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Use of thin film transistor liquid crystal display (TFT-LCD) waste glass in the production of ceramic tiles

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Abstract

In this study, we employ the following operating conditions: varied pressure (25 kgf/cm^2), sintering temperature (900–1200 °C), sintering time (6 h), percentage of thin film transistor liquid crystal display (TFT-LCD) waste glass by weight (0–50%) and temperature rising at a rate of 5 °C/min, to fabricate clay tiles. The sintering characteristics of the clay blended with TFT-LCD waste glass tiles are examined to evaluate the feasibility of the reuse of TFT-LCD waste glass. TFT-LCD waste glass contains large amounts of glass. The TCLP leaching concentrations all met the ROC EPAs current regulatory thresholds. The addition of TFT-LCD waste glass to the mixture, increased the apparent weight loss. The incorporation of 50% TFT-LCD waste glass resulted in a significant increase in the porosity ratio of the specimens compared to the porosity ratio of the ceramic tile containing TFT-LCD waste glass. The main constituent in both the clay tile and the clay with TFT-LCD waste glass samples is quartz. Increasing the temperature resulted in an increase in the flexural strength and resistance to abrasion in the tiles. The porosity ratio decreases as shrinkage increases. The relation between the porosity ratio and the hardness of the tiles used in the study is also shown.

Keywords: Thin film transistor liquid crystal display (TFT-LCD); Waste glass; Leaching concentration; Sintering; Weight loss; Water absorption; Porosity

1. Introduction

According to Taiwan's Environmental Production Administration (EPA), the amount of garbage to be disposed of climbed to 0.75 million tonnes in 2006; therein, waste glass accounted for 5.84% therein [1]. The amount of waste glass being dumped into landfills has accumulated to about 0.52 million tonnes while the amount of thin film transistor liquid crystal display (TFT-LCD) waste glass has reached 6000 tonnes [2].

The structure of TFT-LCD is composed of liquid crystal sandwiched between two glass plates. TFT Glass has as many TFTs as the number of pixels displayed, while color filter glass has a color filter which generates the color. The movement of the liquid crystals is controlled by variations in the voltage between the colored filter glass and the TFT glass. The amount of light supplied by a back light is determined by the amount of movement in the liquid crystals in such a way as to generate color. Both Indium and tin have been used as a diffusion barrier between indium–tin oxide (ITO) and polycrystalline-silicon layers to reduce the contact resistance [3]. These ITO/Si contacts may be utilized in TFT-LCD to reduce the number of fabrication steps. The problem is that TFT-LCD waste glass is not suitable for disposal in landfills, by incineration, or in compost; this makes recycling and re-utilization the best treatment method for its disposal [4,5].

Currently, although landfill disposal is still the main waste management method for TFT-LCD waste glass, this is not a long-term practical solution because of the high cost of transportation and the scarcity of land for landfills. As a result in Taiwan recycling and reuse as construction material has become a more desirable way of treating them in Taiwan. In this study, sintering processes utilized to render TFT-LCD waste glass useful in the making of ceramic tile. The aim of this work is to produce glass–ceramic materials from the TFT-LCD waste glass. The following operating conditions are employed: varied pressing pressure (25 kgf/cm^2), sintering temperature (900–1200 °C), sintering time (6 h), percentage of TFT-LCD waste glass by weight (0–50%) and temperature rising at a rate of 5 °C/min. The sintering characteristics of tile clay blended with TFT-LCD waste glass are examined to determine the feasibility of resource and materialization reuse of TFT-LCD waste glass.

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Table 1
Chemical composition and total heavy metals in the clay and TFT-LCD waste glass

Composition	Clay	TFT-LCD waste glass
SiO_2 (%)[a]	61.5	64
Na_2O (%)[a]	–	0.3
Al_2O_3 (%)[a]	15.84	–
Fe_2O_3 (%)[a]	6.11	–
CaO (%)[a]	0.36	–
MgO (%)[a]	1.31	–
SO_3 (%)[a]	0.02	–
K_2O (%)[a]	2.73	–
Cu (mg/kg)[b]	4	5.1
Zn (mg/kg)[b]	28	0.5
Pb (mg/kg)[b]	ND	3.2
Cr (mg/kg)[b]	6.02	1.07
Cd (mg/kg)[b]	ND	ND

The white clay used was obtained from I-Cheng Pottery Ltd. of Taiwan. ND: no detection.

[a] X-ray fluorescence analysis.

[b] Analyzed by inductively coupled plasma atomic emission spectroscopy after $HF/HClO_4/HNO_3$ digestion.

2. Materials and methods

2.1. Materials

The TFT-LCD waste glass was obtained from a TFT-LCD manufacturing plant in Taiwan. The White clay used was obtained from I-Cheng Pottery Ltd. of Taiwan. The TFT-LCD waste glass and the clay were both crushed to a uniform particle size, then ground until they could pass through a 16 mesh sieve and finally dried. The chemical composition of the raw materials was analyzed by X-ray fluorescence (XRF) and the results are shown in Table 1.

2.2. Experimental procedures

In order to investigate the feasibility of reusing TFT-LCD waste glass to make ceramic tiles, the waste glass content in the clay–TFT-LCD waste glass mixture was varied from 0% to 50% by weight. The mixtures were homogenized in a blender and then molded by pressing at 25 kg/cm^2 to form a 40 mm (L) × 45 mm (W) × 6 mm (H) bar. The results obtained from the laboratory tests can be applied to the commercial size tile since it was constructed by the same component and process. Therefore, the scale up of the brick sample should be acceptable in this study.

The molded specimens were air-dried at room temperature for 24 h, then oven dried at 105 °C (ASTM D 2216) for another 24 h to remove the water content, after which the dried specimens were heated to the designated temperature (900, 1000, 1100 and 1200 °C), at a heating rate of 5 °C/min. This temperature was also maintained for 6 h to bake the samples, after which they were cooled to room temperature.

2.3. Analysis methods

The ceramic tile samples then underwent a series of tests to determine their quality including firing shrinkage, weight loss on ignition, water absorption, bulk density, flexural strength and hardness (CNS 3299). In this test, the plat-like tile sample was mounted at an angle of 22.5° before being subjected to a blast of 80 mesh silica sand. Fixed quantities (30 kg/blast) were employed at 15 min. The samples were weighed both before and after the experiments to as certain the weight loss. The abrasion resistance was measured according to the amount of tile removed by the blasting process [6]. The crystalline phases of all the heat-treated samples and the untreated ground mixture were identified by X-ray diffraction (XRD) analysis. The mineralogy was determined by XRD analysis, carried out by a Siemens D-5000 X-ray diffractometer with Cu Kα radiation and 2θ scanning, ranging between 5° and 70°. The chemical composition was determined by XRF performed with an automated RIX 2000 spectrometer. The specimens were prepared for XRF analysis by mixing 0.4 g of the sample and 4 g of 100 Spectroflux, at a dilution ratio of 1:10. Homogenized mixtures were placed in Pt–Au crucibles, then treated for 1 h at 1000 °C in an electrical furnace. The homogeneous melted sample was recast into glass beads 2 mm thick and 32 mm in diameter. Following criteria evaluation, the tests of toxic characteristic leaching procedure (TCLP) tests, as described in the Taiwan EPA (SW 846-1311 Method) were performed, to quantify the leachability of metals from the clay and TFT-LCD waste glass samples.

3. Results and discussion

3.1. Characteristics of the clay and TFT-LCD waste glass

Fig. 1 shows the particle size distribution of the clay and TFT-LCD waste glass. It can be observed that 20 (wt.%) of the particles in the clay have a median diameter of less than 200 μm and 80% of particles have a median diameter of less than 100 μm. About 3% of the particles in the TFT-LCD waste glass have a median diameter of less than 200 μm and 30% of particles have a median diameter of less than 2 μm. The densities of the clay and the TFT-LCD are 2.43 and 2.33 g/cm^3, respectively.

The chemical composition of the clay and the TFT-LCD waste glass samples was analyzed using XRF and the mineralogical composition was determined with X-ray diffraction. Table 1 presents the chemical composition of the clay and TFT-LCD waste glass. It can be seen that the clay has more SiO_2 and Al_2O_3 than does the TFT-LCD waste glass. The clay, as

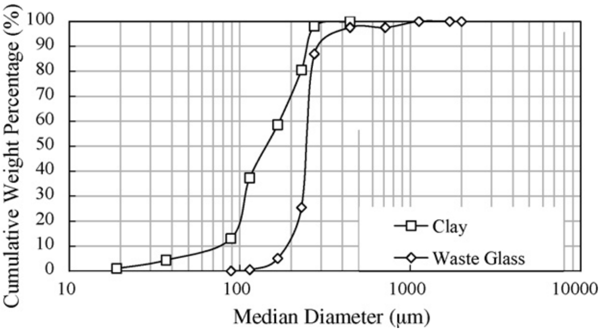


Fig. 1. Particle size distribution of the clay and TFT-LCD waste glass.

Table 2
Leaching concentrations of the clay and TFT-LCD waste glass

	Pb (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Zn (mg/L)
Clay	ND	ND	ND	ND	0.12
Waste glass	ND	ND	ND	ND	0.09
Regulatory limits	5	1	5	15	–

ND: no detection.

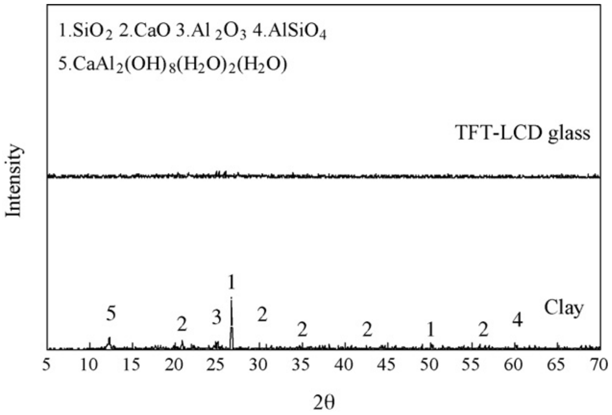


Fig. 2. X-ray diffraction patterns of the clay and TFT-LCD waste glass.

revealed by XRD analysis, is principally constituted of silicon, with aluminum and a small amount of $CaAl_2(OH)_8(H_2O)(H_2O)$. As can be seen, the TFT-LCD waste glass contains large amounts of glass. The TCLP leaching concentrations of the clay and TFT-LCD waste glass all met the ROC EPAs current regulatory thresholds (Table 2) (Fig. 2).

3.2. Loss on ignition of the ceramic tiles

Increasing the amount of TFT-LCD waste glass and the temperature resulted in an increase in the tile's weight loss on ignition, see Fig. 3. Furthermore, the weight loss on ignition is also dependent on the amount of inorganic substances in the clay and the amount of TFT-LCD waste glass that is burnt off during the sintering process. However, the addition of TFT-LCD waste glass to the mixture causes an apparent increase in the loss of weight. It is possibly due to the formation of an unwanted surface, mainly as a result of organic components being burnt off during the sintering process.

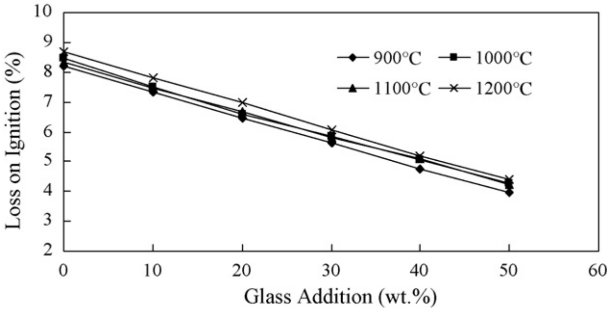


Fig. 3. Loss on ignition of the ceramic tiles.

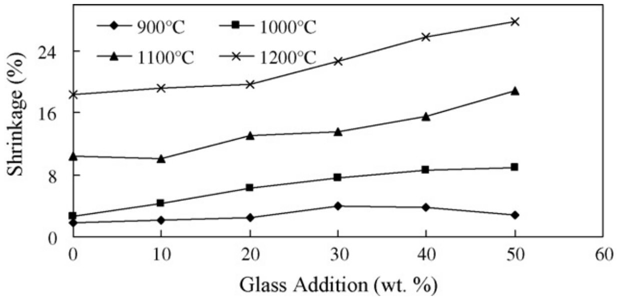


Fig. 4. Shrinkage of the ceramic tiles.

3.3. Shrinkage of the ceramic tiles

The degree of shrinkage is another factor influencing the quality of ceramic tiles. It can be seen in Fig. 4 that the percentage of shrinkage increases with increasing amounts of TFT-LCD waste glass. The firing temperature is another important parameter affecting the degree of shrinkage. In general, increasing the temperature results in an increase of shrinkage (Fig. 4). At 900 °C, there is no apparent decrease in the shrinkage of the tiles when the glass addition exceeds 30%. It is possibly that the formation of necks between the particles tends to increase less obviously as the TFT-LCD waste glass content increases. Thus, the amounts of TFT-LCD waste glass in the mixture and the firing temperature are the two key factors that need to be controlled to minimize the shrinkage during the sintering process.

3.4. Density of the ceramic tiles

The density of samples with different proportions of TFT-LCD waste glass fired at four different temperatures is shown in Fig. 5. As shown, the particle density of the ceramic tiles is proportional to the amount of TFT-LCD waste glass added to the mixture. When the mixture absorbs more water, the ceramic tiles exhibit a larger pore size, resulting in greater density. The firing temperature can also affect the particle density. The results show that increasing the temperature results in an increase in the particle density.

3.5. Water absorption of the ceramic tiles

The CNS 3299 criteria states that a ceramic tile must have less than 17% water absorption. Fig. 6 shows the water absorption results for tiles with different amounts of TFT-LCD waste

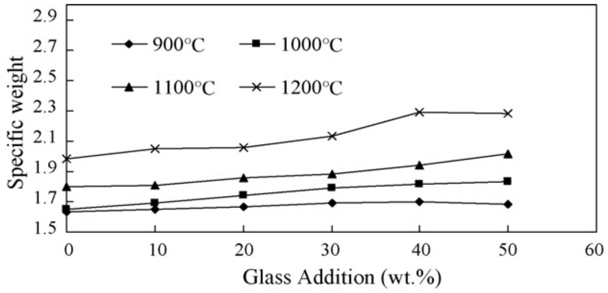


Fig. 5. Density of the ceramic tiles.

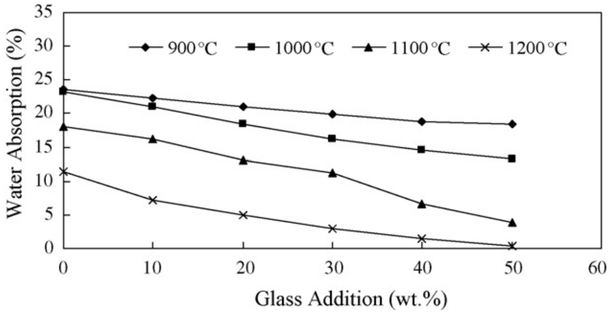


Fig. 6. Water absorption of the ceramic tiles.

glass, at various temperatures. The water absorption decreases as the TFT-LCD waste glass content increases. In comparison, increasing the amount of TFT-LCD waste glass gives rise to a decrease in the water absorption, independently of the firing temperature. These observations suggest that an increase in the sintering rate makes the SiO_2 cause fewer pores in the ceramic tile.

3.6. Porosity of the ceramic tiles

Fig. 7 shows the effect of the firing temperature on the porosity of tiles made with varying amounts of TFT-LCD waste glass. The porosity ratio results show that regardless of the replacement level of TFT-LCD waste glass, the ceramic control samples (i.e. clay without TFT-LCD waste glass) show a significant increase in the porosity ratio over that of the ceramic tile containing TFT-LCD waste glass. This may be due to the SiO_2 content in the TFT-LCD waste glass. Numerous open macro-pores occur when the tiles are fired at low temperatures but these become closed micro-pores because of an increase in the glassy phase that forms due to the reaction with quartz that occurs with an increase in the firing temperature. This means that an increase in the density and a decrease in the porosity with increasing temperature [7,8].

3.7. Hardness of the ceramic tiles

The application of the Vickers hardness test (CNS 3299) requires that tiles, in general, a Mohs' hardness of 5. The hardness of the ceramic tiles is shown in Fig. 8. The Vickers hardness corresponds to values between 3 and 4 on the Mohs' scale when fired at 900 °C. The Vickers' hardness of TFT-LCD waste glass tiles sintered at 1200 °C was sufficiently good to satisfy the CNS 3299 requirements. The hardness results shown in Fig. 8 reveal that regardless of the replacement level, the addition of TFT-LCD waste glass increased the hardness of the ceramic tile sintered at 1200 °C, over that of the control specimen. The rate of increase in the hardness of the ceramic tile was higher when the amount of the TFT-LCD waste glass content increased at above 1000 °C. This difference in the hardness of the specimens may be attributed to the high SiO_2 content in TFT-LCD waste glass, which results in an increased sintering rate and leads to an improvement in the extent of interaction among the particles.

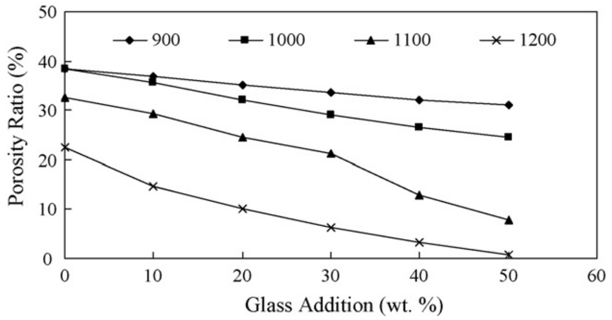


Fig. 7. Porosity of the ceramic tiles.

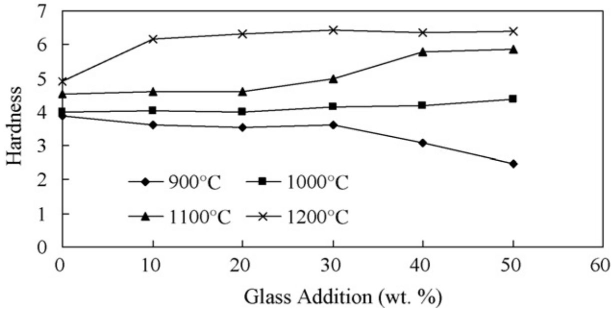


Fig. 8. Hardness of the ceramic tiles.

3.8. Flexural strength of the ceramic tiles

The flexural strength of the tile samples is shown in Fig. 9. The mechanical behaviour correlates well with the other studied parameters. Increasing the temperature results in an increase in the flexural strength in the tiles, see Fig. 9. The temperature increases the flexural strength by means of densification. This behaviour is due to the progressive formation of calcium based crystalline phases (calcium silicates), leading to higher mechanical strength [9]. However, when the sintering temperature is less than 1100 °C the flexural strength of the specimens tends to decrease less obviously as the TFT-LCD waste glass content increases.

3.9. Resistance to abrasion of the ceramic tiles

The results of the abrasion resistance tests are illustrated in Fig. 10. It can be seen that increasing the temperature results in increased resistance to abrasion, see Fig. 10. Also, an amount of 50% TFT-LCD waste glass causes the abrasion resistance of the tile to increase. It is possibly that the Al_2O_3 and SiO_2 and ZrO_2 increase the abrasion resistance of the glaze [10].

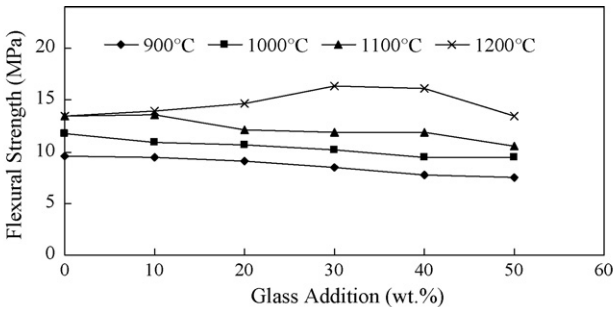


Fig. 9. Flexural strength of the ceramic tiles.

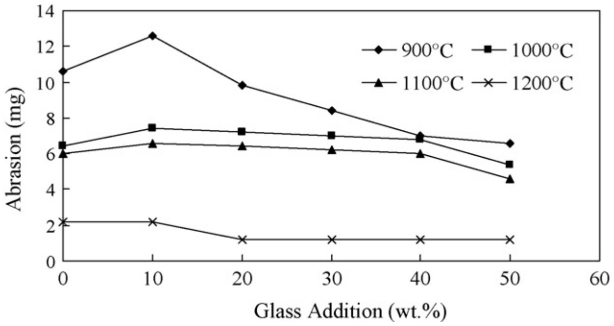


Fig. 10. Abrasion of the ceramic tiles.

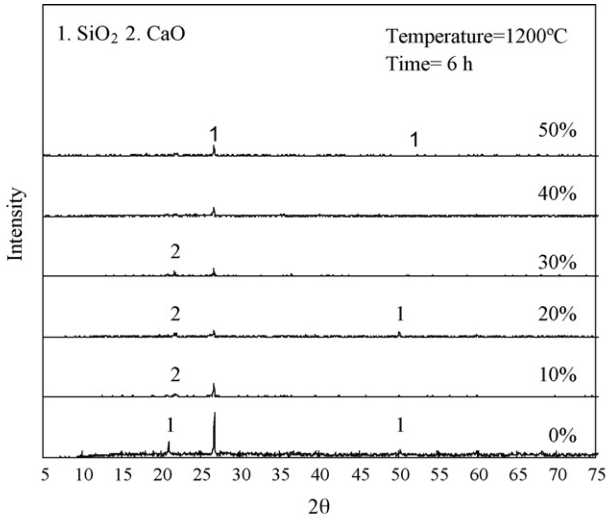


Fig. 11. X-ray diffraction patterns of the ceramic tiles.

3.10. X-ray diffraction patterns of the ceramic tiles

The XRD patterns of samples heated to 1200 °C for 6 h are shown in Fig. 11. The main constituent of both clay ceramic tile and the clay with TFT-LCD waste glass samples, the main constituent is quartz (SiO_2). Samples containing no TFT-LCD waste glass samples were assigned to crystalline phases of quartz (SiO_2). In the clay containing no TFT-LCD waste glass sintered at 1200 °C, the identified crystalline phases are quartz (SiO_2) and traces of CaO. Furthermore, the portion of the glass phase increases with the TFT-LCD waste glass content. No mullite is present at 950 °C, which is in agreement with the results of other researchers [11,12].

3.11. Relation between the porosity and the properties of the tiles

The relation between the porosity and the properties of the tiles can be studied by finding the values that limit the porosity ratio, if any, so as to substitute for the specific weight absorption and hardness requirements. The results are shown in Fig. 12, including the relation between the porosity and shrinkage when the regression coefficient is $R^2 = 0.89$. As expected, the porosity ratio decreases as shrinkage increases. The relation between the porosity ratio and the hardness of the tiles used in the study is also shown. A linear relation of $R^2 = 0.79$ can be observed with data points scattered near the region of higher porosity.

3.12. SEM observation of the ceramic tiles

The microstructure of samples fired at 1200 °C is shown in Fig. 13(a–f).

It can be observed from the micrographs that crystalline materials are embedded in a glassy matrix, meaning that the microstructure of the ceramic tiles was not thoroughly homogeneous. The fractured surface of the sample prepared from TFT-LCD waste glass is very different from that of the control sample. Samples of clay tiles treated at 1200 °C exhibit a poorly sintered structure, with a rough and granular texture caused by the high open porosity (Fig. 13(a)). The clay containing TFT-LCD waste glass fired at 1200 °C showed in a dense and homogeneous microstructure with large glass-like zones (Fig. 13(b)). A denser well-sintered microstructure associated with the formation of elongated cavities can be seen.

Compared to the control sample, the fractured surface of the clay containing 30% TFT-LCD waste glass has a denser well-sintered microstructure with a uniform distribution of pores. Fig. 13(c) shows that the sample contains a greater number of grains than did the control sample. However, a comparison of microstructure of the clay containing 40% and 50% samples (see Fig. 13(e) and (f)) revealed the occurrence of a particle coalescence phenomena as a result of thermal treatment, as evidenced by the formation of necks between the particles. Kanka and Schneider [13] had confirmed the above facts by indicating that, especially in the later stages of the reaction sintering of silica and alumina (>1200 °C), liquid phase sintering produces relatively large prismatic mullite crystals embedded in a fine grained matrix. These results suggest that this dense microstructure may be responsible for the better mechanical properties of the sample.

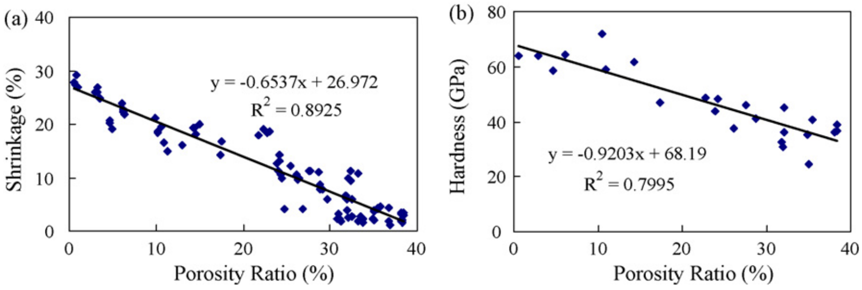
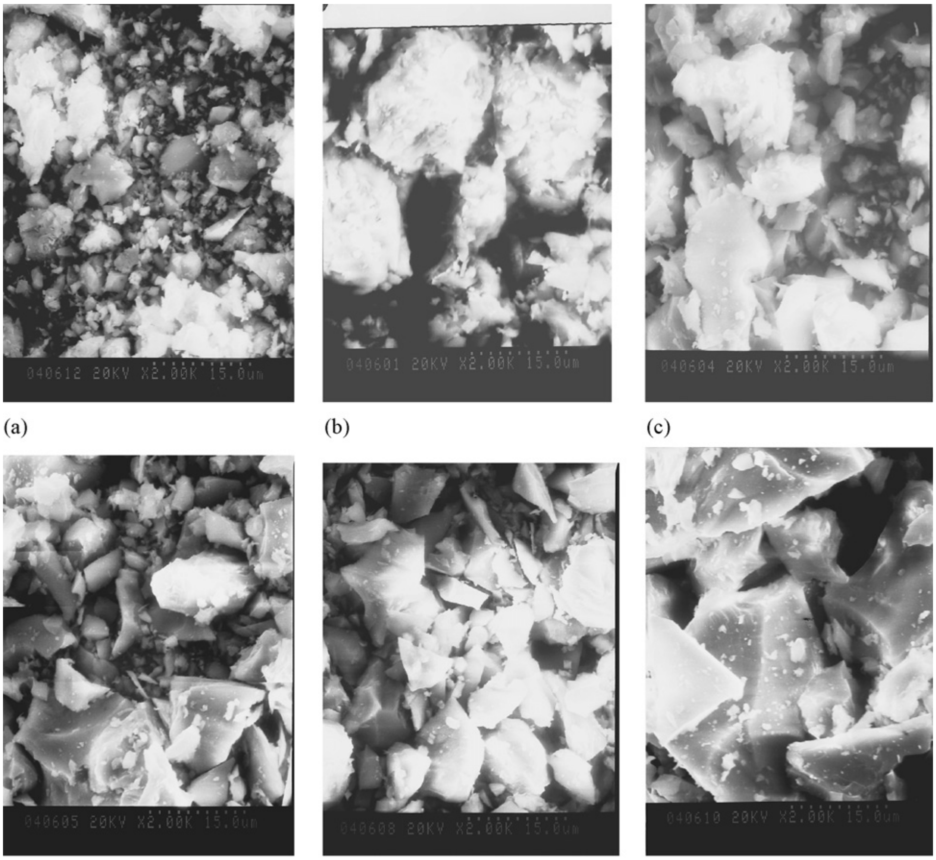


Fig. 12. Relationship between the porosity and the mechanical characteristics: (a) shrinkage and (b) hardness.



(a) (b) (c)

(d) (e) (f)

Fig. 13. SEM observations of the ceramic tiles: (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40% and (f) 50%.

4. Conclusions

In this study we demonstrated that it is possible to utilize TFT-LCD waste glass as a raw material for the production of ceramic tile. On the basis of the reported results, the following conclusion can be drawn:

(1) TFT-LCD waste glass contains a large amount of glass but its TCLP leaching concentration met the ROC EPAs current regulatory thresholds.
(2) The addition of TFT-LCD waste glass to the mixture led to an apparent increase in the loss of weight.
(3) The incorporation of 50% TFT-LCD waste glass resulted in a significant increase in the porosity ratio of the specimens compared to the porosity ratio of the ceramic tile containing TFT-LCD waste glass.
(4) The Vickers' hardness of TFT-LCD waste glass tiles sintered at 1200 °C was sufficiently good to satisfy the CNS 3299 requirements.
(5) Increasing the temperature resulted in an increase in the flexural strength and resistance to abrasion in the tiles.
(6) The main constituent of the clay and clay with TFT-LCD waste glass samples is quartz.
(7) The porosity ratio decreases as shrinkage increases. The relation between the porosity ratio and the hardness of the tiles used in the study is also shown. A linear relation of $R^2 = 0.79$ can be observed, with data points scattered near the region of higher porosity.
(8) A comparison of the microstructure of the clay containing 40% and 50% TFT-LCD waste glass samples revealed the occurrence of a particle coalescence phenomena as a result of thermal treatment, as evidenced by the formation of necks between the particles.

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