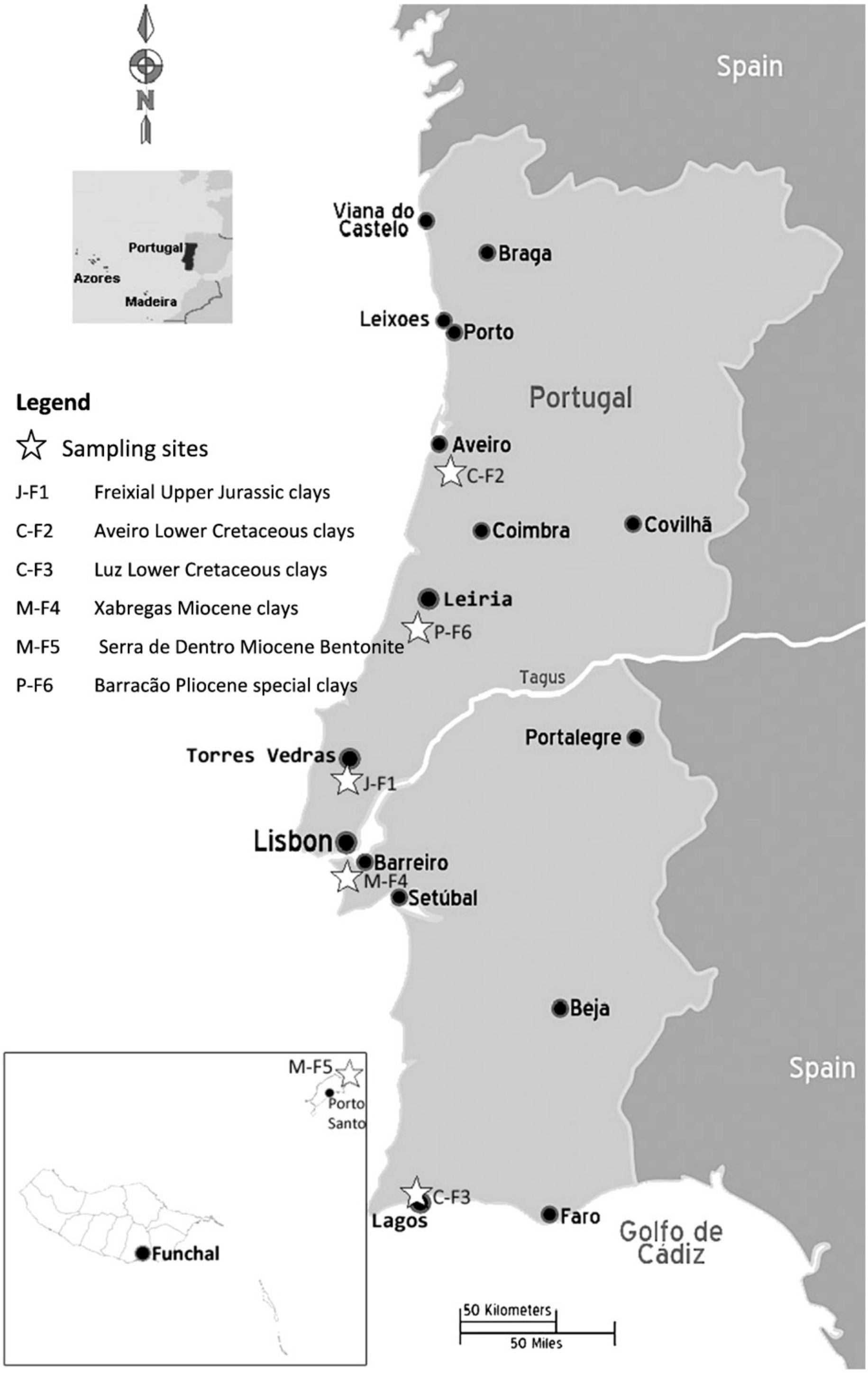

**Fig. 1.** Location of the selected clay-rich formations.

**Table 1**
Bulk granulometry and silt-clay fraction composition (adapted from Rebelo et al., 2010b).

| Samples | Bulk granulometry (%) | | | Silt-clay fraction mineralogy (%) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Detrital tectosilicates | | | | Clay minerals | | | | Carbonates | | | (Hydr)oxides | | |
| | Sand | Silt | Clay | Qtz | Fsp | Pl | An | Mca/Ill | Kln | Sme | Paly | Cal | Dol | Sd | Ant | Crs | Fe |
| J-F1 | 4 | 44 | 52 | 32 | 4 | 1 | – | 34 | 22 | – | – | – | 1 | 1 | – | – | 4 |
| C-F2 | 1 | 23 | 76 | 28 | 4 | 2 | – | 34 | 22 | 5 | – | 1 | – | – | – | – | 4 |
| C-F3 | 18 | 24 | 58 | 7 | 8 | 1 | – | 50 | 11 | 1 | – | 12 | – | – | – | – | 10 |
| M-F4 | 3 | 62 | 35 | 29 | 5 | 7 | – | 21 | 20 | 10 | – | 3 | – | – | – | 2 | 3 |
| M-F5 | 66 | 18 | 16 | 1 | – | – | 21 | 10 | – | 53 | – | 4 | – | – | 2 | – | 9 |
| P-F6 | 3 | 11 | 86 | 12 | 2 | 1 | – | 15 | 63 | – | 3 | – | – | 1 | – | – | 2 |

Qtz = Quartz; Fsp = K-Feldspar; Pl = Na-Plagioclase; An = Anorthite; Mca/Ill = White Mica/Illite; Kln = Kaolinite; Sme = Smectite; Paly = Palygorskite; Cal = Calcite; Dol = Dolomite; Sd = Siderite; Ant = Anatase; Crs = Cristobalite; and Fe = Fe-Oxides.

The bulk granulometry of samples J-F1, C-F2, CF-3 and P-F6 (Table 1) evidenced high amounts of clay-sized particles (>50%) and low contents of sand particles (<5%), with the exception of C-F3 (Table 1). The silt content was the highest in J-F1 (Table 1). M-F4 and M-F5 were characterized by a smaller clay fraction content (<40%) but relatively high contents of the silt and sand fractions (>60%) (Table 1).

Because the bulk materials showed highly variable amounts of sand-sized particles, the initial separation of the silt-clay fraction (<63 μm) from the bulk was considered. This particularity could provide some discomfort during the clay paste application (Rebelo et al., 2010b). Previous studies (Rebelo et al., 2005, 2010a,b) showed that these materials are suitable for therapeutical applications when sieved. Sieving and wet separation is a common treatment for clays that are intended to be used as natural products in several pharmaceutical and cosmetic preparations, which ensures its maximum purity and ease of use (Viseras et al., 2007). Despite the extra effort of sieving and wet separating the original geomaterials, we believe that the increase in quality of the final product justifies it.

Thus, before carrying out the laboratory analysis, each of the studied samples was carefully wet sieved in 63 μm meshes. After drying (at 60 °C), the samples were maintained in closed containers at room temperature.

The mineralogical compositions of separated samples are reported in Table 1. Samples J-F1, C-F2 and M-F4 were characterized by reasonable quantities of quartz and white micas (both around 30%) and lesser quantities of kaolinite. Smectite was present in samples C-F2 and M-F4 in low quantities (5–10%).

Samples C-F3, P-F6 and especially M-F5 (Table 1) contained smaller amounts of quartz (≤12%). Illite was particularly abundant in C-F3 (50% of the <63 μm fraction) and the kaolinite content was significant in P-F6 (Table 1). Sample C-F3 also evidenced a significant content of carbonates and iron (hydr)oxides. Usually, the content of these associated minerals (when present) is <5%. M-F5, a bentonitic material, showed a high smectite content (>50%) and also significant amounts of plagioclases (Table 1). This sample contained significant amounts of iron (hydr)oxides (Table 1).

## 2.2. Abrasivity and plasticity

### 2.2.1. Einlehner abrasivity

The abrasivity was determined using the Einlehner Test. Initially, 50 g of the sieved clays (<63 μm) was dried at 60 °C (during 15–20 min) and dispersed in 400 mL of distilled water until a homogeneous dispersion was obtained (~15 min). The initial mass of the clean and dry standard bronze wire was determined before testing. The weighed wire was assembled into an Einlehner AT 1000 apparatus with the dispersion and, after stirring for 43,500 revolutions (~30 min), the cleaned and dried wire was weighed again. The mass loss (mg) was the measure of Einlehner abrasion. The abrasivity index was determined using the wear area.

### 2.2.2. Atterberg limits

The Atterberg limits ($W_L$, $W_P$ and PI) were determined following the Portuguese norm NP 143-1969. After sieved, 100 g of each sieved samples (<63 μm) was air dried and mixed with water to form a remoulded clay paste. The paste was placed in the standard Casagrande cup and then grooved. The rotation of the apparatus at a set speed was continued until the groove flowed and closed over a specified length. The number of blows of the cup was noted and the sample taken to determine the moisture content. The test was repeated 4 times at decreasing water contents (by air-drying the sample) each time noting the number required to close the groove. A graph of the log of the number of blows against water content was drawn, and the moisture content requiring 25 blows to close the groove, i.e. the liquid limit ($W_L$), was determined.

For the plastic limit test, approximately 20 g of the sieved clays (<63 μm) was mixed on a glass plate with water to make it sufficiently plastic to roll into a ball. The ball was firstly rolled to form a clay thread and then rolled again until it started to crumble at a thread diameter of 3 mm. At this point, the water content gives the plastic limit ($W_P$). The Plasticity index (PI) is the difference between $W_L$ and $W_P$.

## 2.3. Thermal properties

### 2.3.1. Specific heat

The specific heat was determined for each sieved and dried sample by differential scanning calorimetry (DSC) in the Shimatzu® DSC-50 Calorimeter.

### 2.3.2. Cooling kinetics

To produce 60% water-clay pastes, 30 g of sample was mixed with 20 mL of distilled water. The paste was introduced in a closed 50 mL cylindrical Teflon container, was heated at temperature constancy (70 °C) and introduced in a thermostatic bath (Edelstahl Rostfrei®) at 35 °C. The temperature was measured with the Dual Thermometer LT Lutron TM-906A every 30 s until the temperature of the clay paste and the thermostatic bath were identical.

To obtain representative cooling curves of the studied clay pastes, the experimental data were fitted by exponential curves by regression analysis. According to previous studies (Cara et al., 2000; Legido et al., 2007), the curves followed a function of the type $T = A - Be^{-Kt}$ where $A$ is the bath temperature, $B$ is the difference between the starting temperature of the clay and the bath temperature ($A$) and $K$ is the cooling rate. The estimated error of the different samples was calculated:

$$err = \sqrt{\frac{\sum_{i=1}^{n}\left(T_{est,i} - T_{data,i}\right)^{z}}{n}}$$

**Table 2**
Einlehner abrasivity of the clays.

| Samples | Abrasion (mg) | Abrasivity index (g/m$^2$) |
|---|---|---|
| J-F1 | 79 | 258 |
| C-F2 | 72 | 235 |
| C-F3 | 32 | 106 |
| M-F4 | 102 | 334 |
| M-F5 | 39 | 127 |
| P-F6 | 23 | 75 |

**Table 3**
Atterberg limits of the clays.

| Samples | Liquid limit (%) | Plastic limit (%) | Plastic index (%) |
|---|---|---|---|
| J-F1 | 42 | 25 | 17 |
| C-F2 | 67 | 40 | 27 |
| C-F3 | 44 | 29 | 15 |
| M-F4 | 47 | 23 | 24 |
| M-F5 | 108 | 59 | 49 |
| P-F6 | 60 | 33 | 27 |

where $T_{data}$ is the measured temperature, $T_{est}$ the temperature derived from the fitted curve, $n$ the total number of measurements.

### 2.4. Rheology

#### 2.4.1. Sediment volume

The sediment volume (F) was defined as the ratio between the sediment's final (ultimate) volume in mL ($V_u$) and the original volume (in mL) of the dispersion before settling ($V_0$) (Bergaya et al., 2006; Martin, 1993). It was determined following the methodology proposed by the Real Farmacopea Española (2005).

The silt-clay samples (<63 μm) were disaggregated using an agata mortar. The clay–water dispersions were prepared of 6 g clay and 200 mL distilled water, then stirred at 10,000 rpm during 20 min with an Ultra Turrax-T25 stirrer (Ika Labortechnik®). From each clay–water dispersion, 100 mL was extracted and stored undisturbed at room temperature during 24 h in stoppered testing tubes. After 24 h, the final volumes were registered and the corresponding sediment volumes were calculated.

#### 2.4.2. Formulation of clay–water dispersions

The apparent viscosity of 10% clay–water dispersions was measured. The solid phase consisted of 15 g of the sieved samples (<63 μm) and 15 g of Veegum® HV grade (<125 μm). The liquid phase was prepared with 270 mL of distilled water (pH = 5.75, at 20 °C). The clay–water dispersions were homogenized at 1000 rpm (~1–2 min) in a Eurostar Power control-visc P1 overhead stirrer (Ika Labortechnik®) and maintained closed in a thermostatic bath (J.P. Selecta S.A. Precisterm) during 24 h at 40 °C.

The added Veegum® HV (VHV) is a purified smectite with the following mineralogical composition: 53% Al-smectite, 41% Mg-smectite, <5% quartz, and <5% of K-feldspars and traces of calcite (Aguzzi et al., 2005). It was added to all clay-dispersions as stabilizing agent to retard sedimentation and avoid coagulation of the dispersed particles (Viseras et al., 2007). It was added to the solid phase only to perform the apparent viscosity test.

The addition of VHV generally aims at improving the product quality, fulfilling all the required technical specifications. Although these compositional and textural modifications increase the cost of the peloids, they greatly improve the resultant rheological properties. Consequently, the resulting peloids would be easily marketed with economic benefits as is evidenced by a wide number of products fulfilling different therapeutic or cosmetic purposes such as topical health care preparations (Viseras et al., 2007).

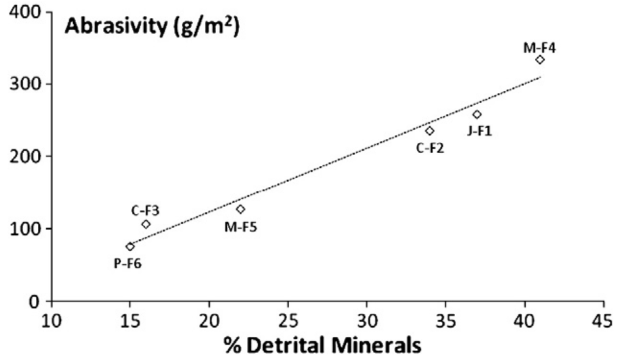

**Fig. 2.** Pearson's correlation between abrasivity index and detrital minerals content.

Different water types influence the original properties of peloids (Veniale et al., 2004). However, this study aimed at characterizing the properties of clays when dispersed in water and not the influence of water types in the properties of the resulting peloid. Therefore, distilled water was used to minimize the effect of different kinds of water (Veniale et al., 2004).

#### 2.4.3. Apparent viscosity

The apparent viscosity of clay–water dispersions formulated with VHV and previously maintained at 40 °C in the thermostatic bath were measured with the viscometer Brookfield Engineering® — DVII + PRO with spindle 03. Three parallel measurements were done in intervals of 30 s at different shear rates (2, 4, 10, 20, 50 and 100 rpm). The measurements were repeated after 24 h at undisturbed conditions, keeping the samples at 40 °C in the thermostatic bath.

## 3. Results and discussion

### 3.1. Abrasivity and plasticity

#### 3.1.1. Einlehner abrasivity

The Einlehner abrasion (at 43,500 rpm) ranged between 23 and 102 mg (Table 2). The abrasivity indices (A.I.) changed between 75 g/m$^2$ (P-F6) to 334 g/m$^2$ (M-F4) (Table 2). The less abrasive materials were C-F3, M-F5 and especially P-F6 with A.I. close to 100 g/m$^2$.

A possible explanation for the higher abrasivity of samples J-F1, C-F2, and M-F4 is their high content in detrital tectosilicates (Table 1). Because these samples include coarse and sharp-edged quartz grains, they produce high abrasion. Consequently, some discomfort is expected when applied to the skin (Rebelo et al., 2010a,b). In fact, the highest abrasivities (>200 g/m$^2$) were observed when the content of detrital minerals (quartz, k-feldspars and plagioclases) was higher than or equal to 34% (Fig. 2).

P-F6, C-F3 and M-F5 would be softer when applied because their content in hard minerals was much lower leading to a less significant abrasivity (Fig. 2). The abrasivity of these samples was comparable to the abrasivity of bentonites recently studied for industrial applications (Klinkenberg et al., 2009). The higher content of <2 μm particles and the presence of a favorable micromorphology (platy shapes and pseudospherical aggregates) were considered important factors because they contribute to softer and less abrasive materials

**Table 4**
Specific heat values of the clays.

| Samples | ΔT (K) | Q/m (J kg$^{-1}$) | Specific Heat (J K$^{-1}$kg$^{-1}$) · 10$^3$ |
|---|---|---|---|
| J-F1 | 91.69 | 64,660 | 0.71 |
| C-F2 | 72.59 | 82,930 | 1.14 |
| C-F3 | 97.14 | 110,000 | 1.13 |
| M-F4 | 93.12 | 94,460 | 1.01 |
| M-F5 | 118.12 | 290,000 | 2.46 |
| P-F6 | 87.21 | 220,000 | 2.52 |

(Klinkenberg et al., 2009; Rebelo et al., 2010a,b).The abrasivity of a clayey material for application to the skin should not exceed 5 g/m$^2$ at 1000 rpm (or 200 g/m$^2$ at 43,500 rpm) (Gomes, 2002). Thus, only C-F3, M-F5 and P-F6 were considered adequate to be applied on the skin without producing an undesirable sensation.

### 3.1.2. Atterberg limits

In the majority of the samples the liquid limit ($W_L$) values varied between 42 and 67% (Table 3). The exception was M-F5, with $W_L$>100%. The studied samples were grouped in high plasticity clays (C-F2, P-F6 and M-F5) when $W_L$ was >50% and in

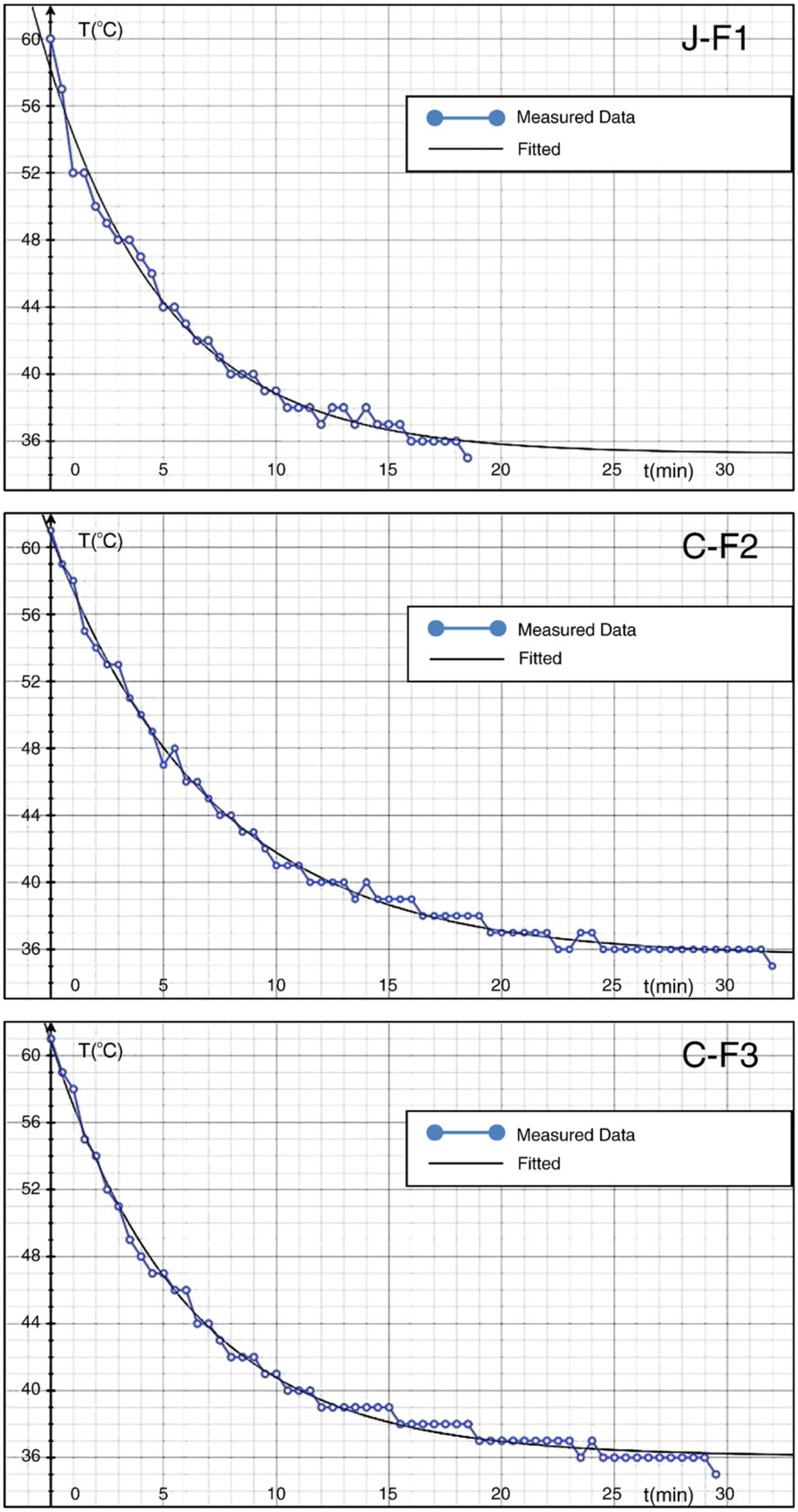

**Fig. 3.** Cooling curves of the clay–water dispersions (formulated with 60% of clay).

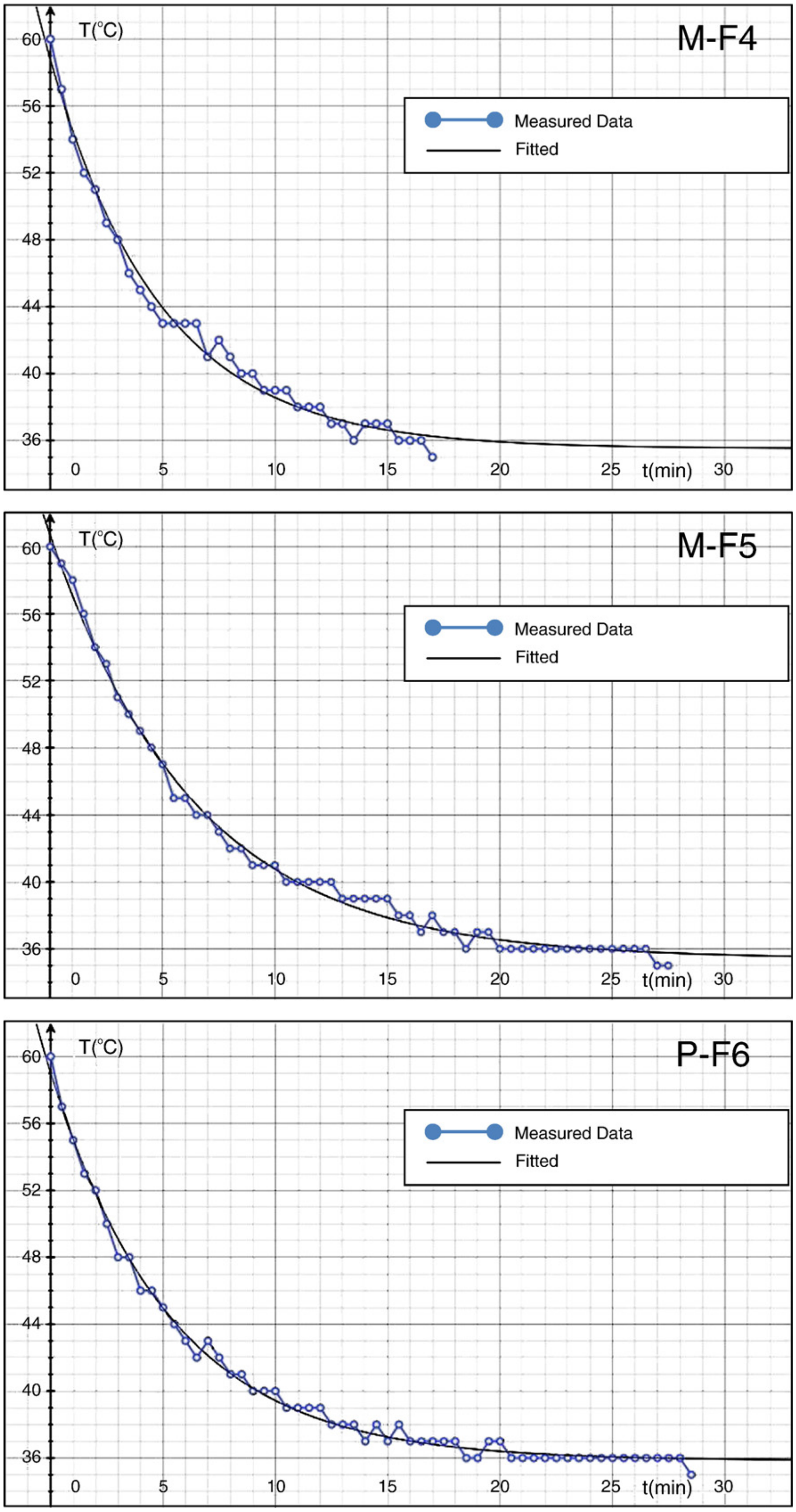

**Fig. 3** (*continued*).

low plasticity clays (J-F1, C-F3 and M-F4) when the $W_L$ was <50% (Bain, 1971).

The plastic limit ($W_P$) was between 23 and 40% for the majority of samples (Table 3). According to Jenkins soils classification (Gomes, 2002), all samples were considered high plasticity soils because their plastic indices (P.I.) were >15%. J-F1 and C-F3 were considered the less plastic, with P.I. ≈ 15%, while M-F5 was the most plastic one with P.I. = 49%.

Samples C-F2, P-F6 and, especially M-F5, showed the best plastic behavior among the studied samples. They should exhibit good water

**Table 5**
Parameters of adjustment and standard error *(err)* of the different clays.

| Samples | *A* (°C) | *B* (°C) | *K* | *err* |
|---|---|---|---|---|
| J-F1 | 35.26 | 22.95 | 0.19 | 0.56 |
| C-F2 | 35.57 | 25.07 | 0.14 | 0.48 |
| C-F3 | 36.07 | 24.71 | 0.17 | 0.46 |
| M-F4 | 35.52 | 23.27 | 0.20 | 0.51 |
| M-F5 | 35.41 | 25.30 | 0.16 | 0.48 |
| P-F6 | 35.85 | 23.18 | 0.19 | 1.30 |

retention capacity and, therefore, should be capable to develop an adequate plastic behavior during their manipulation and spreading. Note that higher liquid limits correspond to higher plastic limits (Table 3). The most adequate raw materials in terms of manipulation and spreading were C-F2, P-F6 and M-F5 because they form pastes with good consistency.

## 3.2. Thermal properties

### 3.2.1. Specific heat

The specific heat ranged between $0.71\times10^3$ and $2.52\times10^3$ $JK^{-1}kg^{-1}$ (Table 4). Samples P-F6 and M-F5 showed the highest specific heat above $2.00\times10^3$ $JK^{-1}kg^{-1}$. Only P-F6 and M-F5 showed specific heat values comparable with some common clays and bentonites for pelotherapy uses (Legido et al., 2007).

### 3.2.2. Cooling kinetics

According to the cooling curves (Fig. 3), the clay pastes M-F5, C-F3, and especially C-F2 were the slowest to cool presenting lower cooling rates ($K$ values$\leq$0.17) (Table 5). These values corresponded to the specific heats (Table 4), except for C-F2 with lower specific heat. The best thermal behavior of this sample at higher water contents was already confirmed by other studies (Table 1) (Cara et al., 2000; Legido et al., 2007).

Clay pastes formulated with M-F4, J-F1 and P-F6 were the fastest to cool presenting very similar cooling rates (Table 5). These results were consistent with the specific heat (Table 4), except for P-F6 which showed a low specific heat. This different behavior of P-F6 with water (fast cooling) and when dried (high specific heat) can be explained by the lack of smectite and a more homogeneous texture when dried (Table 1) (Legido et al., 2007).

## 3.3. Rheological properties

### 3.3.1. Sediment volume

Dispersions of J-F1 and M-F5 showed the highest final volume and the highest sediment volume (about 1.0 mL/mL) (Table 6). These samples yielded flocculated systems when dispersed (Gennaro, 1998). This property is required for the formulation of dispersions with optimal physical stability. Samples J-F1 and M-F5 were also usable to formulate ideal and pharmaceutically acceptable dispersions because no sedimentation or compact sediment formation occurred in these samples (Gennaro, 1998; Martin, 1993).

The dispersions formulated with C-F2, P-F6, C-F3, and M-F4 yielded smaller final volumes resulting in reduced sediment volumes (Table 6). These dispersions were not stable but settled. The formation of a compact sediment at the bottom of the test tube (like a cake) was often observed together with a clear supernatant. To formulate stable dispersions with P-F6, C-F3 and M-F4, dispersing agents had to be added (Gennaro, 1998; Viseras et al., 2007).

**Table 6**
Rheological properties of the dispersions.

| Samples | Final volume (mL) | Sedimentation* volume (mL/mL) | Average apparent viscosity** at 10 rpm (Pas) | |
|---|---|---|---|---|
| | | | t = 0 h | t = 24 h |
| J-F1 | 99 | 0.99 | 3.6 | 3.8 |
| C-F2 | 23 | 0.23 | 4.2 | 4.9 |
| C-F3 | 20 | 0.2 | 2.7 | 3.1 |
| M-F4 | 10 | 0.1 | 2.6 | 3.0 |
| M-F5 | 99 | 0.99 | 3.2 | 3.8 |
| P-F6 | 12 | 0.12 | 2.1 | 2.3 |

* Measured in clay–water dispersions formulated with 3% of clay.
** Measured in clay–water dispersions formulated with clay (5%) and Veegum HV® (5%).

### 3.3.2. Apparent viscosity

The average apparent viscosities (at 10 rpm) of clay–water dispersions (formulated with VHV) were around 3 Pas (Table 6). J-F1 and M-F5 showed good rheological potential in the sediment volume test. The addition of Veegum® HV emphasized this property, with samples showing high apparent viscosity (Table 6). All the other dispersions showed poor stability i.e. smaller apparent viscosities except C-F2. This clay–water dispersion was the most beneficiated by the addition of Veegum® HV as it showed the highest average apparent viscosity at 10 rpm and a small sediment volume (Table 6).

In other studies (Cara et al., 2000; Yvon and Ferrand, 1996) clay pastes used for pelotherapy purposes exhibited viscosities around 4 Pas. Taking into account that the obtained apparent viscosities were beneficiated by the addition of VHV, dispersions formulated with J-F1 and M-F5 (Table 6) demonstrated the best potential to form clay pastes with rheological behavior adequate for treatments.

All the dispersions showed similar flow behavior (Fig. 4). The apparent viscosity curves steeply decreased at shear rates up to 20 rpm (Fig. 4). Thus, the dispersions showed thixotropy behavior implying that all the studied dispersions should flow when agitated and keeping its shape when applied (Viseras et al., 2006). This behavior is a very important property because it leads to the use of clay or clay minerals in several semisolid products such as lotions, creams, ointments, pastes and make-up preparations.

At initial time ($t = 0$) and near zero shear rates, the clay–water dispersions showed apparent viscosities between 10 and 20 Pas (Fig. 4). The highest apparent viscosities (around 20 Pas) were observed for the dispersions formulated with J-F1, M-F5 and especially C-F2 (exceeding 20 Pas). These results confirmed the tendency of J-F1 and M-F5 to form stable dispersions, and thus adequate rheological properties when dispersed. The dispersions formulated with C-F3, M-F4 and mainly P-F6, which already evidenced low stability (Table 6), had also lower apparent viscosities (10 Pas) (Fig. 4).

After 24 h at undisturbed conditions ($t = 24$ h), a slight increase of all dispersions' apparent viscosity was observed (Fig. 4). This tendency was more perceptible at <20 rpm and significant for the clay dispersions formulated with C-F2 and M-F4 (Table 6). This is adequate to produce stable clay–water dispersions without adding dispersing agents. Thus, these formulations should be capable to flow when required remaining at the cutaneous surface during the application (Viseras et al., 2006).

## 3.4. Overview

The mechanical, thermal and rheological properties of the samples are compared in Table 7. M-F5 and P-F6 were the most suitable formulations for therapeutic application. These samples correspond to “Serra de Dentro” and “Barracão Clays” formations. J-F1, C-F2, and C-F3, were considered suitable only in relation to certain properties. These samples correspond to “Freixial”, “Aveiro” and “Luz” formations. To be

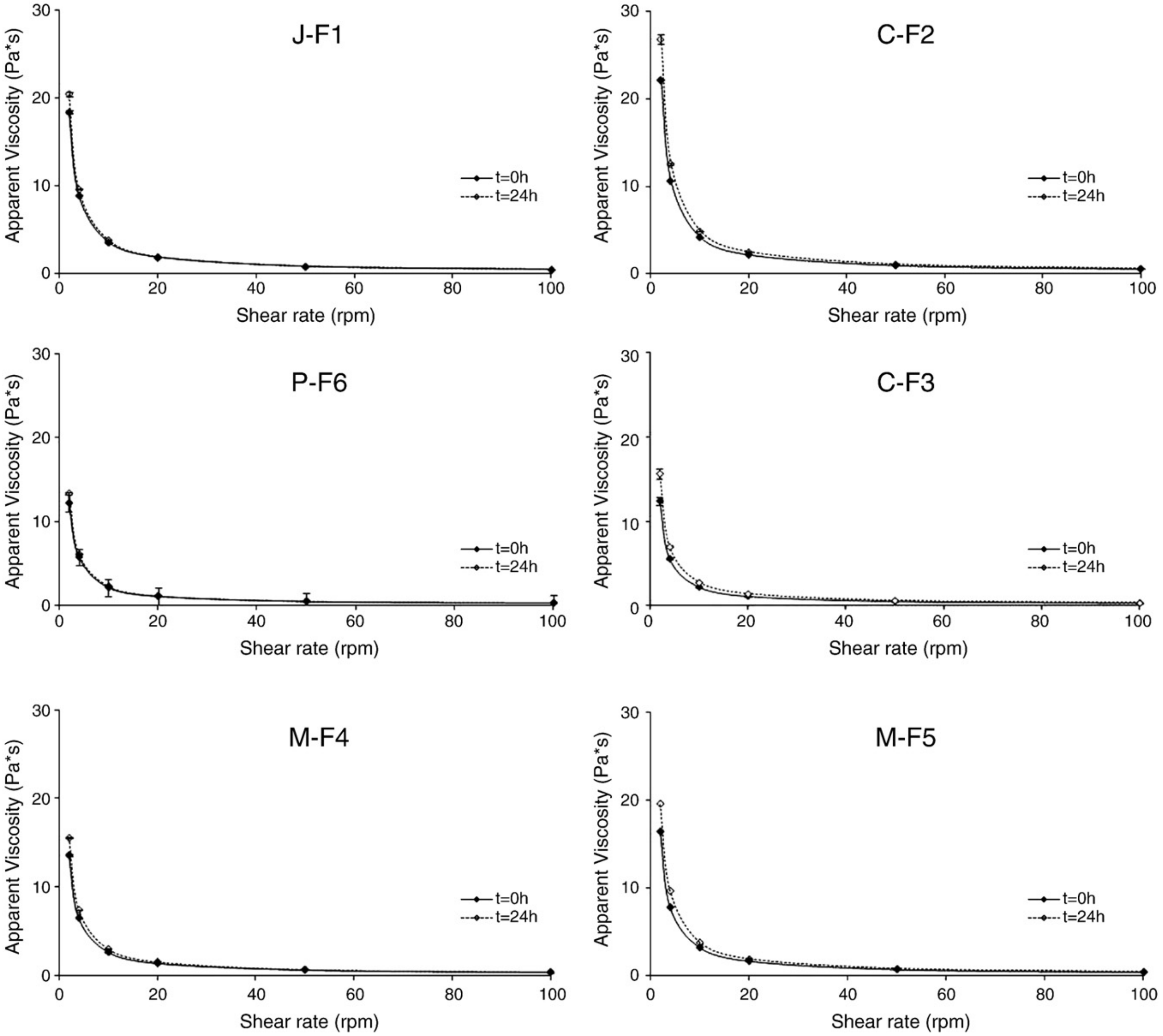

**Fig. 4.** Apparent viscosity curves of the clay–water dispersions (formulated with 5% of clay and 5% of Veegum HV®).

applied in therapeutics their properties have to be improved. M-F4 (corresponding to the "Xabregas" formation) would be unsuitable for application.

## 4. Conclusion

This study aimed at the characterization of mechanical, thermal and rheological properties of some Portuguese geomaterials previously considered suitable for use in Medical Hydrology (Rebelo et al., 2010b). The analysis was performed for the fractions <63 μm. They were characterized in terms of abrasivity, consistency, heat capacity and cooling behavior. The rheological properties, sediment volumes and apparent viscosity of the dispersions were determined.

Samples M-F5 and P-F6 showed good abrasivity, plasticity and specific heat. However, when dispersed in water, only M-F5 showed good sediment volume and cooling behavior while P-F6 revealed a good apparent viscosity. Both samples were considered suitable for

**Table 7**
Suitability of clays in terms of their technical, thermal and rheological properties.

| | Technical | | Thermal | | Rheological | | Overall suitability |
|---|---|---|---|---|---|---|---|
| Samples | Abrasivity | Plasticity | Specific heat | Cooling rate | Sedimentation | Apparent viscosity | |
| J-F1 | ✗ | ✗ | ✗ | ✗ | ✓ | ✓ | Limited |
| C-F2 | ✗ | ✓ | ✗ | ✓ | ✗ | ✓ | Limited |
| C-F3 | ✓ | ✗ | ✓ | ✓ | ✗ | ✗ | Limited |
| M-F4 | ✗ | ✗ | ✗ | ✗ | ✗ | ✗ | Not suitable |
| M-F5 | ✓ | ✓ | ✓ | ✓ | ✓ | ✗ | Suitable |
| P-F6 | ✓ | ✓ | ✓ | ✗ | ✗ | ✓ | Suitable |

✓ (adequate) ✗ (Not adequate).

application. Samples J-F1, C-F2, and C-F3 were considered suitable only in relation to particular properties, showing limited application. J-F1 exhibited good sediment volume and apparent viscosity but unsuitable technical properties. Sample M-F4 was not suitable for any application.

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