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# The characterisation of paper-composite porcelain in a green state

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#### Abstract

A porcelain body traditionally used to produce ceramic art and design objects was re-formulated using additional waste paper. The aim of this study was to develop knowledge into the technological properties of paper-composite porcelain in its green state, for use within the traditional practices of ceramic art and design production.

Characterisation was made by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Two different production methods used by potters, slip casting and free-hand pressing, were used.

The presence of the paper fibre, the paper type and the content amount are the important factors in strengthening development. Significant differences were found in relation to the content amount of paper fibre, between the mother porcelain body and the different content amount of paper fibre in the paper-composite porcelain body.

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## 1. Introduction

Porcelain is vitrified and fine-grained whitewares produced from natural raw materials comprised of clays (mostly of the kaolinite group), quartz and feldspar. It is dense and vitreous, and one of the strongest of all clay bodies, and is an important material in the ceramics field. It can be used for both technical and artistic purposes. However, it can be more difficult to work with than many other types of clay.<sup>2</sup> The purest clays are the least flexible and therefore the hardest to work with during production. A porcelain body is not only difficult to work with in its green state, but also cracks and deforms easily and requires time-consuming precautions during production. For many years, numerous ceramic artists attempted to improve the handling properties of porcelain in a green state by adding different binders.<sup>3</sup> In this process, different types of fibres were mixed as binding media to obtain a new product with improved physical properties. Today, different types of paper fibres are widely used as substances for artistic purposes. For ceramic artists especially, this results in better control over their artistic process in the green state. Paper-composite porcelain, as a kind of *Paper-clay*,<sup>4</sup> fills in these limitations. Unfortunately, the lack of technical information has to be taken into consideration for practical application work when using this material. This especially concerns the different properties obtained by different production methods.

The deficiencies of porcelain in its green state are its low mechanical strength, its fragility, its high shrinkage, and its heavy weight. In practice, all clay materials and clay bodies show a decrease of size in the drying process. The amount of shrinkage depends on many factors; water content, composition of the clay, and the method of producing goods. For this reason, substances are added to the plastic raw materials to prevent drying shrinkage. The shrinkage ratio is an important factor in ceramics because the reduction in size that invariably accompanies the drying and firing of pieces of pottery causes problems. Thus, high shrinkage is a serious problem for the industrial potter/ceramic designer and for the ceramic artists, who must produce finished pieces to a pre-determined size. Drying shrinkage is also an important property that causes cracks, warping, and distortion of the ware. Consequently, knowledge on drying shrinkage is

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very important to get the right shape and size of finished goods.

The heavy weight is another problem in porcelain clay: lightweight clay bodies give better workability and more freedom to the artists to produce their ceramic art/design work. Besides, the lighter weight ceramics are easier to handle especially for transportation, installation and finally to the consumers.

### 2. Aim and methods

The aim of this study is to contribute to better understanding of paper-composite porcelain. We also want to find out how the paper fibre affects the technical properties such as linear drying shrinkage, weight-loss from its wet to its dry state and its mechanical dry strength, and to compare the differences when using two different production methods.

This study is part of an extended study partly presented in a previous paper in which the characterisation of paper-composite porcelain body in a fired state was made by X-ray diffraction (XRD) and scanning electron microscopy (SEM).<sup>5</sup>

In the present paper, the final characteristics of the papercomposite porcelain and a mother porcelain body in their green state are characterised and are compared. The raw materials in the green state are analysed and characterised with respect to their mineralogical composition using XRD and microstructural SEM analysis. The technological properties observed are: linear drying shrinkage, weight-loss ratio and mechanical strength in the green state.

Using SEM techniques, this study carried the investigation of the microstructure of a paper-composite porcelain body, and the mineral composition was analysed by XRD.

The basic raw materials are kaolin, feldspar, quartz, copy/print waste paper, and other mixed waste papers. The raw materials, paper fibre and porcelain clay materials are mixed together in different proportions. In this study, two common production methods, slip casting and free-hand pressing were used to get information on the differences in the properties. XRD test samples are prepared only by the free-hand press method. The production methods of this study are carried out as similarly as possible to the traditional practices of ceramic artists to ensure technological transfer. Functional-ware and various artistic objects with asymmetrical and complicated thin-walled shapes are often produced by the use of the slip forming method. The problem of slip casting is that it needs intensive labour thus making it more difficult to implement in large-scale production or by free shaping of artistic objects. The free-hand pressing method is a type of plastic forming, implying a simple manual method. This method is nowadays mainly used to produce artistic objects or in small scale industrial production.<sup>6</sup> In this study, a free-hand pressing method is used to produce the test bars from the plastic mass and is closer to the normal artistic production method of plastic forming than machine pressing.

## 3. Experimental procedure

### 3.1. Porcelain raw materials

Porcelain has been studied as a mother body. The starting raw materials were kaolin (ECC International Standard Porcelain, Imerys Minerals Ltd., UK), FFF Finnish flotation feldspar (Partek Industry Mineral Ltd., Finland) and Finnish flotation quartz (Partek Industry Mineral Ltd.).

## 3.2. Waste paper as additional raw material of paper-composite porcelain

In this study, only waste paper was used in combination with a porcelain body. Two different types of waste papers were selected due to easy availability. The first is a copy/print paper waste (CP), and the second is other paper waste (HP) that mixes all sorts of paper.

### 3.3. Sample preparation

The mineralogical composition of the mother porcelain powders used is composed of 50% kaolin, 25% feldspar, and 25% quartz.

The test batches were mixed with two different paper types (CP and HP) with three different paper ratios (50, 70, and 90% by volume; and 6.8, 14.6, and 39.8% in weight), and a base porcelain body (mother porcelain, M) with no paper fibre added. The formulations of paper-composite porcelain bodies are shown in Table 1.

Both CP and HP were reduced to pulp before being mixed with the porcelain powders. The waste paper was first soaked in hot water and beaten to disintegrate the fibres. Using a large mesh screen to get a pulp with 20% water, the porcelain powders were then added and squeezed to get rid of excess water. The excess water was recycled. The starting powders were mixed with various ratios in a mixer for 3 h. The content of added water was 30 wt.% to produce samples by free-hand pressing. The content of added water was 45 wt.% to produce the samples by the slip casting method. In order to enhance slip stability a commercial organic deflocculant, Dolapix PC 67 (Zchimmer&Schwarz GmbH and Co., Germany) was introduced in amounts of 0.25 wt.%, based on the weight of the powder. Test bars from each test batch for hand pressing were made with dimensions  $25 \text{ mm} \times 25 \text{ mm} \times 115 \text{ mm}$  according to the international standard test method (ASTM C326-76). The clay batch was made in a one-sided plaster mould and

Paper-composite porcelain formulations (wt.%)

	MCP1	MCP2	MCP3	MHP1	MHP2	MHP3
Kaolin	46.60	42.70	30.10	46.60	42.70	30.10
Feldspar	23.30	21.35	15.05	23.30	21.35	15.05
Quartz	23.30	21.35	15.05	23.30	21.35	15.05
CP	6.80	14.60	39.80	_	_	_
HP	-	_	-	6.80	14.60	39.80

the open surface was smoothed using a splint. Just after demoulding, the samples were measured for their weight and length. Test bars were dried for 24 h at normal room temperature. After air-drying at room temperature for 24 h, they were further dried in an oven for 24 h at 110 °C. The weight and length of the wholly dried samples were then measured. The characterisation quality assurance was adopted according to ISO-8402.

### 3.4. Experimental techniques

### 3.4.1. X-ray diffraction (XRD)

X-ray diffraction was used for the qualitative determination of the crystalline phases present in CP and HP paper, the porcelain raw materials (kaolin, feldspar and quartz), and the green paper-composite porcelain bodies MCP2, MCP3, MHP2 and MHP3. This was performed using a Siemens D 5000 diffractometer operating at 45 kV and 45 mA. Using monochromatic  $CuK_{\alpha}$  radiation,  $\lambda = 0.154060$  nm. The X-ray scan was made over a range of  $2\theta$  values of  $15-60^{\circ}$  with data acquisition for 2.0 s at intervals of  $0.05^{\circ}$ . The X-ray intensities were recorded using a computer system and commercial software Diffract AT. Crystalline phases were identified by comparison with standard reference patterns from the Powder Diffraction File PDF-2 database sets 1-52, maintained by the International Centre for Diffraction Data (ICDD).

#### 3.4.2. Scanning electron microscopy (SEM)

Microstructural examination of surfaces were carried out using a CamScan S4-80DV analytical scanning electron microscopy equipped with an Oxford Instruments EXL Link microanalysis system. This technique was used for a porcelain green body, as well as paper-composite porcelain green bodies, to reveal microstructures and observe topographical contrast in the secondary electron imaging (SEI) mode. Gold coating of the specimens was carried out using an electron beam evaporation system (Model: S150B, Edwards High Vacuum Ltd., UK).

## 3.4.3. Linear drying shrinkage, weight-loss and mechanical strength

The physical properties in its green state were characterised according to the international standard test methods with respect to linear drying shrinkage (according to ASTM C326), and weight-loss as the weight change (ASTM C373).<sup>9</sup> An Instron universal testing machine was used to determine mechanical strength in a three-point bend mode, which was tested according to ASTM C689.<sup>10</sup> Test bars were obtained in a plaster mould. Just de-moulded as well as wholly dried test bars were measured for their weight to 0.001 g and length. The linear drying shrinkage was determined by the difference in the length of the test bar before and after drying. The thickness and length were measured using a vernier caliper to 0.01 mm.

All tests were performed at normal room temperature. The test results were recorded using an average value (mean value) of five measurements (one measurement on each of the five specimens). In this paper, the standard deviation of the mechanical strength is reported. Every experimental step in this study kept the test conditions as similar as possible so that a fair comparison could be made.

### 4. Observations and results

### 4.1. X-ray diffraction

The results from XRD phase analysis (see Table 2) confirmed that the phases present were within the expected range.

Representative XRD diffractograms of the samples are illustrated in Figs. 1–3. In Figs. 1–3, the major phases show the distinct peaks marked in the XRD patterns.

Fig. 1 shows the XRD patterns of the CP and HP raw samples. Major crystalline phases are marked as Ca (calcite), Ce (cellulose), K (kaolinite) and T (talc), respectively in the diffractogram. The mineralogical constituents of the two papers were approximately the same with the exception of kaolinite, and talc, which were present in HP. The mineral additives of the paper used in this study were kaolin (kaolinite, Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O), calcium carbonate (calcite, CaCO<sub>3</sub>) and talc (3MgO·4SiO<sub>2</sub>·H<sub>2</sub>O). Certain additives, such as calcium carbonate, kaolin, talc and titanium dioxide (TiO<sub>2</sub>), are used to improve the opacity and brightness of paper. They usually come in a fine powder form; like pigments, they become entrapped between the fibres and improve the surface smoothness of a sheet for printing, or to reduce shrinkage in three-dimensional paper techniques. 11 Major components of the CP raw sample were calcite and cellulose  $(C_6H_{10}O_5)n$ ). Traces were magnesioferrite (MgO·Fe<sub>2</sub>O<sub>3</sub>) and sodium calcium silicate (Na<sub>2</sub>O·CaO·SiO<sub>2</sub>). It is assumed that magnesioferrite is from a pigment of print ink. However, in any case it did not show any significant peak in dried green MCP samples. Major components of the HP raw sample were calcite, cellulose, talc and kaolinite as CP. The XRD analysis of waste paper showed pure calcite mineral in every sample.

The mineralogical composition of the porcelain raw materials, such as kaolin, feldspar and quartz, were characterised

Table 2 XRD analysis of the mineral components from green samples

1 6 1				
Phase				
Calcite, cellulose, magnesioferrite, sodium calcium silicate				
Calcite, cellulose, kaolinite, talc				
Kaolinite, quartz, rutile, hematite, muscovite				
Albite, quartz, microcline				
Quartz, albite, larnite, anorthoclase				
Kaolinite, quartz, calcite, orthoclase, tarasovite				
Kaolinite, quartz, calcite, orthoclase, tarasovite, nacrite, dickite				
Kaolinite, quartz, calcite, orthoclase, tarasovite, albite				
Kaolinite, quartz, calcite, orthoclase, tarasovite, albite				

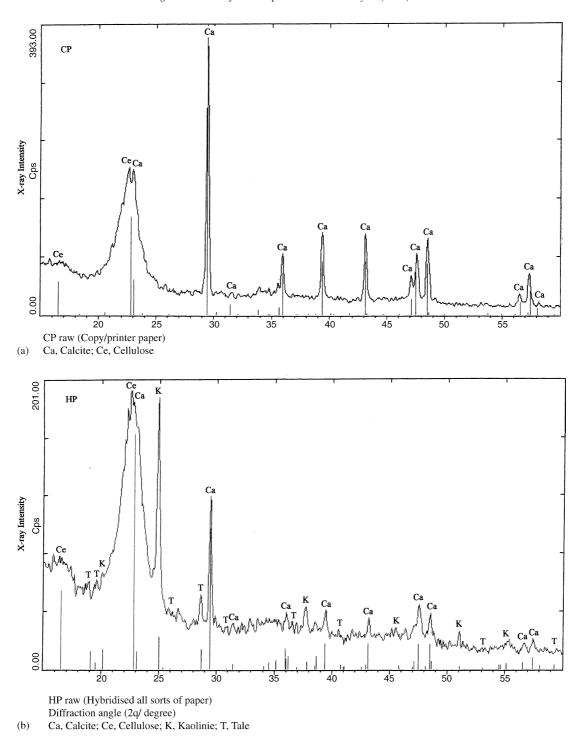


Fig. 1. X-ray diffraction patterns in CP and HP raw samples.

by XRD, as well as chemical composition. Fig. 2 shows the XRD patterns of kaolin, feldspar and quartz raw samples.

The XRD analysis shows that the kaolin raw sample contains mainly kaolinite and minor quartz (SiO<sub>2</sub>). Other traces were rutile (TiO<sub>2</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>) and muscovite (KAl<sub>2</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(OH)<sub>2</sub>). From the analysis of kaolin, the precise nature of iron minerals could not be determined. Feldspar raw sample contained albite, quartz and microcline (K<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·6SiO<sub>2</sub>) as its major components. The quartz raw

sample showed definitely clear quartz peaks as its major component. The traces were albite  $(Na_2O \cdot Al_2O_3 \cdot 6SiO_2)$ , larnite  $(Ca_2SiO_4)$  and anorthoclase  $((Na,K)AlSi_3O_8)$ .

Fig. 3a and b shows XRD patterns as a function of the composition in the paper-composite porcelain bodies. The analysis showed that the compositions of all MCP and MHP samples consisted of kaolinite, quartz, calcite, orthoclase  $(K_2O\cdot Al_2O_3\cdot 6SiO_2)$  and tarasovite (mica-smectite: NaKAl<sub>8</sub>(Si,Al)<sub>16</sub>O<sub>40</sub>(OH)<sub>8</sub>·2H<sub>2</sub>O) as the major components

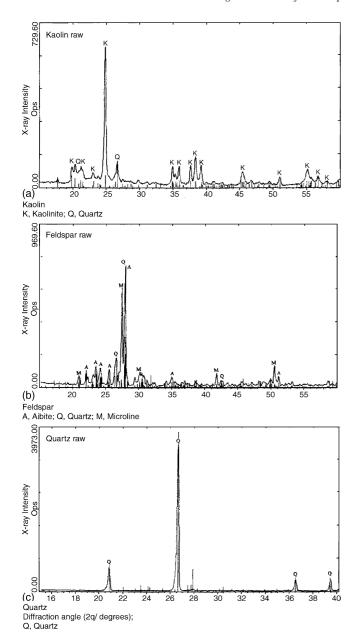


Fig. 2. X-ray diffraction patterns in the porcelain raw materials in a green state.

in their green state. Raw material compositions consisted of equal amounts of kaolin, feldspar and quartz in MCP2 and MHP2, MCP3 and MHP3, respectively, with a variation in the CP and HP contents. The increased content amounts of CP or HP in the paper-composite porcelain sample batches showed a significant chemical influence in increasing calcite peaks in the composition of both MCP and MHP green samples. MCP3 and MHP3 green samples showed stronger calcite peaks than MCP2 green and MHP2 green samples. However, the MCP3 green sample showed stronger calcite peaks than the MHP3 green sample. It is clearly displayed that the increasing calcite peak was directly proportional to increasing CP or HP in a porcelain body.

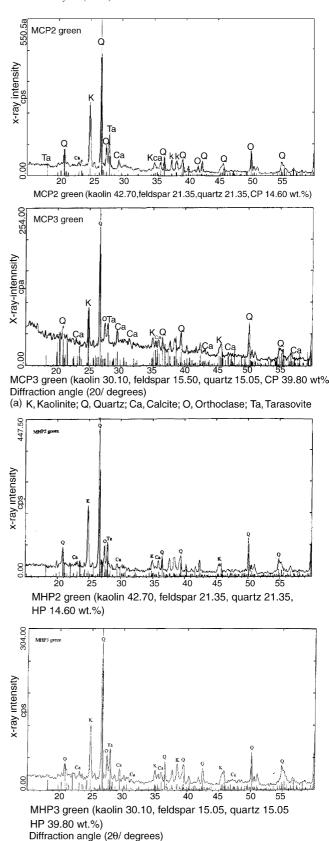


Fig. 3. (a) X-ray diffraction patterns in MCP paper-composite porcelain dried samples in a green state and (b) X-ray diffraction patterns in MHP paper-composite porcelain dried samples in a green state.

(b) K, Kaolinite; Q, Quartz; Ca, Calcite; O, Orthoclase; Ta, Tarasovite

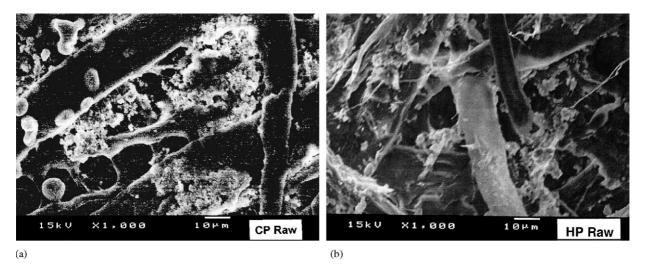


Fig. 4. SEM photomicrographs of the surfaces on the CP and HP raw samples (a) CP raw and (b) HP raw.

Examination of the peaks leads to the conclusion that the major crystalline phases presented in the green paper-composite porcelain samples were kaolinite, quartz, calcite, orthoclase and tarasovite (marked as K, Q, Ca, O and Ta, respectively, in the diffractogram) despite the different amounts or different types of paper contents in the bodies. However, nacrite (Al $_2O_3$ ·2SiO $_2$ ·2H $_2O$ ), and dickite (Al $_2O_3$ ·2SiO $_2$ ·2H $_2O$ ) were found only in the MCP3 green sample as traces that did not show in any other paper-composite porcelain green samples. Albite (Na $_2O$ ·Al $_2O_3$ ·6SiO $_2$ ) was found in MHP2 and MHP3 as a trace that did not show any significant peaks in the MCP green samples. The features of the MHP2 and MHP3 green samples with XRD patterns were very close to each other; and all the major components and traces were the same.

### 4.2. Scanning electron microscopy

This study examined the microstructures of samples in the green state in order to understand developments on how cellulose from the waste paper influences the paper-composite porcelain structure. The surface morphologies of samples were carefully examined by SEM techniques on the two kinds

of fresh paper raw samples (CP and HP), porcelain raw materials (kaolin, feldspar and quartz) and green surfaces of M, MCP and MHP samples.

The characteristic green surface microstructures of the CP and HP raw samples are shown in Fig. 4a and b. Fig. 4a is a scanning electron micrograph of a CP raw sample. The fibres are long, and the thickest fibre is approximately <80 μm. The morphology shows a part of the transverse side, near the bottom and left side. The cell walls of CP fibres are thin, and the lumens large, thus, these fibres have mostly hollow cores. 12 Fig. 4b shows that the HP paper fibres have been trodden. In general, it is believed<sup>13</sup> that trodden paper fibre increases the mechanical strength and increases the interfibre bonded area between fibres by making them more flexible. The strength of paper depends on the total number of bonds between the interfaced surfaces of the fibres. The trodden fibres form a more compact structure with less empty space: trodden fibres bond together much better and produce a stronger structure than non-trodden fibres. The morphology of the HP raw sample also shows many inter-fibres bonds.

The morphologies of the porcelain raw materials are shown in Fig. 5a-c. Particle size distribution of kaolin is

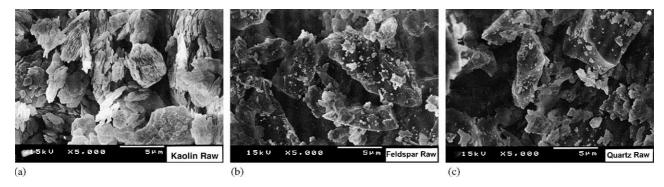


Fig. 5. SEM photomicrograph of the porcelain raw materials (a) Kaolin, (b) Feldspar and (c) Quartz.

70% <2 μm of wt.% (ECC International Standard Porcelain, Imerys Minerals Ltd.). Feldspar is 40% <10 μm, 20% <20 μm, and 30% <40 μm of wt.%. Particle size distribution of quartz is 50% <20 μm, 30% <5 μm, and 10% <45 μm of wt.%. Both feldspar and quartz are ceramic grade 200 mesh (Partek Industry Mineral Ltd.). The paper cellulose fibre is a hollow tube-like structure and can siphon moisture into itself, acting like a sponge. Since the clay particles are mainly smaller than paper fibre, small clay particles are easily siphoned into the fibre tubes; clay minerals and paper fibre are mixed together. Clay particles also cover the paper fibres, as shown in Figs. 6 and 7.

The microstructures of M, MCP and MHP green samples are shown in Figs. 6 and 7. Fig. 6a shows the surface of the M without CP or HP. The microstructure of the M green sam-

ple is fibre-free. The morphologies of the paper-composite porcelain bodies in the green state are shown in Fig. 6b–i. The fibrous structures display strongly binding fibres, an interlocking of the fibres and formation of fibre bridges. <sup>15</sup> The inter-fibre bonding in the structures of MCP3 sample is shown in Fig. 6f, while Fig. 6d shows a fibrous tunnel in the structure of MCP2 sample body.

SEM examinations revealed that the fibrous structure increases proportionally to increasing amount of paper in the composites. Fig. 6e shows MHP2 sample, which has a much more increased fibrous structure than MHP1 shown in Fig. 6c. Fig. 6f—i show that the highest amount of paper-combined bodies, MCP3 and MHP3, displayed a more fibrous structure than MCP1 and MHP1, or MCP2 and MHP2 green samples (Fig. 6b—e).

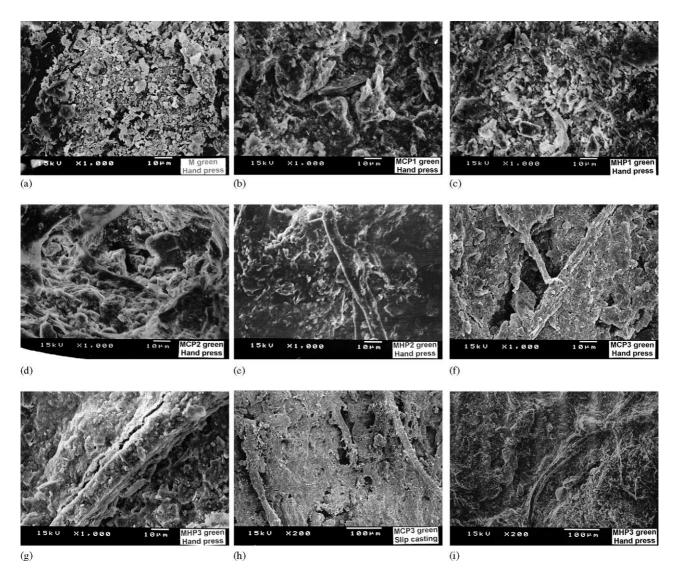


Fig. 6. SEM photomicrographs of the M mother porcelain and paper-composite porcelain green samples. (a) M green free-hand press, magnified  $1000\times$ , (b) MCP1 green free-hand press, magnified  $1000\times$ , (c) MHP1 green free-hand press, magnified  $1000\times$ , (d) MCP2 green free-hand press, magnified  $1000\times$ , (e) MHP2 green free-hand press, magnified  $1000\times$ , (f) MCP3 green free-hand press, magnified  $1000\times$ , (g) MHP3 green free-hand press, magnified  $1000\times$ , (h) MCP3 green slip casting, magnified  $200\times$  and (i) MHP3 green free-hand press, magnified  $200\times$ .

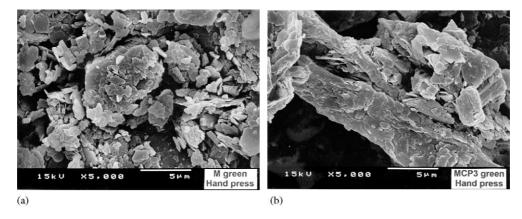


Fig. 7. SEM photomicrographs of the M mother porcelain and MCP3 paper-composite porcelain green samples produced by free-hand press casting method (a) M green free-hand press, magnified  $5000 \times$  and (b) MCP3 green free-hand press, magnified  $5000 \times$ .

As shown in Fig. 6h and i, the orientation of the fibrous structure is random in the paper-composite porcelain sample. Hence, the fibrous structure distribution in the paper-composite porcelain is not very homogeneous. The composite material obtained is very heterogeneous: 16 bonding between fibres and matrix is created during the manufacture of the composite material. This has a fundamental influence on the mechanical properties of the composite material. The paper fibre influenced the heterogeneity in the formation of the paper-composite porcelain sample, which is a non-uniform distribution of fibres in the matrix.

Fig. 6f and h show that the MCP3 sample has a coarser pore structure than the MHP3 samples (Fig. 6g and i). The MHP3 sample has a denser and better-packed surface morphology, while MCP3 shows a rough and highly porous surface. The MHP1 sample shows a denser structure that consists of finer particles compared with MCP1. The MHP1 body structure is more similar to the M body structure than MCP1 is to M.

Fig. 6f and h showed that there were no significant differences in the microstructure between the samples produced by the two different production methods; slip casting and free-hand press casting. The type of paper fibre (compare from Fig. 6h to i) or the amounts of paper (compare from Fig. 6a–c to f–i) in the paper-composite porcelain influenced the observed body structures.

In Fig. 7, SEM images show the morphologies of M and MCP3 green samples at the same magnification. Figs. 7a and b show the typical surface structure changes achieved by combining the paper fibre in porcelain. The high porosity fibrous structure is clearly visible in the structure of the MCP3 green sample, which also illustrates the degree of the heterogeneity in its microstructure. It was also observed that clay minerals covered the paper fibres in the paper-composite porcelain body structure (Fig. 7a).

Through the SEM examinations, a fibrous structure was characterised in a paper-composite porcelain body, in its green state, and has a different body structure to its mother porcelain body. The structure of the paper-composite porcelain body had fibre binders formed in the construction of fibre

bridging. This result is related to the interaction between the clay raw materials and paper fibre during the paper-composite porcelain clay preparation process. These observations indicate that once the body preparation process is finished, the effect of the paper fibre is as a binder and results in a complex network structure in the paper-composite porcelain body. This is believed to give the strength to its body properties in its green state.

## 4.3. Linear drying shrinkage, weight-loss and mechanical strength

Table 3 lists the average values of the linear drying shrinkage from wet to dry, weight-loss from wet to dry, mechanical green strength and the standard deviation of mechanical green strength from the respective results. The result of mechanical strength represents the average based on a number of individual tests.

### 4.3.1. Linear drying shrinkage

Table 3 show that with the exception of the MCP3 press, all MCP and MHP samples have a lower shrinkage ratio than the M sample in both production methods. The production method, amount of paper fibre in the composition, and type of paper fibre were the major factors influencing the linear drying shrinkage of MCP and MHP samples.

From the results, the production method is a minor factor in influencing the drying shrinkage of paper-composite porcelain when the amount of paper fibre is small. However, the production methods become an important concern in the MHP samples when the amount of paper fibre is increased.

All MHP samples show less shrinkage ratio than the MCP samples. These results show that the type of paper fibre is an important factor in influencing the drying shrinkage in paper-composite porcelain.

The water content in body composition is an important factor for controlling the drying shrinkage. In this study, the samples prepared for slip casting have a water content of 45 wt.% while samples for free-hand press casting have 30 wt.%. In

Table 3
Physical properties of M (mother porcelain), MCP and MHP (paper-composite porcelain) samples in the green state produced by free-hand press and slip casting methods

	Linear drying shrinkage from wet to dry (%)	Weight-loss from wet to dry (%)	Mechanical strength (MPa, N/mm <sup>2</sup> )	Standard deviation of mechanical strength
M press	4.3	16.0	5.9	0.3
M slip	4.8	16.0	5.8	0.3
MCP1 press	4.1	21.0	7.8	0.5
MCP1 slip	4.1	25.9	7.6	0.5
MCP2 press	4.2	21.1	9.6	0.5
MCP2 slip	4.5	30.1	9.4	0.4
MCP3 press	4.3	22.5	10.0	0.4
MCP3 slip	4.7	37.7	9.7	0.4
MHP1 press	3.5	21.4	9.1	0.5
MHP1 slip	3.5	25.2	9.0	0.3
MHP2 press	3.5	22.1	10.2	0.4
MHP2 slip	3.7	25.4	10.0	0.3
MHP3 press	3.6	22.2	11.5	0.5
MHP3 slip	4.3	25.4	11.4	0.5

the two production methods, the samples produced by a freehand press casting method showed a smaller shrinkage than the samples produced by a slip casting method.

### 4.3.2. Weight-loss

The test results of weight-loss from wet to dry showed that in the green state all MCP/MHP samples have a lighter weight and higher weight-loss ratio than the M samples. Furthermore, an increase of the amount of paper fibre in the MCP/MHP samples body composition had an effect on the increase in the weight-loss as shown in Table 3. The weight-loss increased slightly in the MCP/MHP samples when produced by the free-hand press casting method.

This result indicates that the most important feature is that when the paper fibre is combined as an additive and as a binder in the body composition, this clearly increases weightloss ratio in the green state.

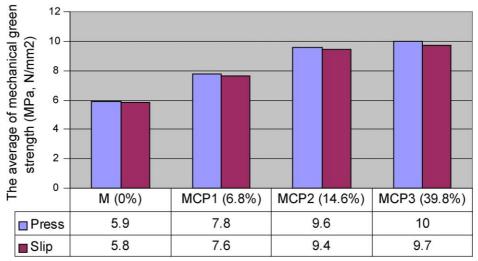
### 4.3.3. Mechanical strength

Table 3 shows that the MHP samples have a higher mechanical strength than the MCP samples.

In the mechanical green strength test, it was observed that no MCP/MHP samples were completely broken into two pieces. Instead, they cracked in the middle of the bar but the paper fibres still held the cracked bar together. Multiple bonding fibres were observed directly in the cracks of the paper-composite porcelain bars. Comparably, all M samples were completely broken into two pieces.

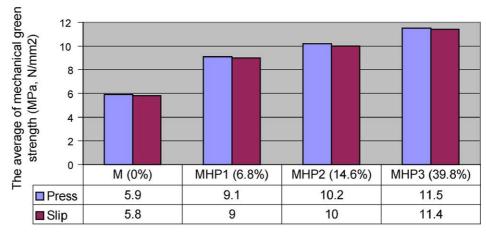
Figs. 8–11 show that the mechanical green strength is significantly increasing with the increase of the paper fibre amount in the body composition.

The characteristic green surface microstructures of the M and MCP/MHP press samples are shown in Figs. 6 and 7. The MHP press samples in Fig. 6c, e, g, and i showed that the MHP press samples have a less porous and better-



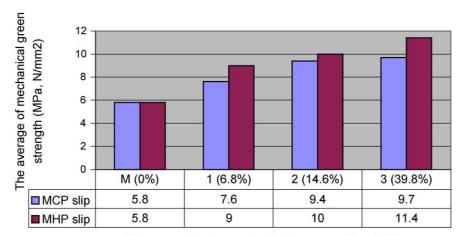
The amount of paper fibre in the composition (wt.%)

Fig. 8. Mechanical green strength; M and MCP samples produced by two different methods.



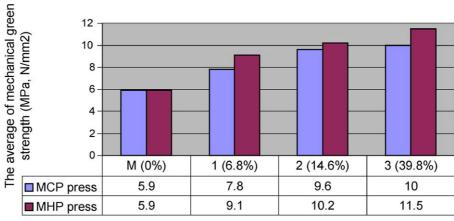
The amount of paper fibre in the composition (wt.%)

Fig. 9. Mechanical green strength; M and MHP samples produced by two different methods.



The amount of paper fibre in the composition (wt.%)

Fig. 10. Mechanical green strength; M, MCP and MHP samples produced by free-hand press casting method.



The amount of paper fibre in the composition (wt.%)

 $Fig.\ 11.\ Mechanical\ green\ strength;\ M,\ MCP\ and\ MHP\ samples\ produced\ by\ slip\ casting\ method.$ 

packed surface morphology, while the MCP press samples showed a rougher and more porous structure. All these green morphologies match the green strength behaviour shown in Figs. 8–11.

A clearly uniformed formation and a low shrinkage rate are very important in achieving a dense green surface morphology. The MHP slip/press samples have a higher mechanical strength than the MCP slip/press samples. The microbonding structure in Fig. 6 is considered when understanding the result. With the denser and less porous green microstructure of MHP slip/press samples as in Figs. 8-11, the lower green strength of the MCP slip/press samples was expected. The effects of the amount of paper fibre in the body composition were significant. In Figs. 8 and 9, the type of production method and the type of selected paper fibre are not the major factors for the green strength. The primary factors are the adding of paper fibre as a binder in the porcelain, and the amount of paper fibre added in the body composition. So far, the slightly higher strengths appeared in the samples produced by the free-hand press casting method rather than the samples produced by the slip casting method, and MHP samples rather than MCP samples.

In Figs. 10 and 11, all MCP/MHP press/slip samples are clearly stronger than the M press/slip samples in the green state. The biggest differences in mechanical green strength are almost double in MCP3/MHP3 press samples compared to the M press sample.

All MCP/MHP press/slip samples showed that their green strength increases according to the increase in weight-loss ratio and shrinkage ratio. The increasing amount of the paper fibre in the body composition also implied an increase in the green strength, the weight-loss ratio, and the drying shrinkage ratio.

All test results from the physical properties provided evidence that the MCP/MHP press/slip samples have less shrinkage, a lighter weight and a higher mechanical strength than the M press/slip samples, except for the MCP3 press sample which showed same dry shrinkage ratio as the M press. It is believed that the reason for lower shrinkage, a lighter weight and a higher mechanical strength of the paper-composite porcelain is that the paper fibres act as binders in the microstructure. The strong inter-fibre bonding, interlocking fibres, build fibre bridging between the clay particles and bind them together, which influences the properties of the paper-composite porcelain.

## 5. Conclusions

This study characterised the material properties of papercomposite porcelain in its green state. It concludes that papercomposite porcelain is practically attractive because of its high strength, high weight-loss and low drying shrinkage. The use of paper fibre in the porcelain resulted in a 3.53% drying shrinkage ratio in the MHP1 slip sample compared to 4.8% in the M slip sample. The highest weight-loss in the paper-composite porcelain was 37.67% in the MCP3 slip sample compared to 16.04% weight-loss in the M slip sample. The highest green strength in the paper-composite porcelain was 11.5 MPa in the MHP3 press sample while 5.9 MPa in the M press sample. Between the two different types of production methods, the samples produced by the free-hand press casting method showed a lower shrinkage ratio and a higher green strength than the samples produced by the slip casting method.

The role of paper fibre is as a binder and it results in a complex network structure in paper-composite porcelain. It gives a higher green strength, a lighter weight and a lower green shrinkage in the paper-composite porcelain that gives better working characteristics in the green state than that of its mother porcelain. This makes it beneficial for usage in the traditional practices of ceramic art, and it may be worth developing it for industrial ceramic design production. It is believed that the origins of these effects are fibre bridging, fibre binding, and an interlocking of the fibres in the microstructure of the paper-composite porcelain. The bonding between fibres and matrix is created during the preparation process of the samples. This has a fundamental influence on the technical properties of the paper-composite porcelain in the green state.

Considering all properties, it can be concluded that the major factors in influencing the technical properties were not only the role of paper fibre itself in the structure of paper-composite porcelain but also the amount of paper fibre in the body composition, the type of paper fibre, and the production method.

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### References

- Santacruz, I., Nieto, M. I., Moreno, R., Ferrandino, P., Salomoni, A. and Stamenkovic, I., Aqueous injection moulding of porcelains. *J. Eur. Ceram. Soc.*, 2003, 23(12), 2053–2060.
- Lightwood, A., Working with Paper Clay and Other Additives. The Crowood Press, Wiltshire, 2000, p. 27.
- 3. Peterson, S., The Craft and Art of Clay (3rd ed.). L. King Pub, London, 1999, pp. 151–153.
- 4. Gault, R., Paper Clay. A&C Black, London, 1998, p. 37.
- Kim, J. A., The characterisation of paper composite porcelain in a fired state by XRD and SEM. J. Eur. Ceram. Soc., 2004, 24(15–16), 3823–3831.
- Hlaváč, J., The Technology of Glass and Ceramics [Glass Science and Technology], Vol 4, ed. K. Nemecek. Elsevier, Amsterdam, 1983, p. 260.

- 7. ASTM C 326-82, Standard Test Method for Drying and Firing Shrinkage of Ceramic Whiteware Clays. ASTM International, 1997.
- ASTM C 373-88, Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products. ASTM International, 1999.
- ASTM C 689-80, Standard Test Method for Modulus of Rupture of Unfired Clays. ASTM International, 1999.
- 11. Dawson, S., *The Art and Craft of Papermaking*. Aurum Press, London, 1993, p. 34.
- Whitney, R. P., Chemistry of paper. In *Paper-Art & Technology*, ed. P. Long. World Print Council, San Francisco, 1979, pp. 36–44.
- 13. Heller, J., *Papermaking*. Watson-Guptill Publications, New York, 1978, pp. 56–62.
- 14. Gartside, B., Paper clay. New Zealand Potter, 1993, 35(3), 32-33.
- Chen, P. W. and Chung, D. D. L., Low-drying-shrinkage concrete containing carbon fibres. Composites Part B, 1996, 27(3–4), 267–274.
- Gay, D., In Composite Materials [Materiaux Composites], ed. S. V. Hoa and S. W. Tsai. 4th ed. CRC Press, LLC, Florida, 2002, pp. 3–4.