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# Texturation of model clay materials using tape casting and freezing

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## Abstract

The present work aimed to investigate the processing of textural clay based materials using tape casting together with freezing. Two model raw materials were used, namely: BIP kaolin from France and ABM montmorillonite from Mediterranean region. The mixtures of both clays were studied, whereby, the amount of montmorillonite was 0, 5, 10, 20 or 50 mass%. After tape casting, the as-obtained green bands were frozen into liquid nitrogen, lyophilized and then fired at 1050 °C or 1200 °C.

The amount of montmorillonite appeared as a critical parameter that controls the cohesion of the dry products. For montmorillonite content ≥20 mass%, the products exhibited multiple cracks after lyophilisation. With lower montmorillonite content, the cohesion of the dry products was satisfactorily and a macroscopic cross-linked surface texturation was observed. After calcination at 1050 °C or 1200 °C, the texturation appeared well defined. Moreover, calcination at 1200 °C increased the densification of products and the occurrence of a glassy phase was noted.

The combination of both tape casting and freezing (freeze tape casting) is a promising way to develop various clay-based and composites materials exhibiting unique microstructure organization and characteristics with potential application in the field sustainable and environmentally friendly filtration, adsorption or catalysis.

*Keywords:* Texturation; Kaolin; Montmorillonite; Tape casting-freezing; Lyophilisation

## 1. Introduction

Clays can be defined as natural raw materials mainly constituted with clay minerals as major components. They are used for a wide range of application ranging from traditional to advanced ceramic materials as well as for drilling fluids, cosmetics, pharmaceutical and medical applications [1–9] The main advantage of such readily available resources is their environmentally friendly character in most cases and furthermore their recyclability since they can easily be re-used and therefore match sustainability requirements. The basic knowledge on clay minerals is a key point to clearly understand the level of their tunable characteristics regarding various applications. It is well-established that most clay minerals are layered hydrous magnesium or aluminum silicates, also called phyllosilicates [10], which impart plasticity to clays and which are divided in two groups:

- 1:1 or Te–Oc phyllosilicates whereby the structural unit is composed of one tetrahedral sheet (silicon cations) that is covalently linked to one octahedral sheet (aluminum or magnesium cations) through apical tetrahedral oxygens. Kaolinite is a typical clay mineral belonging to this group and its ideal structural formula is [$Si_4O_{10}Al_4(OH)_8$]. Their characteristic layer-to-layer distance (d-spacing) is 7.1-7.3 Å and only few cations substitution is observed here.
- The 2:1 or Te–Oc–Te phyllosilicates in which the structural unit contains one central octahedral sheet sandwiched between two tetrahedral sheets. Their d-spacing varies from 10 to 14 Å depending on their interlayer characteristics. Many substitutions can occur in octahedral and tetrahedral sheets, thus leading to charge deficit per unit cell ranging from 0.3 to 1.8. The net negative resulting from these isomorphous

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substitutions is compensated for by interlayer cations, less or more hydrated (mainly K, Na, Ca and Mg). The latter interlayer species can be easily exchanged since they are loosely held, which is the case for smectites and more precisely montmorillonites having the general formula $[Si_8O_{20}Al_{3.5-2.8-y}Mg_{0.5-1.2}(OH)_4M_{0.5-1.2}]$ (M = interlayer cation). Also montmorillonite are swelling minerals because the hydration degree of interlayer is very sensitive toward surrounding moisture. These characteristics can partly explain their higher reactivity compared to 1:1 phyllosilicates.

In ceramic industry, kaolinite (main constituent of kaolins) is considered as a refractory clay mineral with low plasticity compared to montmorillonite [11,12]. In fact, the latter brings more plasticity and ensures a good cohesion in green ceramic bodies; also montmorillonite allows lowering the sintering temperature due to the presence of alkaline and earth-alkaline cations (fluxing agents). But the swelling character of these montmorillonites [13] is very detrimental for ceramic products because during the drying stage, the loss of physisorbed-water is associated with a significant shrinkage that promotes cracks development and propagation. For this reason, the amount of montmorillonite is always reduced in wide diffusion ceramic bodies (less than 3 mass%). Besides, montmorillonites have been widely used to develop textural materials.

Regarding aforementioned points, the present work aims to explore a different processing including montmorillonite amount $>5$ mass% with the scope to take advantage of the natural aspect ratio and shape phyllosilicates to develop textural clay-based materials. Kaolin and montmorillonite model raw materials have been used in order to limit interactions with commonly associated minerals or impurities. To our knowledge, such investigation has not been explored in literature.

## 2. Experimental

### 2.1. Materials

Two raw model clays are used in the present study: BIP kaolin and ABM montmorillonite. Their chemical and mineralogical compositions are presented in Tables 1 and 2. The BIP kaolin is mainly constituted with kaolinite clay mineral as expected (silica/alumina ratio=1.3) and also contains few amount of associated minerals (micaceous phases and quartz). In the case of ABM montmorillonite, the major clay mineral is an aluminous montmorillonite whereby the interlayer cations are calcium, magnesium as well as potassium ions. The physical characteristics of these model clays are given in Table 3.

### 2.2. Processing

Tape casting is used for the elaboration of the various samples with the aim to enhance the natural texturation of clay platelets. Since kaolins exhibit less plasticity and cohesion in green bodies in comparison with other clays, a binder and a plasticizer have been used namely PVA (vinyl polyacetate) and PEG (polyethylene glycol). Preliminary tests show that the appropriate amount of each additive is 5.5 mass% (with respect to the clay content). The samples studied in this work are made of BIP kaolin—ABM Montmorillonite mixture with 0, 5, 10, 20 and 50 mass% of montmorillonite labeled respectively KM0, KM5, KM10, KM20 and KM50. The desired amounts of kaolin and montmorillonite are first added in deionized water in order to reach a solid content of 50 mass%. After a vigorous mixing during 5 min, the plasticizer and binder are added, and then the slurry is homogenized for additional 5 min. The as-obtained slurry is maintained under roll-mixing in order to ensure the homogeneity and to prevent bubbles formation (de-airing) within the slurry prior to its use. The tape casting equipment is constituted with a single blade in motion over a table made off with marble. Once the container is filled with the slurry, the casting is performed at previously monitored casting rate (1 cm/s in this case) and desired gap to ensure the final thickness of the green band. The as-obtained band (Fig. 1(b)) is divided in smaller samples, then quenched into liquid nitrogen ($T = -196$ °C). These samples are kept within a freezer at −24 °C before drying through lyophilisation. The lyophilisation apparatus used in this work is from

Table 2
Mineralogical composition of the raw clays (mass%).

| | **ABM montmorillonite** | **BIP kaolin** |
|---|---|---|
| **Montmorillonite** | 90 | / |
| **Illite–Mica** | < 8 | 16 |
| **Kaolinite** | – | > 78 |
| **Quartz** | < 2 | 5 |

Table 3
Physical characteristics of the raw clays.

| | **BIP kaolin** | **ABM montmorillonite** |
|---|---|---|
| **BET Specific surface area ($m^2/g$)** | 11.10 ± 0.79 | 107.67 ± 0.79 |
| **Grain size (μm)** | $d_{10}=2.82$<br>$d_{50}=8.99$<br>$d_{90}=27.88$ | $d_{10}=1.64$<br>$d_{50}=9.04$<br>$d_{90}=31.42$ |
| **Density ($g/cm^3$)** | 2.600 ± 0.004 | 2.257 ± 0.001 |

Table 1
Chemical composition of the raw clays (mass%).

| | **$SiO_2$** | **$Al_2O_3$** | **$TiO_2$** | **$Fe_2O_3$** | **CaO** | **MgO** | **$K_2O$** | **$Na_2O$** |
|---|---|---|---|---|---|---|---|---|
| **ABM Montmorillonite** | 56.57 | 17.90 | 0.36 | 4.25 | 2.65 | 5.96 | 1.24 | < 0.20 |
| **BIP Kaolin** | 48.10 | 36.90 | < 0.05 | 0.26 | < 0.20 | 0.17 | 1.90 | < 0.20 |

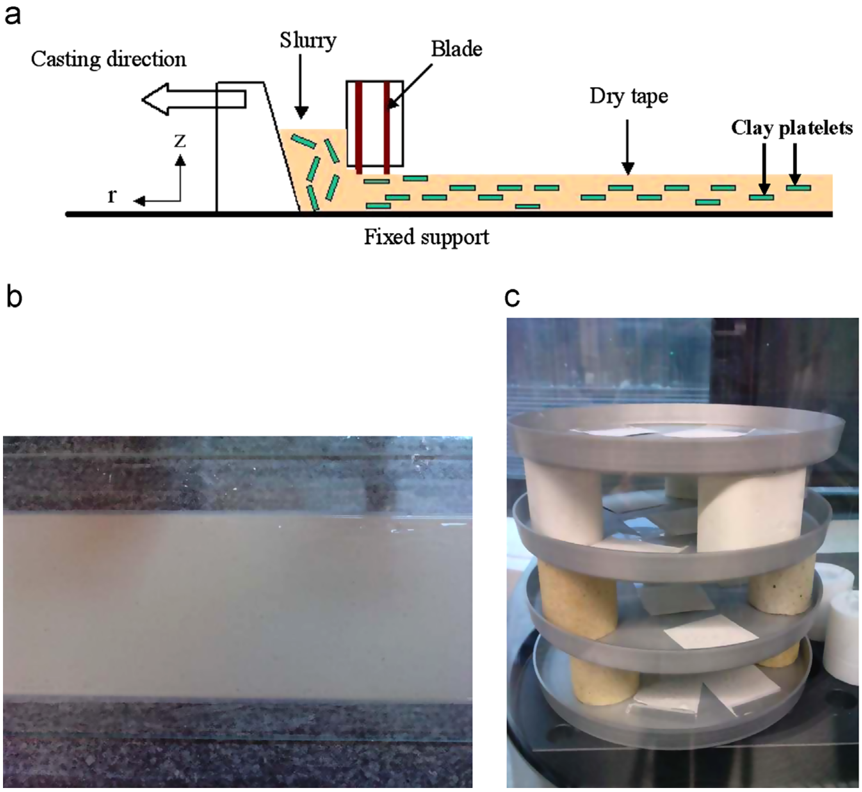

Fig. 1. (a) Graphical representation of the tape casting process used in the present work, (b) examples of a green tape casting band and (c) samples into the lyophilisation chamber.

xxx and allows to perform the sublimation of ice, the operation is completed when the pressure is stabilized at 0.0010 mbar ((Fig. 1(c))). The dry sample are characterized and submitted to calcinations at 1050 °C and 1150 °C. The main interest to manufacture products by combining tape casting, freezing and lyophilisation is the potential to enhance microstructure preferential organization as well as to avoid micro-cracks occurrence noted in conventional air drying processes.

### *2.3. Characterization techniques*

The observation of some samples microstructure was performed using a Stereoscan 260 apparatus equipped with a PGT Prism energy dispersive spectrometry analyzer. Prior to their observation, the samples were dried at 60 °C for one week and metallization was conducted through the sputtering of a nanometric layer of platinum onto the sample surface.

The surface parameters (essentially typical roughness) and texturation degree were characterized using an interferometric optical microscope (Nanosurf, FOGALE Nanotech company, Nîmes, France). Its main advantage is the characterization at macroscopic level of the surface rugosity. A computer generated hologram is used to focus the beam onto the sample. After the correction of noise of the obtained-images, the Ra parameters were extracted. The images presented have been previously corrected and submitted to the 3D representation using the provide software (mountains).

The Brunauer, Emmett and Teller [14,15] method was used to determine the specific surface area of the samples, using a TriStar II device from Micromeritics. Measurements were carried out after 16 h degassing-step at 150 °C, on dried samples previously crushed and sieved to 100 µm.

X-ray diffraction (XRD) diagrams were obtained on powdered samples with a Brucker-AXS D5000 powder diffractometer using K$\alpha_1$ radiation of Cu and a graphite back-monochromator. XRD experiments were achieved in step-scan mode from 3° to 45° ($2\theta$) with a counting time of 10.1 s/0.02° step. Crystalline phases were identified by comparison with Powder Diffraction Files (PDF) standards from The International Center for Diffraction Data (ICDD).

## 3. Results and discussion

The as-obtained green bands are shown in Fig. 1. The samples surfaces are regular and do not show residual bubbles. When the samples are quenched into liquid nitrogen, there microstructure is preserved, but during the lyophilisation, the sublimation of ice leave some macroscopic texturation all over the samples surfaces. In the case of KM20 and KM50 some cracks appear and lead to the damaging of these samples. The latter trend is consistent with the fact that in kaolinite-montmorillonite mixtures, the montmorillonite content should not exceed 20 mass% in order to ensure the conservation of macroscopic and microscopic organization of the structure. The BET specific surface area changes induced by the calcination of the various samples at 1200 °C are given in Table 4. It is noted that the specific surface are quite similar in all green samples except for sample KM50. Also after firing, the decrease of specific surface area is noted in all cases, down to a limit value near to 0.8 $m^2$/g. It is likely that the physical parameters of samples are affected only when the montmorillonite content is greater than 20 mass%. The swelling character of montmorillonite appears to govern the KM50 sample behavior during lyophilisation. The plasticity effect seems to be limited under such drying conditions (low pressure and temperature) and therefore, the cracks propagation cannot be avoided.

The SEM images of the samples KM0, KM5, KM10 and KM20 are similar in term of clay platelets organization. The general trend is shown in Fig. 2. The natural alignment of clay platelets is observed in all cases while an additional microstructural organization is observed due to the ice preferential crystallization during the freezing step. This textural organization is also confirmed by the interferometric characterizations (Fig. 3) which

Table 4
Physical properties of the different textured-products.

| | 100 | 5/95 | 10/90 | 20/80 | 50/50 |
|---|---|---|---|---|---|
| **S.S. BET green products ($m^2$/g)** | 10.7 ± 0.2 | 10.9 ± 0.1 | 10.9 ± 0.05 | 11.11 ± 0.06 | 21.4 ± 0.2 |
| **S.S. BET fired products ($m^2$/g)** | 1.05 ± 0.01 | 0.8 ± 0.008 | 0.9 ± 0.01 | 0.8 ± 0.006 | – |

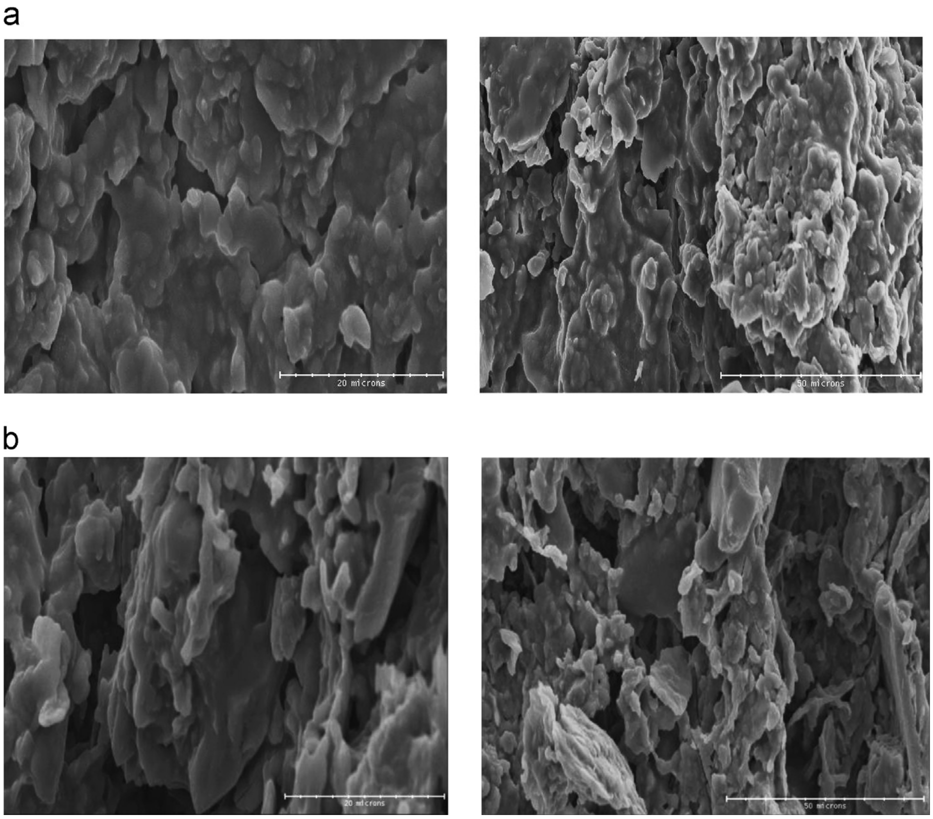

Fig. 2. SEM images of KM20 sample fired at 1200 °C (a)// and (b)⊥ to the band surface.

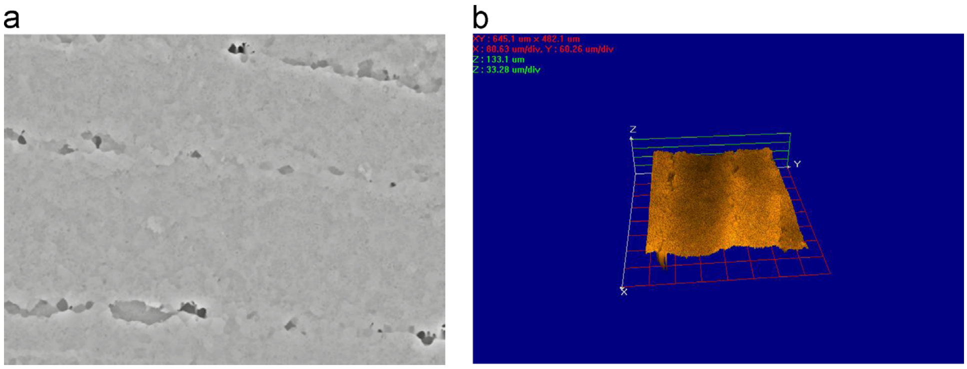

Fig. 3. Interferometric optical microscopy images (a) 2D and (b) 3D views.

allow having more precise information on the macroscopic organization. The resulting microstructure is close to the well-known repulsion of solid particles during the propagation of the ice solidification front found in literature [16–22]. The preservation of such organization despite the rapid freezing into liquid nitrogen is probably due to the less amplitude of particle motion in these samples in comparison to particles in suspensions (or slurries). The surface roughness is higher in samples fired at 1050 °C than in the case of those fired at 1200 °C. This may result from the densification of the latter samples in presence of a higher amount of liquid phase as can be observed onto related SEM images (Fig. 4). Actually, montmorillonite clay provides the media with alkaline and fluxing agents, which enhance the occurrence of a viscous liquid phase in the range of 1100–1200 °C [6,12,23–27]. The resulting liquid phase at high temperature tends to flow within the samples and therefore may contribute to their consolidation as well as to the inhibition of initial microstructure organization. Again the montmorillonite amount appears as a key parameter to reach a good compromise in terms of sample consolidation and sample texturation. From the studied samples, it results that the amount of montmorillonite clay need to be less than 20 mass% to ensure the preservation of macroscopic texturation of sintered samples.

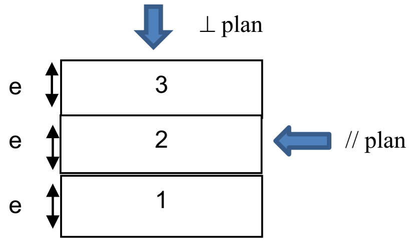

Fig. 4. Schematic representation of the multilayer design.

Further development has been made using the slurries KM0, KM5 and KM10, to manufacture a multilayer sample using tape casting of successive bands. The width of each layer is set at 500 μm and the 1st, 2nd and 3rd layers are respectively made of KM0, KM5 and KM10. A delay time of 5 min has been used between of each subsequent layer. As can be seen in Fig. 5, the macroscopic texturation is maintained after firing at 1050 °C and 1200 °C. The surface roughness is still close to 45 μm (Fig. 6). SEM images of the multilayer width and parallel to the casting direction, does not exhibit any layer mismatch or debonding (Fig. 5). The latter is consistent with a good accommodation between layers using the suggested processing which appears as a promising route for the shaping of unique texturation microstructure devoted to catalysis or filtration applications with strong anisotropic properties.

## 4. Conclusion

The processing of textural clay based materials has been performed using tape casting together with freezing and lyophilisation. The two model commercial raw materials used, namely: BIP kaolin and ABM montmorillonite have been combined with 5.5 mass% of polyvinyl alcohol (PVA a) and 5.5 mass% of polyethylene glycol to reach the adequate flowing state. The amount of montmorillonite has been varied from 0, 5, 10, 20 to 50 mass%. The texturation state was observed on dry and fired (1050 °C and 1200 °C) products using interferometric and scanning electron microscopies.

(1) The amount of montmorillonite is a critical parameter that controls the cohesion of the dry products. Below 20 mass% of montmorillonite, the cohesion of the dry products are

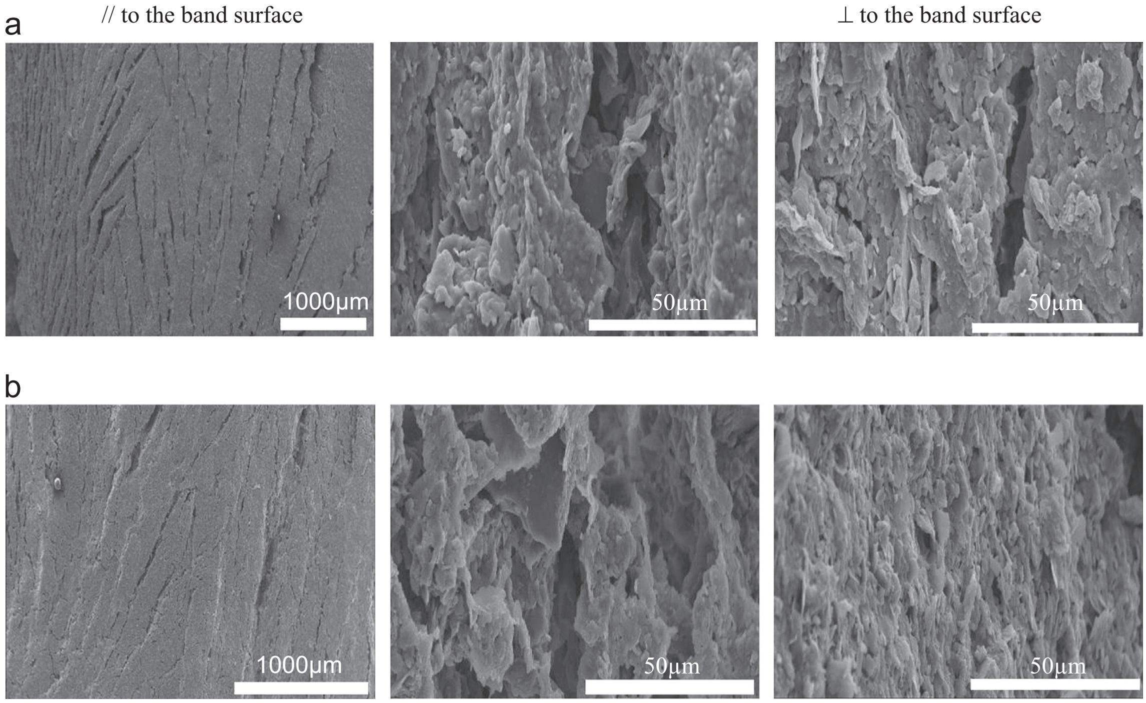

Fig. 5. SEM images of the multilayer sample calcined at (a) 1200 °C and (b) 1050 °C.

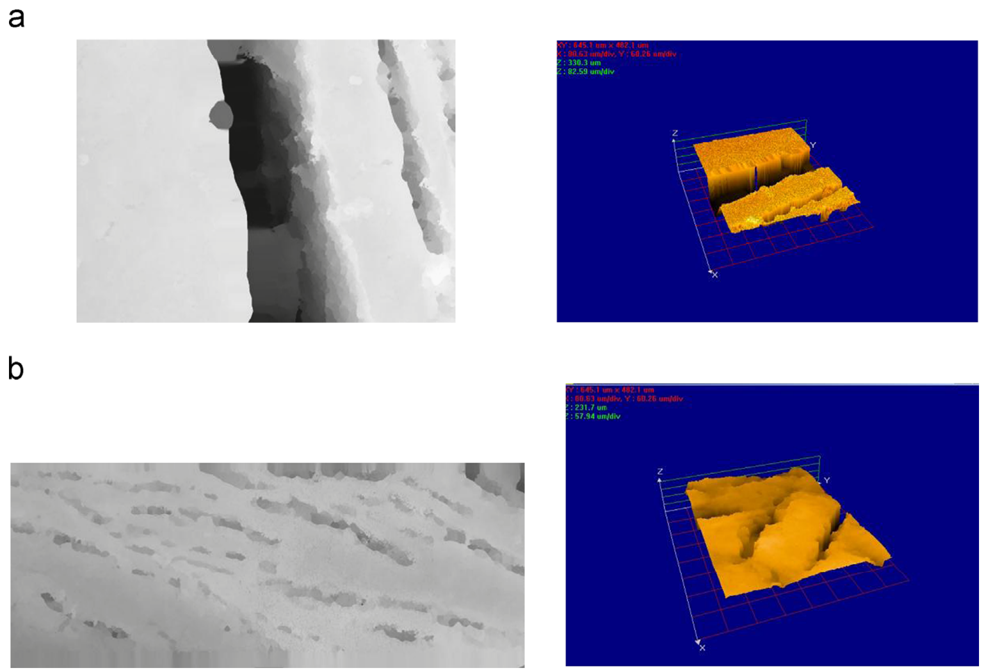

Fig. 6. Interferometric optical microscopy images (2D and 3D views) of the multilayer sample calcined at (a) 1050 °C and (b) 1200 °C.

satisfactorily and macroscopic cross-linked surface texturation is noted. Above 20 mass% of montmorillonite, the products exhibit multiple cracks after lyophilisation and could not be further manipulated.

(2) After calcination at 1050 °C, the additives (PVA and PEG) are degraded and the texturation appears more clearly. In addition, in samples KM5 and KM10, consolidation seemed to be more effective and clay platelets are well-observed parallel to the casting surface. Increasing the calcination temperature to 1200 °C tended to increase the densification of products and the occurrence of a glassy phase was noted. Besides, the texturation of products was roughly modified.

Therefore, it can be assumed that the combination of both tape casting and freezing is a promising way to develop various clay-based and composites materials with unique texturation and characteristics with potential application in the field of low energy and environmentally friendly filtration, adsorption or catalysis.

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