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The physical and physicochemical properties of some Turkish thermal muds and pure clay minerals and their uses in therapy

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Abstract: The physical and physicochemical properties of thermal muds (peloids) from 20 spas in Turkey were defined and compared with those of naturally pure clay minerals, smectite, illite, sepiolite, and kaolinite, to define the suitability of their use in pastes, masks, creams, and/or mud baths. The liquid and plastic limit values of the peloids show medium to high plasticity. The values of the pure clay minerals vary from 110 to 369 and 60 to 130, respectively, being higher than those of the peloid samples except for illite and kaolinite. The peloid samples show very soft, soft, semihard, hard, and fluid properties according to the consistency index. The CEC values of the peloids vary from 10.11 to 36.01 meq/100 g. The abrasivity of the peloids and clay minerals ranges from 0.58 to 3.12 mg/m^2 and 0.05 to 0.37 mg/m^2, respectively. The viscosity values of the peloid samples are variable and the thixotropic values are considerably higher in some peloid samples. In the pure clay minerals, sepiolite shows high values. The oil absorption capacity of sepiolite is higher than that of the other clay minerals. The peloids with high CEC, swelling, and absorption capacity may be suitable for the removal of oils, toxins, and contaminants from the skin.

Key words: Abrasivity, consistency limits, absorption, peloid, therapy, viscosity

1. Introduction

The physical properties of peloids, such as the ease of use, ease of removal from the skin, and the potential for irritating the skin, are important parameters in the determination of their suitability for use in cosmetics or therapy (Summa and Tateo, 1998; Viseras and Lopez-Galindo, 1999; Cara et al., 2000a, 2000b; Carretero, 2002; Veniale et al., 2004, 2007; Carretero et al., 2006, 2007, 2010; Carretero and Pozo, 2007, 2009, 2010; Lopez-Galindo et al., 2007; Tateo and Summa, 2007; Dolmaa et al., 2009; Karakaya et al., 2010, 2016a; Matike et al., 2011; Rebelo et al., 2011).

The physical and physicochemical properties of peloids play a key role in their use as masks, cures, pastes, and bandages. Peloids prepared as clay/water mixtures can display different properties such as plasticity, consistency, acquisition of colloidal state, and thixotropy, depending on the clay mineral type and the peloid content. The rheological properties of peloids, such as fluidity and consistency, depend on the mineralogical composition and maturing conditions (Carretero et al., 2006). Those parameters affect the chemical reaction and heat transfer between the peloid and the body (Yvon and Ferrand, 1996; Bettero et al., 1999). The rheological properties and the stickiness of the muds used in pelotherapy are important. The viscosity of the mud increases with the addition of Ca- and Mg-sulfate fluids and decreases in association with other fluids (Viseras et al., 2006). Gomes and Silva (2007) explained the use of clay minerals, specifically for local applications dermocosmetic applications. Carretero and Pozo (2009) reported that the use of various clay minerals in hot springs and therapy depends on the grain size, low hardness, rheological properties, high moisture content, cation exchange capacity (CEC), and heat retention properties. The high proportion of the smectite group minerals in peloids makes them suitable for use in healing applications due to their swelling potential (water absorption), surface area and CEC (enabling the retention of unwanted elements), and specific heat (enabling the application of the mud bandage/mask for long periods of time) (Cara et al., 2000a, 2000b). Peloids containing carbonate group minerals, on the other hand, are especially suitable for psoriasis because they improve the subcutaneous circulation and suitable layering of the epidermis (Lopez et al., 2008). The apparent viscosity is observed in many cosmetic products that are used,

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similarly to peloids, in contact with the epidermis (Viseras et al., 2006).

Peloids are used in spas for patients with musculoskeletal system problems to reduce/prevent aches, to improve the quality of life, and in cosmetics. Therefore, therapeutic applications do not only benefit from the heating effect (vein widening, sweating, and heartbeat and respiration enhancement), but also the healing effect of the peloid from absorption by the skin (Quintela et al., 2012). Clay minerals, e.g., kaolinite, smectite, palygorskite, sepiolite, and talc, are defined in pharmacopoeias, and being accepted medicines they could contribute in pharmaceutical formulations as active principles and/or excipients (Gomes et al., 2015 and reference there in).

Peloids (thermal mud) have been used in many Turkish thermal resorts for healing, therapy, and cosmetic uses, from ancient times to the present day (Karakaya et al., 2010, 2016a, 2016b). Peloid materials with different mineralogical, chemical, and physicochemical properties show different therapeutic and cosmetic effects, and their effects also depend on which materials are used. The physicochemical and chemical properties of peloids and their therapeutic effects can vary due to the different compositions of the materials used and their effects also depend on how the materials are used. There are few detailed studies on the suitability of peloids in Turkey. For the first time, Karakaya et al. (2010) studied solely the mineralogical and chemical properties of nine spa peloids. In this study, the rheological and physicochemical properties of peloids are investigated and compared with those of pure clay minerals such as smectite, illite, kaolinite, and sepiolite to make recommendations for the preparation of suitable peloids. Additionally, it is also aimed to suggest which types of clay minerals can be used for healing, wellness, and cosmetics because clay minerals and clay/water mixtures are the main controlling factors of peloid properties and uses.

2. Materials and methods

Twenty-three peloid samples were taken from different spa centers together with a volcanic center in Turkey (Figure 1). All physical and physicochemical analyses of the peloids and naturally pure clay minerals were made in the peloid laboratory of the Department of Geological Engineering of Selçuk University, except for particle size analysis. The peloid samples were dried, washed with distilled water, and sieved under water to separate the silt-clay size (<63 µm) fraction from the bulk materials. Distribution of the silt-clay fraction was studied using the Micromeritics SediGraph 5200 Particle Size Analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA) in the SEM laboratory of Anadolu University (Eskişehir, Turkey). Mineralogical analyses of the bulk samples were made by X-ray diffraction using randomly oriented powders and oriented samples (<2 µm).

After drying of wet and sieved samples, they were homogenized, dried, and pulverized for 5 min in a porcelain ball mill for the analyses. The naturally pure clay

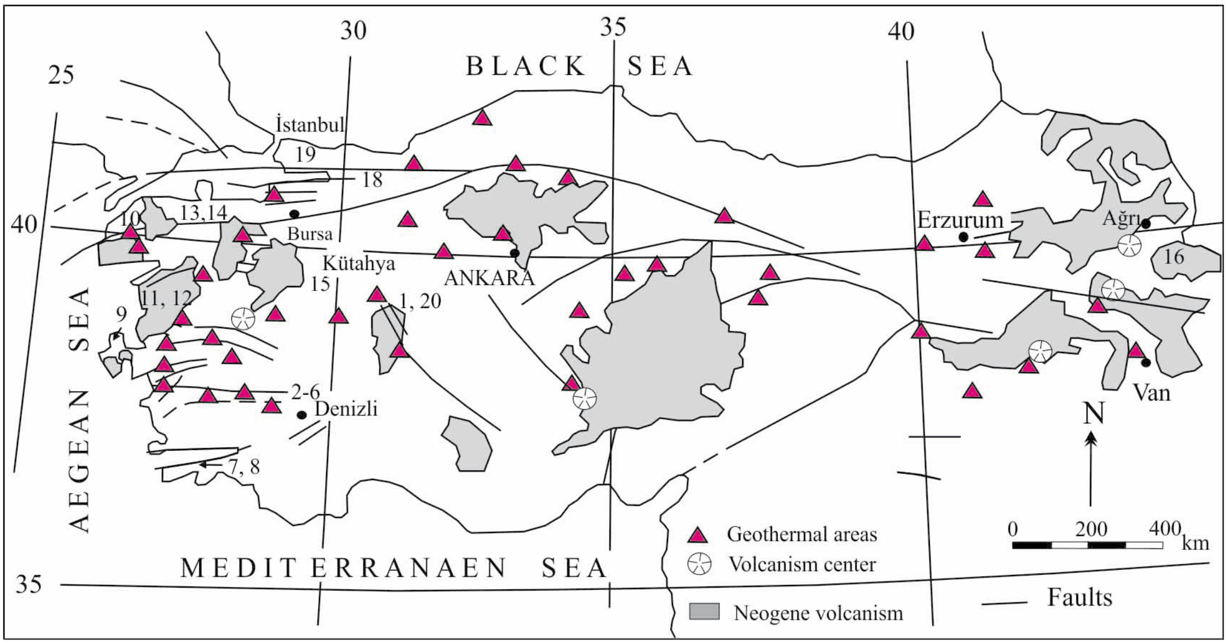

Figure 1. Location of the peloid samples and main tectonic lineaments, volcanic centers, and geothermal areas of Turkey (simplified from Şimşek, 2015).

minerals, with mineralogical and chemical properties as previously defined by Çelik et al. (1999), Karakaya MÇ et al. (2001, 2011a, 2011b, 2012), and Karakaya N et al. (2011) were collected from different areas of Turkey. The pure illite and smectite samples were collected from the vicinity of Ordu in the northern part of Turkey (Çelik et al., 1999; Karakaya MÇ et al., 2011a, 2011b). The kaolinite and sepiolite samples were taken from the Konya and Ankara regions located in central Turkey, respectively (Karakaya et al., 2001; Karakaya N et al., 2011). The pure clay minerals, smectite, illite, sepiolite, and kaolinite, were used for comparison of their physical and physicochemical properties with those of the peloids. The mineralogical compositions and types of the samples were published by Karakaya et al. (2016b).

The consistency of the peloid and clay minerals was determined with the Casagrande system using the Atterberg method in accordance with the ASTM 4318-00 standard (ASTM, 1994). The samples were dried in an oven at 50 °C and sieved to <63 µm. The consistency indexes (Ic) of the studied peloids were calculated with the equation [Ic = (LL – wn)/LL – PI], where LL is the liquid limit, wn is the natural water content (%), and PI is the plasticity index (Means and Parcher, 1963). The naturally present water content was calculated from the weight loss at 50 °C. The activity index (AI) shows the change in volume of the clays associated with the change in water content. It is calculated from the ratio of the plasticity index to the weight of the <2 µm clay size fraction (%) (Skempton, 1953) and is expressed as a percentage.

The moisture content of the peloid samples was measured in accordance with the relevant Turkish standard (Turkish Standards Institution, 1978). The moisture of the sample was determined from 1 g of sample after drying for 1 h at 105 ± 5 °C. The dry mass and the moisture content of the sample were then calculated.

The CEC values of the peloids were determined by means of the ammonium acetate method as described by Busenberg and Clemency (1973).

The oil absorption tests were carried out following the relevant Turkish standard (Turkish Standards Institution, 1997) using surface oil absorption tester Model AI 3016 (Angel Instruments, Sharanpur, India) at 20 °C and 50% room temperature and humidity, respectively. Cotton oil was used in the experiment; every drop of 0.0015 mL was dripped using the syringe of the 2.03 kg cylinder. The cylinder was rolled over the sloped surface (approximately 33.4 cm) and some of the oil was absorbed by the sample. Five measurements were taken from each sample, and an average was taken; the measurement error was ±0.3. Samples of 100 g were prepared from the bulk samples using the quartering method.

The apparent viscosity of the material was measured with a Brookfield viscometer on a 10% peloid-water dispersion. The dispersion was prepared by mixing 15 g of sieved (<63 µm) peloid sample with 360 mL of distilled water. This methodology is concordant with the ASTM (2010) standards, better describing non-Newtonian materials. The apparent viscosity measurements were carried out at different turning speeds. The apparent viscosities of the samples kept in a 40 °C hot water bath were measured using a Brookfield LVDVIII+PRO Ultra Rheometer (Brookfield, Middleboro, MA, USA) and a number 73 spindle. The measurements were made in 30-min intervals at different cutting ratios (2.5, 5, 10, 20, 50, and 100 rpm). The measurements were repeated after 24 h. The thixotropic index is defined as the ratio of the viscosity at 2.5 rpm to the viscosity at 20 rpm (Singer and Galan, 1984). The thixotropic percentage is the percentage ratio of the viscosity difference from 5 rpm to 20 rpm to the second viscosity.

The abrasivity of the sieved (<63 µm) peloid and pure clay samples was determined on 50 g of sample (< 63 µm) dried for 15 min at 60 °C and disaggregated in 400 mL of distilled water until a homogeneous dispersion was obtained using the Einlehner AT 1000 Abrasivimeter (Angel Instruments), as defined by Klinkenberg et al. (2009) and Rebelo et al. (2011). Before and after the testing, the mass of the clean and dry bronze wire was measured. The dispersed sample was stirred at 43,500 revolutions for 30 min. The mass loss (mg) of the wire, as the accepted Einlehner abrasion and abrasivity index, was calculated as the ratio of the wear area to the mass loss.

The Brunauer–Emmett–Teller (BET) surface areas of samples were measured by standard multipoint techniques using Gemini VII 2390 V1.03 equipment (Micromeritics Instrument Corporation). The samples were subjected to a degassing process conducted at 150 °C under vacuum for 3 h to attain a constant weight. Surface area values were determined using the BET equation (Brunauer et al., 1938) using a P/Po range of 0.06–0.30 of the branch of the isotherm and pore size distribution was determined from the desorption branch of the isotherms. The degassing of the powder samples was performed under vacuum (10^{-2} Torr) at temperatures ranging from 50 to 150 °C.

3. Results

3.1. Mineralogical properties

The mineralogical composition of the peloids is generally homogeneous and composed mainly of smectite, illite, and mixed-layer illite-smectite, with smaller proportions of quartz and feldspar, calcite, dolomite, and amorphous silica and rarely of kaolinite, halite, serpentine, and gypsum (Karakaya et al., 2016a). The proportion of the clay minerals is generally between 50% and 60%, and the most abundant clay mineral is Ca-montmorillonite (Table 1).

Table 1. Mineralogical composition (rare components were omitted) of the samples (Karakaya et al., 2016b).

Sample number	Mineralogy and mineral contents (wt.%)
P-1	Sme(60)+Cal(12)+Ms/Bt(10)+Fsp(8)+Qz(5)+Kln(3)+Dol(2)
P-1/1	Sme(65)+Cal(15)+Ms/Bio(8)+Fsp(6)+Qz(6)
P-2	Sme(65)+Cal(13)+Dol(8)+Ms/Bt(6)+Qz(4)+Kln(4)
P-3	Cal (95)+Sme(3)+Dol(2)
P-5	Sme(38)+Ms/Bt(30)+Cal(13)+Fsp(9)+Qz(5)+Kln(3)+Dol(1)+Gp(1)
P-5/1	Cal(34)+Ms/Bt(32)+Sme(18)+Fsp(5)+Qz(4)+Kln(4)+Dol(2)+Gp(1)
P-6	Sme(36)+Ms/Bt(27)+Cal(22)+Qz(5)+Dol(4)+Fsp(3)+Kln(3)
P-6/1	Sme(58)+Cal(20)+Ms/Bio(16)+Qz(2)+Dol(2)+Fsp(1)+Kln(1)
P-6/2	Sme(47)+Cal(23)+Ms/Bio(18)+Qz(4)+Dol(3)+Kln(3)+Fsp(2)
P-7	Sme(31)+Dol(18)+Cal(17)+Srp(10)+Kln(8)+Qz(7)+Py(5)+Gp(4)
P-8	Sme(42)+Srp(18)+Cal(9)+Ms/Bt(8)+Dol(6)+Kln(6)+Qz(5)+Fsp(4)+Hl(2)
P-9	Sme(66)+Hl(11)+Cal(8)+Fsp(7)+Qz(5)
P-10	Sme(14)+Fsp(21)+Qz(28)+Ms/Bt(18)+Hem(10)+Kln(5)+Py(4)
P-11	Sme(52)+Ms/Bt(21)+Fsp(9)+Qz(8)+Dol(6)+Kln(4)
P-12	Sme(57)+Ms/Bt(15)+Cal(11)+Fsp(8)+Qz(4)+Kln(3)+Gp(2)
P-14	Sme(32)+Ms/Bt(22)+Cal(17)+Fsp(11)+Qz(7)+Kln(4)+Py(4)+Hl(2)
P-15	Sme(36)+Ms/Bt(26)+Cal(12)+Kln(10)+Dol (7)+Qz(4)+Fsp(3)+Gp(2)
P-16	Sme(73)+Fsp(6)+Qz(6)+Kln(4)+Gp(4)+Py(4)+Cal(3)
P-16/1	Sme(47)+Cal(37)+Fsp(6)+Qz(4)+Kln(4)+Gp(2)
P-16/2	Sme(61)+Ms(11)+Fsp(7)+Qz(6)+Kln(4)+Gp(4)+Py(4)+Cal(3)
P-17	Sme(60)+Cal(15)+Fsp(12)+Kln(4)+Qz(4)+Py(4)
P-18	Sme(52)+Cal(40)+Fsp(3)+Qz(3)+Do(2)
P-19	Man(90)+Sep(10)
P-19/1	Man(82)+Spe(18)
P-20	Ms/Bt(37)+Cal(18)+Sme(7)+Fsp(26)+Qz(12)
P-20/1	Ms/Bt(38)+Cal(17)+Sme(11)+Fsp(21)+Qz(13)

Bt: Biotite, Cal: calcite, Dol: dolomite, Fsp: feldspars, Gp: gypsum, Hem: hematite, Hl: halite, Hyl: halloysite, Ilt: illite, Kln: kaolinite, Man: magnesite; Ms: muscovite, Qz: quartz, Sme: smectite, Sep: sepiolite, Srp: serpentine, Py: pyrite (abbreviations from Whitney and Evans, 2010).

3.2. Particle size distribution

The particle size distributions of the peloid samples are highly heterogeneous. The fraction below 2 µm of peloids P-2, 5/1, 6, 11, 15, 16, 17, and 18 are less than 50% (Table 2). For the fraction under 2+5 µm (fine silt and clay) determined in P-16, the content of this fraction is 77%. The samples with the highest fraction content of fine sand are P-2, 5/1, 6, 11, 15, 16, 17, and 18. The fraction content below 20 µm is less than 50% in P-10, 11, and 15.

3.3. Consistency properties

The consistency parameters are the key factors in the adhesion strength (or bond strength) between the particulate material grains, the slip resistance against load and stability, changing stiffness with water, and the stiffness acquired from different waters. The liquid limit and plastic limit values of the samples vary (Figure 2; Table 3). The consistency limits of samples P-3 and P-10 could not be determined because they have high calcite concentration (<10% clay) and contain almost no clay. Peloid samples P-2, 12, and 16 have the highest liquid limit values, while P-5, 8, 11, 18, 19, and 20 have the lowest values. The liquid limit values of the peloid samples are between 22% and 84%, which may indicate very low smectite content (Table 3). The liquid limit values of montmorillonite, illite,

Table 2. Particle size distribution of the peloid samples (μm).

	P-1	P-1/1	P-2	P-5	P-5/1	P-6	P-7	P-8	P-9	P-11	P-12	P-13	P-14	P-15	P-16	P-17	P-18	P-19	P-20	P-20/1
>63	0.3	0.3	0.1	0.3	0.1	0.2	0.1	0.1	0.2	0.3	0.5	0.3	0.2	0.1	0.2	0.2	0.1	0.4	0.3	0.3
63–50	1.5	0.0	0.0	0.0	0.0	0.0	0.0	1.8	0.0	0.0	0.1	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0
50–10	8.1	7.9	20.0	5.0	22.1	20.0	0.1	0.0	1.8	21.9	9.0	13.0	2.9	27.0	1.0	15.0	36.0	0.0	9.9	10.2
10–2	27.2	28.2	45.7	23.1	31.9	41.0	7.5	1.9	6.0	26.1	25.0	22.0	20.1	36.0	83.1	27.0	31.9	5.0	24.1	23.1
<2	64.4	63.6	34.2	71.6	45.9	38.8	92.3	98.0	92.0	51.7	65.6	64.7	76.8	36.9	15.7	57.8	32.0	94.8	65.7	66.4

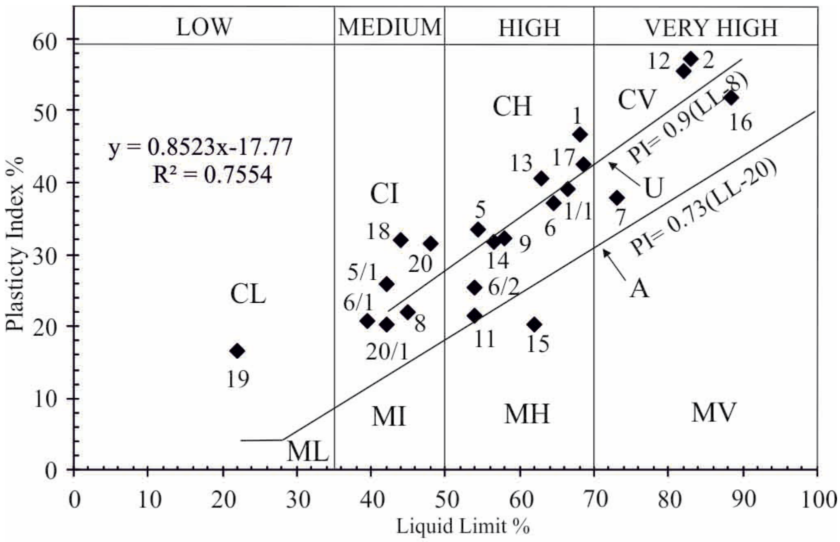

Figure 2. Plasticity of the peloid samples. Explanation: for fine materials, L: low, I: middle, H: high, V: very high, M: extremely high plasticity. Line A is an empirical boundary for classification of cohesive soils (Bain, 1971). CV, CH, CI, and CL: Very high, high, intermediate, and low plasticity clays, respectively; ML and MH, silt and organic soils of low and high plasticity. The A line separates clay type materials from silt and the U line shows the upper bound of the ground.

kaolinite, and palygorskite are 100-900, 60-120, 30-110, and 160-230, respectively (Mitchell, 1993). The plastic limit values of the samples (5.1% to 41.5%) are lower than the limit values given by Mitchell (1993) for clay minerals. The liquid limit, plastic limit, plasticity index, activity index, and consistency index are considerably lower in P-19, which contains 90% magnesite. According to the liquid limit and plasticity limit values of the studied peloid samples, one sample is CL (low plasticity clay), six samples are CI (intermediate plasticity clay), eight samples are CH (high plasticity clay), three samples are CV (very high plasticity clay), and the other five samples are MH (high plasticity silt), as shown on the graph by Holtz and Kovacs (1981, references therein) (Figure 2; Table 3). The investigated peloids generally have a high clay content and medium to high plasticity. Samples P-11 and P-15 have a higher proportion of silt size material and plot in the high plasticity silt area of Figure 2. Samples P-7 and P-16 plot on the clay–silt boundary shown by line A. The consistency limits of the peloid samples were compared with measurements made on pure clay minerals (Tables 3 and 4). The liquid limit values of the pure clay minerals range from 110 to 125 in smectite, 32 to 35 in illite, 286 to 369 in sepiolite, and 43 in kaolinite (Table 4). The plastic limit values of the peloids are significantly lower than those of the pure clay minerals, which could be attributed to the high quantities of nonclay components in the peloids (Tables 3 and 4).

According to the consistency index, samples P-5 and 19 are fluid; P-5/1, 6/2, and 18 are very soft; and the other peloids are soft, semihard, and hard in character (Table 3) (Means and Parcher 1963). Samples P-6 (immature) and P-6/2 (pool) show similar properties. The AI represents the change in volume depending on the water content

Table 3. Consistency limits and other physical characteristics of the peloid samples.

Sample number	Liquid limit (LL %)	Plastic limit (PL %)	Plasticity index (PI %)	Plasticity expandability potential	Activity index (AI %)	Consistency index (I_c)	Swelling (%)	Consistency status
P-1	68.00	20.87	47.13	HPL/HS	0.60	0.73	8.71	SR
P-1/1	66.50	27.00	39.50	VHPL/HS	1.09	0.28	8.80	Soft
P-2	83.00	25.36	57.64	VHPL/HS	1.68	0.53	8.91	Soft
P-5	54.50	20.65	33.85	HPL/MS	0.47	-0.19	8.80	Fluid
P-5/1	42.00	15.72	26.30	HPL/MS	0.57	0.04	6.70	VS
P-6	64.50	26.92	37.58	HPL/HS	0.96	0.51	9.20	SR
P-6/1	39.50	18.55	21.00	HPL/LS	0.49	0,31	4.70	Soft
P-6/2	54.00	28.38	25.60	HPL/MS	0.71	0.12	6.70	VS
P-7	73.00	34.74	38.26	VHPL/HS	0.41	0.77	8.10	Rigid
P-8	45.00	22.77	22.23	IPL/LS	0.23	0.35	3.40	Soft
P-9	58.00	25.36	32.64	HPL/MS	0.35	0.95	7.50	Rigid
P-10	Not determined (nonplastic)						0.40	SR
P-11	54.00	32.33	21.67	HPL/LS	0.42	0.82	4.50	Rigid
P-12	82.00	25.92	56.08	VHPL/HS	0.85	0.41	8.30	Soft
P-13	63.00	22.12	40.88	HPL/HS	0.63	0.61	9.50	SR
P-14	56.50	24.40	32.10	HPL/MS	0.42	0.73	6.10	SR
P-15	62.00	41.52	20.48	HPL/LS	0.55	0.91	8.50	Rigid
P-16	88.50	36.24	52.26	VHPL/HS	3.29	0.70	8.40	SR
P-17	68.50	25.47	43.05	HPL/MS	0.75	0.90	5.10	Rigid
P-18	44.00	11.61	32.40	HPL/MS	1.01	0.25	4.70	VS
P-19	22.00	5.12	16.90	IPL/LS	0.18	-0.62	0.90	Fluid
P-20	48.00	16.20	31.80	HPL/MS	0.51	0.70	7.70	SR
P-20/1	42.00	21.49	20.50	IPL/LS	0.31	0.59	7.10	SR

VHPL: Very highly plastic clay, HPL: highly plastic clay, IPL: intermediate plastic clay, HS: high swelling, MS: medium swelling, LS: low swelling; measurement errors of the consistency parameters and swelling are ±0.2 and 0.3, respectively. SR: Semirigid, VS: very soft.

and is defined as the ratio of the plasticity index to the weight percentage (%) of the clay size by weight (<2 µm) (Skempton, 1953). Apart from six of the studied peloid samples (P-1/1, 2, 6, 12, 16, and 18), the activity values are lower than 0.75 in the samples (Table 4).

In the studied peloid samples with high carbonate mineral content, the swelling percentage could not be determined for P-3 and is significantly lower for P-10, at approximately 0.4%, due to their high carbonate and nonclay mineral content. The swelling percentage of the other samples varies from 3.4% to 9.5% (Table 1). In the samples with high smectite content, the swelling percentage is generally high. Some samples containing high levels of smectite show low swelling capacities, which could be partially attributed to the smectite being Ca-smectite showing high to medium crystallinity. The moisture content of one of the peloid samples is greater than 50% (P-16), while that of the other samples is 16%–59% (except P-3).

3.4. Oil absorption

The oil absorption capacities of the peloid samples are between 26.51% and 59.95%. There are no correlations between the oil adsorption and CEC in the peloids or between BET and oil adsorption. Generally, the samples with high moisture content also show high oil absorption capacities (Table 5). The water and oil absorption capacities of the materials used as peloids were compared to those of various pure clay minerals (Table 5). The moisture of the studied peloids is similar to that of smectite and kaolinite, higher than illite, and lower than sepiolite. From the perspective of oil absorption, all peloid samples are noticeably lower than sepiolite and, except for a few samples, all capacities are lower than those of other clay minerals. The studied peloids absorbed oil in a shorter time compared to the clays (Table 5).

Table 4. Some consistency limits of examined pure clay minerals.

	Consistency limits			Plasticity expandability potential
Mineral	Liquid limit	Plastic limit	Plasticity index	
Ca-Smectite	111.0	65.8	45.2	VHPL/HS
Ca-Smectite	110.0	65.2	44.8	VHPL/HS
Na-Ca-Smectite	125.0	60.6	64.4	VHPL/HS
Illite-1	35.0	29.7	5.3	IPL/LS
Illite-2	32.0	23.6	8.4	IPL/LS
Sepiolite-1	286.0	109.0	177.0	VHPL/HS
Sepiolite-2	369.0	130.0	239.0	VHPL/HS
Kaolinite	43.0	39.0	4.0	IPL/LS

Explanations were given in Table 1.

3.5. Abrasion properties

The Einlehner abrasion (at 43,500 rpm) of the peloid and pure clay samples ranges from 24 to 102 mg and 2 to 7 mg (Table 3). The abrasion index of the peloids varies from 0.58 to 3.12 g/m^2. The highest abrasion index was observed in sample P-10, while P-19 showed the lowest value. The abrasivity of the pure clay minerals is lower than that of the peloid samples. The abrasion index of the sepiolite and kaolinite is lower than that of illite and smectite (Table 5).

3.6. Viscosity and thixotropy properties

The apparent viscosities of the studied peloids were 9.03–90.66 Pa s in the first measurement at 2.5 rpm. During the measurements after 24 h, values of 7.02–88.30 Pa s were obtained (Table 6). The highest viscosities (at 2.5 rpm) were observed in samples P-6, 8, 9 16, 10, 14, 18, and 20. There is a general parallelism in the graphs of the measurements taken after 24 h, with a slight decrease or increase of the apparent viscosity in samples allowed to stand for 24 h (Figures 3 and 4). Where the viscosity curves do not match after wait time, samples other than P-1/1, 2, 3, 6, and 19/1 showed an increase in the viscosity values after 24 h. This indicates that the clay/water dispersions are appropriate to use in the implementation process. Samples P-1, 1/1, 5, 6/1, 6/2, 7, 11, 12, 15, and 16 with viscosity values very close to or somewhat close to 4 Pa s at 10 rpm also show suitability for use when required to stay on the skin (Viseras et al., 2006). Samples numbers P-13 and P-14, and partially P-15, have lower thixotropic properties than the other peloid samples (Table 4). Because peloid samples P-1/1, 2, 5/1, and 15 do not show a change in viscosity behavior after 24 h, their flow behavior will not change considerably over time. The viscosity properties of the studied peloids were compared with those of pure clay samples. The measurements were completed on pure smectite (one pure Ca and two Na-Ca montmorillonite), three illites, two sepiolites, and one kaolinite (Figure 4). The viscosity of Na-Ca-smectite is higher than that of Ca-smectite, while the sepiolite viscosity is higher than that of the other clay minerals. The lowest viscosity is 2.8 Pa s in the kaolinite sample at 2.5 rpm. The most suitable value at 10 rpm was determined for the Na-Ca-smectite sample. All samples showed an increase in viscosity after being allowed to stand for 24 h. The highest viscosity was observed in sepiolitic clays, showing 9–10 Pa s at 10 rpm, which is higher than the 4 Pa s value; however, viscosity values too low for use as peloids were observed in the samples of Ca-smectite and kaolinite, and partially in illite (Figure 4).

Thixotropic studies were carried out on the peloids as fluid muds, which lose their fluidity and start to solidify when not moving but return to their fluid state when stirred. The thixotropic values taken initially and after 24 h are generally similar. Thixotropy is important for peloids used in masks. It provides information on the cracking and falling period of the mud spread on the skin.

3.7. BET surface area and CEC properties

BET surface areas for the majority of the samples are greater than 20 m^2/g; samples P-1, 2, 16, 20, and 20/1 show greater values. The lowest values were obtained for samples P-10, 11, and 19 (Table 3). The highest BET values were determined in smectites and sepiolites while kaolinite and illite had the lowest values from pure clay samples.

The CEC of the studied samples is 10.11–36.01 meq/100 g. Sample P-19 containing 90% magnesite shows the lowest CEC value, and sample P-10 shows the lowest smectite content (Table 3).

4. Discussion

The peloids and pure clay minerals have very high, high, intermediate, and weak plasticity values. The particle sizes

Table 5. Moisture, oil adsorption capacity, duration, abrasivity, abrasivity index, BET surface area, and CEC of the analyzed peloid and pure clay minerals.

Sample number	Moisture %	Oil adsorption capacity (mL/100 g)	Oil adsorption duration (±5 s)	Abrasion (mg)	Abrasivity index (g/m^2)	BET surface area (m^2/g)	CEC (meq/100 g)
P-1	36.45	33.19	39.74	36	133	42.46	26.79
P-2	46.54	39.94	54.30	37	136	55.88	36.01
P-5	36.54	39.95	35.62	34	134	26.86	30.89
P-6	43.09	46.60	39.08	46	153	22.26	31.07
P-7	46.39	46.61	29.12	46	181	20.67	33.83
P-8	33.22	33.26	39.54	41	122	28.49	29.12
P-9	33.20	33.27	47.01	58	153	21.47	33.34
P-10	16.96	26.57	52.63	98	312	8.12	10.11
P-11	29.91	33.22	48.41	69	193	13.49	19.58
P-12	43.09	43.15	34.13	43	131	26.80	24.41
P-13	33.22	29.92	55.42	55	159	30.40	28.84
P-14	39.86	43.23	32.71	71	195	22.34	27.20
P-15	46.47	46.46	26.83	62	186	20.92	29.06
P-16	59.91	59.95	10.01	40	125	34.67	32.66
P-17	43.25	33.23	49.21	55	167	29.72	35.54
P-18	40.06	30.00	29.33	59	178	22.47	26.30
P-19	32.43	36.00	25.74	24	63	15.78	10.87
P-20	25.76	32.00	30.22	76	254	80.35	32.61
P-20/1	29.80	34.00	35.28	73	251	65.57	33.48
Ca-smectite	55.00	71.00	20.78	7	28	73.60	nm
Na-Ca-smectite-1	57.00	73.00	23.34	6	30	86.22	nm
Na-Ca-smectite-2	74.00	83.00	23.15	5	21	108.53	nm
Illite-1	32.00	38.00	21.10	7	37	17.92	nm
Illite-2	39.00	45.00	18.40	6	30	30.24	nm
Illite-3	31.00	35.00	22.30	5	29	21.78	nm
Kaolinite	45.00	54.00	27.98	2	5	32.90	nm
Sepiolite-1	73.00	150.00	16.29	2	6	198.88	nm
Sepiolite-2	60.00	130.00	18.54	3	7	211.00	nm

CEC values of Benetutti mud (Cara et al., 2000a) and Morinje mud (Mihelčić et al., 2012) are 30 and 18.0 meq/100 g, respectively. nm: Not measured.

of some of the peloids are suitable for peloid applications because the clay content is between 70% and 80% (Veniale et al., 2007) (Table 2). Therefore, the most suitable peloids without mechanical grinding were P-5, 7, 8, 9, 14, and 19. Other samples are not suitable, but their application may be advisable especially if sand-sized particles are separated from the material before application.

The low-plastic clays that plot below the theoretical line are low and medium plasticity clay and silt (Bain, 1971) (Figure 2). There is a strong positive correlation (r = 0.86) between liquid limit and plasticity index in the peloid samples. A high percentage of clay fraction and water absorption capacity also result in high liquid limit values. The varying plastic limits of the peloid samples are due to different clay contents. Therefore, depending on the plasticity properties of the peloids, some of them will dry in a shorter time, crack, and show more fluidity. The majority of the peloids have plasticity indexes above 15% and liquid limits above 50% (except for P-8), and are therefore suitable as peloids. Similar to the liquid limit values, the plastic limit values are lower than the values determined by Mitchell (1993), which is due to the peloids containing

Table 6. Viscosity of peloid samples at different shear rates (rpm).

Sample / shear rate (rpm)	TÇ-1		TÇ-1/1		TÇ-2		TÇ-5		TÇ-5/1	
	0 h	24 h	0 h	24 h	0 h	24 h	0 h	24 h	0 h	24 h
2.5	18.10	23.21	17.49	16.29	16.68	16.68	28.28	37.91	39.31	40.51
5.0	9.63	13.14	8.52	7.89	8.16	8.24	14.14	17.45	20.06	21.41
10.0	**5.27**	**7.12**	**4.12**	**3.89**	3.49	2.35	**6.82**	8.07	11.21	11.31
20.0	2.81	3.99	2.05	1.93	1.74	1.67	3.28	3.74	6.01	5.91
50.0	1.28	1.81	0.82	0.78	0.81	0.32	1.31	1.46	2.61	2.61
100.0	0.72	1.01	0.43	0.41	0.17	0.17	0.71	0.79	1.41	1.41
Thixotropy	6.44	5.82	8.54	8.44	9.59	6.97	8.62	10.14	6.58	6.82
Sample / shear rate (rpm)	TÇ-6		TÇ-6/1		TÇ-6/2		TÇ-7		TÇ-8	
	0 h	24 h	0 h	24 h	0 h	24 h	0 h	24 h	0 h	24 h
2.5	64.21	54.22	19.22	21.58	16.22	19.43	36.71	41.12	64.38	70.40
5.0	33.16	29.15	9.80	10.94	10.31	14.01	17.45	19.36	27.58	31.79
10.0	17.62	15.51	**4.97**	**5.51**	9.75	8.16	8.42	9.33	12.03	14.19
20.0	10.34	8.81	2.54	2.76	4.95	5.18	4.16	4.61	5.84	6.64
50.0	5.30	4.51	1.06	1.10	2.45	2.57	1.79	1.95	2.62	2.78
100.0	3.85	3.27	0.55	0.55	1.28	1.37	1.05	1.09	1.54	1.62
Thixotropy	6.23	5.95	6.57	6.83	3.28	2.38	8.82	8.92	11.02	10.60
Sample / shear rate (rpm)	TÇ-9		TÇ-10		TÇ-11		TÇ-12		TÇ-13	
	0 h	24 h	0 h	24 h	0 h	24 h	0 h	24 h	0 h	24 h
2.5	70.00	76.42	79.83	46.94	37.30	50.35	37.11	43.15	32.09	48.12
5.0	32.39	36.51	45.30	30.18	16.55	23.07	18.05	20.86	19.06	25.21
10.0	15.34	17.30	26.83	14.49	7.72	10.58	8.63	10.08	12.03	13.10
20.0	7.49	8.50	14.99	9.63	3.71	5.04	4.19	4.91	7.27	7.15
50.0	3.00	3.46	7.54	4.43	1.55	2.08	0.17	2.04	3.71	3.91
100.0	1.58	1.82	4.39	3.08	0.89	1.19	0.95	1.11	2.56	2.16
Thixotropy	9.35	8.99	5.32	4.87	10.05	9.97	8.86	8.79	4.41	6.42
Sample / shear rate (rpm)	TÇ-14		TÇ-15		TÇ-16		TÇ-17		TÇ-18	
	0 h	24 h	0 h	24 h	0 h	24 h	0 h	24 h	0 h	24 h
2.5	54.21	66.20	14.04	15.40	22.06	19.56	23.07	26.68	56.96	69.40
5.0	35.11	32.11	7.72	8.22	10.10	9.81	8.22	9.03	25.37	29.99
10.0	24.62	19.62	**4.26**	**4.61**	**5.52**	**5.02**	**3.86**	**4.31**	12.03	14.19
20.0	16.18	12.10	2.58	2.56	2.76	2.62	1.91	2.21	5.99	6.87
50.0	9.72	6.51	1.27	1.24	1.10	1.10	0.92	0.95	2.54	2.92
100.0	7.31	4.82	0.78	0.78	0.55	0.55	0.58	0.55	1.54	1.63
Thixotropy	3.23	5.52	5.44	6.02	7.79	7.47	12.08	12.07	9.51	10.10
Sample / shear rate (rpm)	TÇ-19		TÇ-19/1		TÇ-20		TÇ-20/1			
	0 h	24 h	0 h	24 h	0 h	24 h	0 h	24 h		
2.5	22.06	18.02	45.53	48.39	90.66	88.30	20.06	26.08		
5.0	11.03	10.42	23.16	34.90	61.07	70.02	18.12	23.07		
10.0	**8.52**	**7.36**	11.93	18.15	28.63	32.11	18.50	17.55		
20.0	2.76	2.23	6.26	9.55	8.03	17.82	10.28	12.03		
50.0	1.10	1.03	2.71	4.17	2.19	8.01	6.02	6.92		
100.0	0.55	0.10	1.50	2.28	1.11	5.13	4.66	4.96		
Thixotropy	7.99	8.08	7.30	7.16	12.60	4.29	9.51	10.81		

Bolded values are appropriate for peloids; measuring error is ±0.2.

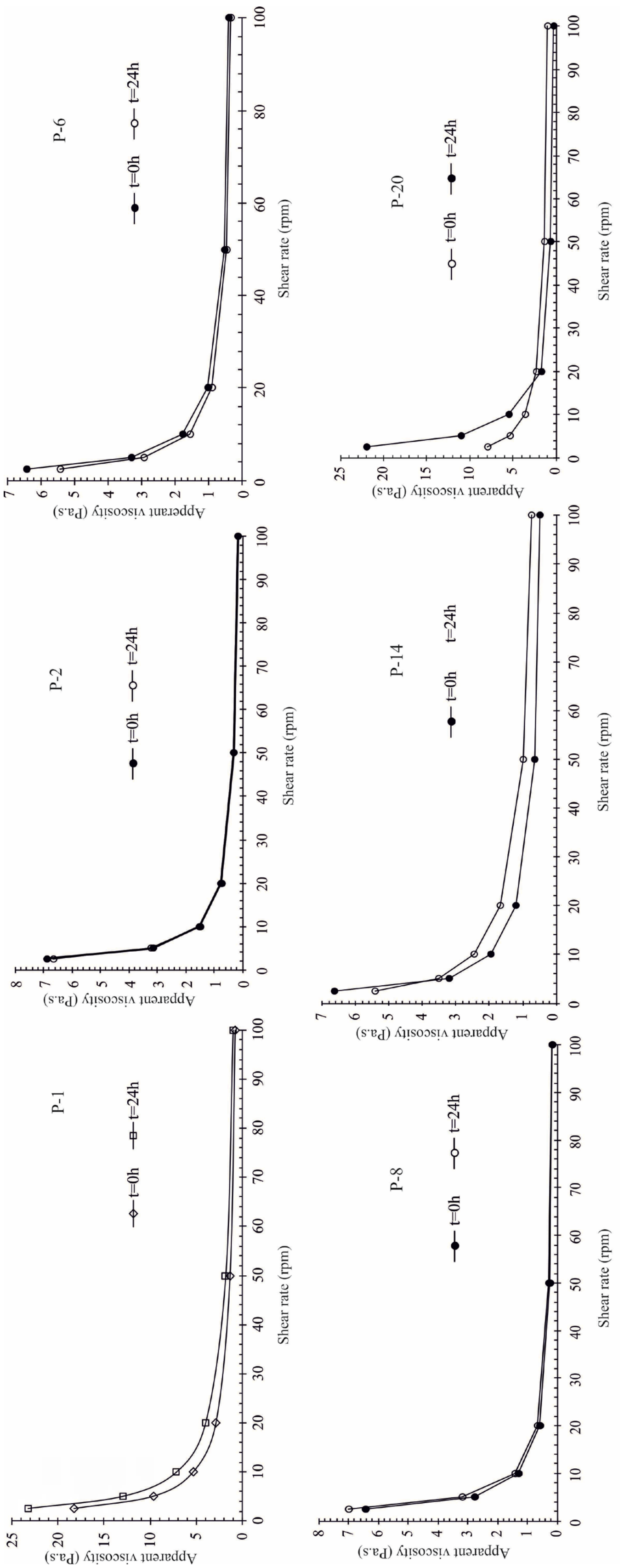

Figure 3. Apparent viscosity curves of some peloid samples.

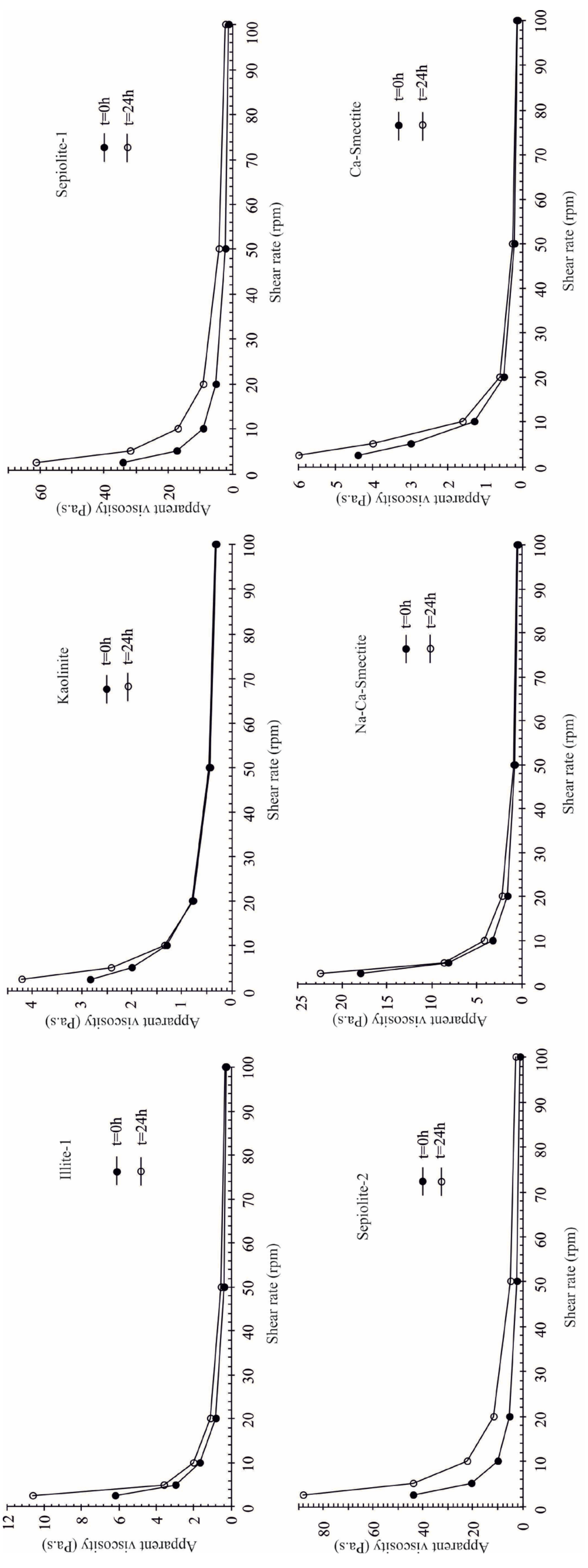

Figure 4. Apparent viscosity curves of the pure clay minerals.

nonclay materials and low smectite (montmorillonite) contents. Because the plasticity provides information on how the material will behave and change shape when applied, the suitability of the components should be analyzed. Plasticity is related to the mineral type, water content, grain size, and CEC of clay minerals. Materials with low plasticity show poor adhesion to the skin surface, so they easily flow through the skin and thermal therapy effects on the body will be low. Snethen et al. (1977) stated that the liquid limit and plasticity index are the best indicators of potential swelling and classified the swelling potential of the material as low, intermediate, or high swelling capacity. When the limits given by Snethen et al. (1977) are taken into account, samples other than P-6/1, 8, 11, 15, and 19 have low swelling potential, and the others have intermediate or high potential. The experimentally determined swelling percentage is generally comparable with the swelling potentials (Table 1).

Skempton (1953) reported AI values of 0.3–0.5 for kaolinite, 0.5–1.2 for illite, 0.5–1.2 for palygorskite, and 1.5–7.0 for montmorillonite. He also classified clays according to the AI values as AI < 0.75 for inactive clays, 0.75 < AI < 1.25 for normal clays, and AI > 1.25 for active clays. Apart from two peloid samples (P-2 and 16), the AI in all peloids is <1.25, reflecting inactive clays. Four peloids (P-1/1, 6, 12, and 17) were defined as normal clays, while the other peloids were defined as inactive clay or peloids with low montmorillonite content (Skempton, 1953; Mitchell, 1976). When inactive peloid samples are mixed with water, they will show low swelling ratios. The workability of the material depends on the consistency and activity index, and it is important to determine the properties that create problems when in contact with skin. It is clear from the limits given above that workability increases with an increase in montmorillonite. For that reason, soft or semihard peloids are advisable, but fluid or very soft peloids are difficult to keep in place on the skin due to their fluidity. Hard peloids are not suitable for use as pastes, masks, or bandages. High moisture percentage was generally found in samples with high smectite content. Some of the samples with high smectite content showed relatively low swelling capacities, possibly due to the smectite being Ca-smectite. The swelling potential of one the samples is less than 50%, whereas the others were high (apart from P-3 and 10). Pastes with high clay mineral content show a high swelling potential and can retain large quantities of water and heat, making them suitable for use in pelotherapy (Yvon and Ferrand, 1996). Therefore, clay-rich peloids with a high moisture content also have a high smectite content and consequently high CEC values (Veniale et al., 2004).

The higher abrasivity of samples P-5/1, 10, 14, 15, 20, and 20/1 may be related to the high content of detrital tectosilicates and nonclay minerals (Tables 1 and 2). The hardness of the minerals, i.e. quartz, feldspar, dolomite, and pyrite, in the samples may lead to too much abrasion. Therefore, these samples may cause some discomfort or irritation when used as masks (Rebelo et al., 2011). The abrasivity of the peloid samples is higher than or comparable to that of the pure clay samples. The low abrasivity of the clay minerals may be related to their low hardness and particle size and micromorphology (platy shapes and pseudospherical aggregates) (Klinkenberg et al., 2009; Rebelo et al., 2011). The types and amounts of hard minerals and the degree of rounding or grinding of sharp edges also have great influence on the abrasivity (Klinkenberg et al., 2009). It is recommended that the abrasivity of a clay material for application onto skin should not exceed 200 g/m^2 at 43,500 rpm (Gomes, 2002; Rebelo et al., 2011). Thus, nearly all of the peloid samples can be considered as suitable peloids without producing an undesirable sensation, except for P-10, 20, and 20/1. The pure clay minerals show the lowest abrasivity. Therefore, they do not cause any irritation or scratching of the skin. The lower abrasivity of sepiolite and kaolinite than of illite and smectite may be related to their micromorphologies.

Clay pastes used in pelotherapy should have apparent viscosities of approximately 4 Pa s at 10 rpm and peloids with very low viscosities are not suitable for use in therapy (Cara et al., 2000b; Yvon and Ferrand, 1996). Viscosities closest to this value were measured in samples P-1, 1/1, 6/1, 15, and 16. Samples 2, 5, 6/2, 7, 11, 12, and 19 were fairly close (Table 4; Figure 3). Furthermore, samples P-6/1, 11, 13, 17, 20, and 20/1 showed increased thixotropic values after 24 h, demonstrating that the peloid material tends to solidify over time. The materials in the samples show decreasing thixotropy (P-1, 2, 3, and 6/2) and tend to become partially fluid over time. The apparent viscosity curve shows a sudden decrease in the shear stress at 20 rpm; the dispersions have a thixotropic character. This causes the peloids to flow when mixed with water and preserves their shape when applied to the skin (Viseras et al., 2006). This behavior of the materials shows that the clays are suitable for many semisolid medical/cosmetic creams, ointments, pastes, gels, and makeup (Rebelo et al., 2011). The increase in the viscosity values after 24 h could cause difficulties for the removal of the material from the skin, working, and drying. The viscosity and thixotropic properties are important for choosing a peloid. The thixotropic properties cause solid particles to remain in suspension and resist sinking. These properties decrease when the suspension becomes active and increase when the suspension is inactive. Samples P-3, 6/2, 13, and 14, and partially 15, have very low thixotropic values compared with the other peloid samples. Samples P-8, 11, 18, and 20/1 have thixotropic values higher than the other samples (Table 4). A high viscosity in peloids could mean that the peloid cannot be not spread evenly on the skin and will crack in a shorter time. Very high viscosity and thixotropy, however, make the peloid too sticky (fluidity is very reduced) and therefore shaping/working the peloid is more difficult, drying times are longer, removal from the skin after drying is harder, and removal from the container (or storage) is more difficult, an unwanted situation.

In the literature, CEC values of various clay minerals vary depending on structural properties from 10 to 160 meq/100 g (Grim, 1968). The clay minerals with the highest CEC values are the smectite and vermiculite group minerals. Other clay minerals have a CEC value of 10–50 meq/100 g (Grim, 1968). There is an intermediately positive (r = 0.82) correlation between CEC and the smectite content of the studied samples. The smectite minerals are accepted as the clay minerals with the highest ion exchange capacity (Grim, 1968). The CEC values of the studied peloids are lower than those of the clays used as peloids by Veniale et al. (2004) (virgin clay = 63), but many samples have higher values than Benetutti mud (Cara et al., 2000a) and Morinje mud (Mihelčić et al., 2012) (Table 3). The CEC of peloids suitable for the use in therapy was given by Rebelo et al. (2005) and Quintela et al. (2012) as 16–25 meq/100 g and 10–30 meq/100 g, respectively. Therefore, the majority of the investigated samples are suitable because their CEC values are above these results. High moisture capacity is an important characteristic of medicinal muds. High values of CEC permit the mud to trap a higher amount of these elements, e.g., Ca, Mg, and Sr (Karakaya et al., 2010). Compared with other clay minerals commonly used for therapeutic or cosmetic purposes, the investigated samples have higher CEC than kaolinite (5–15 meq/100 g) and a value similar to illite and sepiolite (10–40 and 10–45 meq/100 g, respectively), but lower than that of montmorillonite (80–120 meq/100 g) (Christidis, 2011). Especially when applied directly to the skin, the peloids with high CEC can play a role in removing toxins, bacteria, and unwanted components by absorbing them but can also carry a health risk as this can change the compounds into harmful compounds (Carretero et al., 2006, 2007; Tateo and Summa, 2007; Matike et al., 2011).

Peloids with CEC values lower than 15 meq/100 g have a low absorption capacity and cannot absorb ions from the skin, but they also can transfer some ions from the peloid to the skin depending on the concentration (Matike et al., 2011).

The oil absorption capacity can be used to eliminate excessive oil and toxins from the skin. It is used effectively in the treatment of skin conditions such as boils, acne, ulcers, abscesses, and seborrhea (increased secretion from the sebaceous glands) (Carretero et al., 2006). Peloids with high oil absorption and moisture capacity can cause dryness of the skin and therefore should not be kept on the skin for a long period of time in the case of dry skin types. The water retention/absorption capacity and similarly the moisture content are parameters related to the organic matter and smectite content and should be considered when packaging and applying the peloid to the skin. The positive relationship between the oil absorption and the moisture content of peloid samples is related to the clay minerals, specifically to the smectite content. As a result, the oil and partially the moisture capacity do not have an apparent relationship with the oil absorption time and absorption can take longer for materials with higher capacity. Therefore, the oil absorption capacity should be taken into account when the application method is considered, especially for skin treatments. Peloids with high oil absorption capacity are useful for the absorption of excess oils from oily skin or skin with acne when they are used as masks or bandages. However, they may be unsuitable for normal to dry skin because they may cause too much drying and loss of the natural moisture of the skin. Such peloids, when mixed with pure smectite, will not be a problem for normal to dry skin and will not cause dryness.

Smectite-rich peloid and pure smectite and sepiolite samples have high BET surface areas. The low BET values of kaolinite and illite samples may be related to nonexpanding properties and having only external surfaces of the minerals. The BET surface areas of the minerals vary from 10 to 70 m^2/g, while smectite group minerals have extensive internal as well as external surfaces, giving high specific surfaces areas (800 m^2/g; Carter et al., 1986). Low BET values of some smectite-rich peloids may be sourced from low particle size, low layer charge, pore water chemistry, and particle aggregation (Yong and Warkentin, 1975). Preparing peloids from low CEC and BET clays is unsuitable for skin cleansing, while clay with high CEC is more suitable for removing toxins, bacteria, and other unwanted components from the skin. Sepiolite with high BET can be added to peloid materials for use in treating some skin problems (acne, seborrhea, eczema, etc.).

5. Conclusions

The viscosities of some of the peloids are higher or lower than the viscosity values required. Sepiolite showed the highest values, and its use in large quantities in peloids is therefore unsuitable. The Na-Ca-smectite has a more suitable viscosity. Spa centers using or planning peloid therapy should take the characteristics of peloids, such as unsuitable physical parameters, into account. The variations of the CEC of different peloid types are due to the clay mineral content. Peloids should be prepared from clays with high CEC and BET values, which are more suitable for removing toxins, bacteria, and other unwanted components from the skin. Sepiolites can be added to peloid materials for the use in treating some skin problems (acne, seborrhea, eczema, etc.). Peloids with high oil absorption properties are not suitable for use on normal to dry skin or skin without an acne problem because they will cause the skin to dry excessively and the natural moisture will be reduced. The viscosity of pure sepiolite is higher than that of the other clay minerals, while kaolinite shows the lowest viscosity. The viscosity of some peloids is not appropriate for therapeutic application. All samples displayed an increase in viscosity after 24 h. The viscosity values were too low in Ca-smectite and kaolinite, and partially in illite, for the use as peloids. The abrasivity of most of the peloids is appropriate for use in masks or bandages and pure clay minerals can be added to the peloids to prepare more suitable materials. Finally, the usage areas of peloids should be determined on the basis of their clay types and physicochemical features.

Acknowledgments

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