INFLUENCE OF INCORPORATION OF POWDER OF PRINTED CIRCUIT BOARDS ON TECHNOLOGICAL PROPERTIES AND MICROSTRUCTURE OF TRIAXIAL CERAMICS

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ABSTRACT: *Using the methodology of experiments with mixtures, seven formulations of clay, phyllite, and printed circuit boards (PCB) were obtained to study the influence of this waste on triaxial ceramic tiles. Each formulation was processed under conditions similar to those used in the ceramic tiles industry, and characterized for fired modulus of rupture (FMoR) and water absorption (WA). The samples sintered at 1180°C were also subjected to analysis by XRD and SEM. The lowest resistance was observed in samples with 40% residue, while the highest strength occurred for samples with 14% residue, which reached average values of mechanical strength and water absorption of 35.0 MPa and 2.0%, respectively. The microstructure showed that it is possible to use waste of PCB in triaxial ceramic, which exhibits a fluxing behavior and it has an important effect on the sinterability and the development of appropriate microstructures.*

Key-words: mixture experiments; printed circuit boards; ceramic tiles, ceramic properties.

INTRODUCTION

New electro-electronic facilities and technologies have contributed to a serious environmental problem regarding the elimination and disposal of obsolete or unused equipment. This has caused a major concern in reuse and recycle different classes of waste as raw materials(1-3).

The printed circuit boards (PCB), which are part of the essential components for the operation of electrical and electronic equipment (EEE) are a class of waste whose management is not simple, contrasting to plastic and metal skeletons. Moreover, PCB represent a residue which is potentially dangerous and difficult to recycle (4-6).

Studies about recycling of waste of electrical and electronic equipment (WEEE), especially the waste of printed circuit boards (WPCB) have been performed worldwide. This occurs because PCB represents only 3% weight of total components of EEE, but show great heterogeneity in chemical composition and has great potential pollutant and toxic. For these reasons, different ways of obtaining and processing this waste have been studied[7-10], as well as its application in various materials, either as filler in polymer matrix composites[7,11], partial substitute for aggregate in concrete [12], or as reinforcement in asphalt [13].

An important feature of this residue is to contain significant amounts of metals, including sodium and potassium. In the sintering temperature of ceramic bodies, these metals may act as fluxes, contributing to the glass phase formation in sintering , and replacing raw materials such as feldspars [14,15].

An opportunity to potentialize a better cost-benefit and optimize the physico-chemical properties of WPCB is to use it as a component in triaxial ceramics. Thus, the experimental design, especially experiments with mixtures, can contribute to a better understanding of the effects of waste in ceramic matrix [16,17]. This technique allows studying the factors involved in the experiment and their interactions. So, if processing conditions are kept constant, the variables become the fractions of the components in the mixture. Thus, it is possible to observe how each component of the mixture influences the final result [18-20].

Previous studies using techniques with experiments have used mixtures of triaxial ceramic projects with up to ten compositions[10]. This number still corresponds to many experiments, which requires considerable human and material resources.

This research uses only seven experiments [7] to study the effect of WPCB fraction on the properties of triaxial ceramics system, containing clay and phyllite.

MATERIALS AND METHODS

As raw materials, two clays, a phylllite and WPCB were employed. Clays and phyllite were provided by Mineração Paraná Ltda. (Tijucas do Sul, PR) [21]. The printed circuit boards were provided by University of Region of Joinville (UNIVILLE). The clays were mixed in the ratio 1.5:1 to correct plasticity and facilitate statistical analysis on a triaxial project. The residual powder was obtained from milling of green PCB.

An experimental design was defined with Statistica 9.0 Software. An arrangement {3,2} with a centroid point, totalizing 7 mixtures was used.

The mixtures were subjected to wet grinding for 36 h (residue less than 3% on 325 mesh sieve), followed by drying for 24 h, granulation for 7.0 ± 0.5 wt%, uniaxial pressing at 40 MPa (EMIC, 10 ton press) and sintering at 1180 ° C for 2 h, heating rate of 5 ° C / min and natural cooling.

Fired Modulus of Resistance (FMoR) was determined in three-point bending tests (EMIC 30 ton test machine). For each mixture, the final test result was taken as the average of the measurements carried out on ten test bars. Water absorption (WA) was determined via boiling in water for 2 h, using a digital scale Denver DE 100A with a resolution of 1 mg. For each mixture, the final value was taken as the average of five pieces.

Samples fractured in test FMoR were observed by SEM; samples polished and attacked with HF 10% for 300 s were subjected to XRD (monochromatic radiation of Co).

The requirements of the NBR 13818 (1997) were observed in order to evaluate the applicability of the material (Table 1)

Table 1. Classification for ceramic tiles according to WA and FMoR.

Classification	Name	WA (%)	FMoR (MPa)
Porcelain	BIa	≤ 0.5	≥ 35
Stoneware	BIb	0.5 – 3.0	≥ 30
Semi-stoneware	BIIa	3.0 – 6.0	≥ 22
Semi-porous	BIIb	6.0 – 10.0	≥ 18
Porous	BIII	> 10.0	≥ 15

Source: adapted from NBR 13818 : 1997.

Data were analyzed by the software Statistica 9.0 to obtain the regression models for each property and their respective response surfaces.

RESULTS AND DISCUSSION

Experimental Design

By processing requirements, it was decided that the proportion of each component in the ceramic mixture should vary between 40 and 80% clay, 20 to 60% phyllite and 0 to 40% WPCB. This system gave a narrow composition triangle, shown in Figure 1.

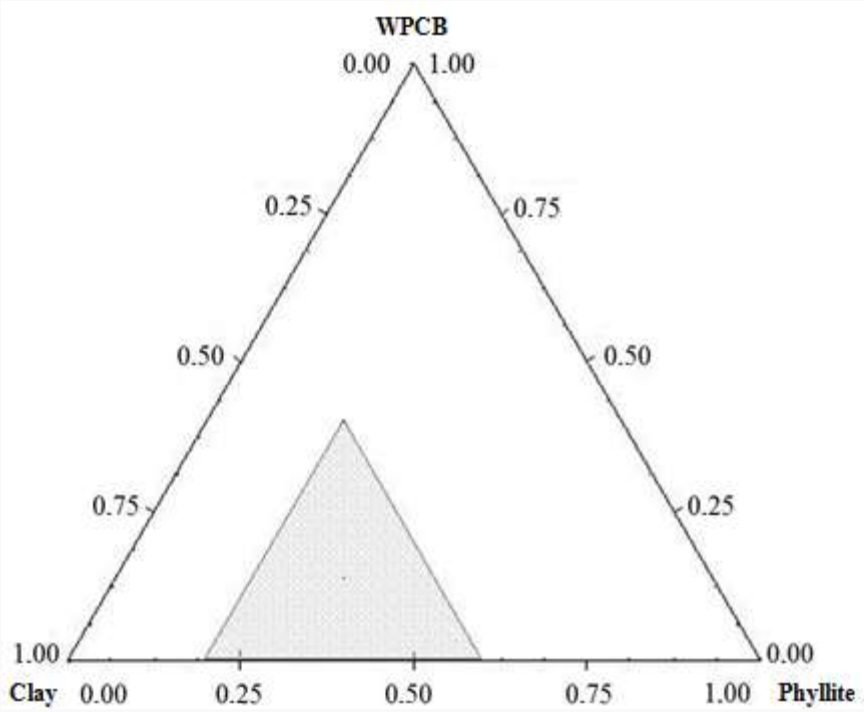

Figure 1: Triaxial system of clay mix, phyllite and e-waste and the region studied (grey triangle).

In this restricted area (also called “pseudocomponent triangle”) a simplex arrangement {3,2} was established with a central point, summing up seven composition described in Table 2.

Measurements of the properties and data analysis

Table 3 presents the values obtained for FMoR and WA. From these values and the chemical composition of each mixture, regression equations according to the mathematical models[16] were calculated. A selection was made from those with a significance level lower of 8%. Equations (A) and (B) are the end result (x_1 is the fraction of clay, x_2 is the fraction of phyllite, and x_3 is the fraction of WPBC, expressed as original components).

Table 2. Triaxial formulations contain clay, phyllite and WPCB.

Mixture	Raw Materials		
	Clay (%)	**Phyllite (%)**	**WPCB (%)**
1	**0.80**	**0.20**	**0.00**
2	**0.40**	**0.60**	0.00
3	0.40	0.20	**0.40**
4	0.60	0.40	0.00
5	0.60	0.20	0.20
6	0.40	0.40	0.20
7	0.53	0.33	0.14

Table 3. Measured values of FMoR and WA.

Mixture	FMoR (MPa)	WA (%)
1	18.83±1.97	8.10±0.38
2	31.21±3.20	5.95±0.39
3	8.56±0.88	0.04±0.01
4	27.98±2.62	7.72±0.35
5	32.26±4.18	3.29±0.41
6	29.86±3.67	0.27±0.02
7	35.00±4.10	2.07±0.09

$$FMoR = 13{,}76x_1 + 44{,}71x_2 - 255{,}32x_3 + 471{,}83x_1x_3 + 256{,}84x_2x_3 \quad (A)$$

$$WA = 9{,}51x_1 + 2{,}17x_2 - 14{,}06x_3 \quad (B)$$

Table 4 shows the analysis of variance based on the statistical parameters for those equations, using statistical standards (p-value, multiple coefficient of determination, R^2, and coefficient of multiple determination adjusted, R_A^2) (16,17).

It is seen that all models are statistically significant at the stipulated level ($p \leq$ significance level) and have low variability (high coefficient of multiple determination). The errors could be considered randomly distributed, with mean tending to zero, which suggests a constant variance for the estimates of the properties. Based on this analysis, equations (A) and (B) may be regarded as suitable models for describing the effect of the raw materials the properties FMoR and WA.

Table 4. Analysis of variance.

Properties	**Model**	**R^2**	**R^2_A**	***p* value**
FMoR	Quadratic	0.9972	0.9837	0.0807
WA	Linear	0.8530	0.7795	0.0216

Response surfaces to FMoR and WA

The quadratic model was considered adequate to represent the FMoR, according to the analysis of variance, Table 4, because p value was similar to the established significance level (0.08 ≈ 0.0807). The model can explain more than 98% of the variability of the measurements, since R^2 and R^2_A found were 0.9972 and 0.9837, respectively, so that the factors which affect the behavior of the material to this property are the components of the mixture and their interactions.

According to the results obtained it can be observed that the lower resistance found, 8.56 ± 0.88 MPa, corresponded to samples with 40% residue (mixture 3), while the maximum strength, 35.00 ± 4.10 MPa was regarding samples with 14% residue. This indicates that the residue contributes to improve the property, but in excess it impairs the performance of this material and the mechanical strength observed by three point bending.

For WA, the linear model was considered appropriate according to the analysis of variance, Table 3. The p value is less than the stipulated level of significance (0.0216 <0.08), and R^2 and R^2_A (0.8530 and 0.7795, respectively) can be accepted, although not being adequate values for these parameters. It is found that the residue contributes to reduce the absorption, while the other components contribute to enhance it.

Figure 2 illustrates FMoR and WA in a response surface. The region with a maximum value of FMoR (34 MPa) has the following composition: 58-68% clay, 20 to 60% phyllite and 0-18% of the WPCB (45-70% clay, 0 to 100% phyllite and 0-45% of WPCB in pseudo), and mixtures with WA less than 2,0% are obtained for areas with 40 to 52% clay, 20 to 44% phyllite and 20-40% WPCB (0-30% of clay 0-60% of phyllite and 50-100% in the pseudocomponent chart).

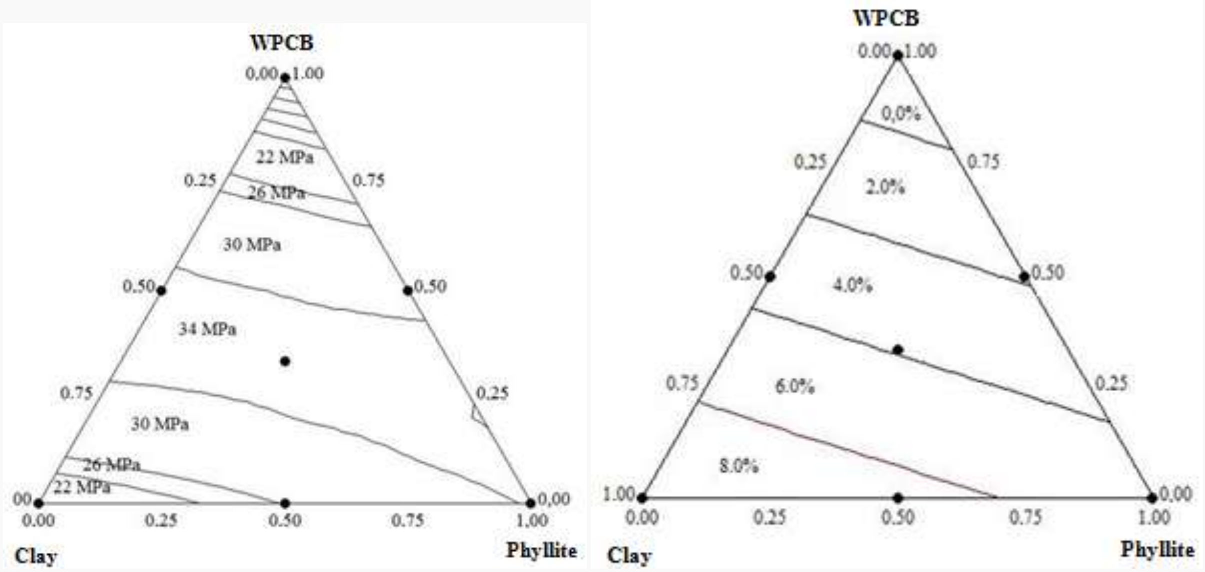

Figure 2: Response surface to FMoR (left) and WA (right).

Material applicability

The NBR 13818 (1997) classifies the ceramic tiles according to WA and FMoR. Table 1 described the types of ceramic tiles and the required values for these properties.

Thus, according to those characteristics the material can be classified as stoneware or semi-stoneware, since there are regions of the response surface, where the two requirements are met. It is also observed that even in regions where WA was obtained semi-porous ceramic, FMoR was above what is determined by the standard, showing the strengthening the residue provided the material.

Other studies(7,10) have claimed that incorporation of the residue in polymer composites increases the material strength, and the reinforcement is given by the power dissipation WPCB. It can be said that the WPCB increased the mechanical strength of the ceramic material, which can be confirmed by the analysis of the microstructure.

Microstructural analysis

Figure 3 shows SEM micrographs of fracture of samples 1, 7, 6 and 3, with residue content of 0, 14, 20 and 40% respectively. It is observed that the mixture did not achieve an efficient sintering, as evidenced by no existence of glassy phase. This can be attributed to the small fraction of the mass flux of material, since the phyllite used has low amount of fluxing component (≈10% of feldspar)[21].

Sample 7 shows better sinterability, but there are small pores, which are irregular and interconnected. In this case, a proper value of FMoR (35.00 ± 4.10 MPa) and WA (2.0 ± 0 09) was achieved. Sample 6 shows a similar behavior. On the other hand, sample 3, despite presenting a very low WA (0.05 ± 0.009%), a FMoR of only 8.56 ± 0.88 MPa was measured. This can be attributed to the high amount of waste, which contributes to form a glassy phase, which reduces both FMoR and WA.

To complement this analysis, Figure 4 shows the XRD patterns obtained for samples 7, 6 and 3 after polishing and acid treatment. It is seen the presence of quartz and mullite in all samples. The main theories explaining the mechanical properties of ceramic are related to the amount of mullite present in the material[21]: larger amounts of mullite generate higher mechanical strength.

The intensity of the peaks generated by samples 7 and 6, with 14 and 20% residue, respectively, shows the residue does not hinder the formation of mullite. In contrast, the peak intensity in sample 3, with 40% residue, is clearly reduced which may explain the mechanical behavior. It is also observed that the amount of quartz decreases as the residue content is increased, and presence of amorphous phase is higher, the higher is the amount of WPCB.

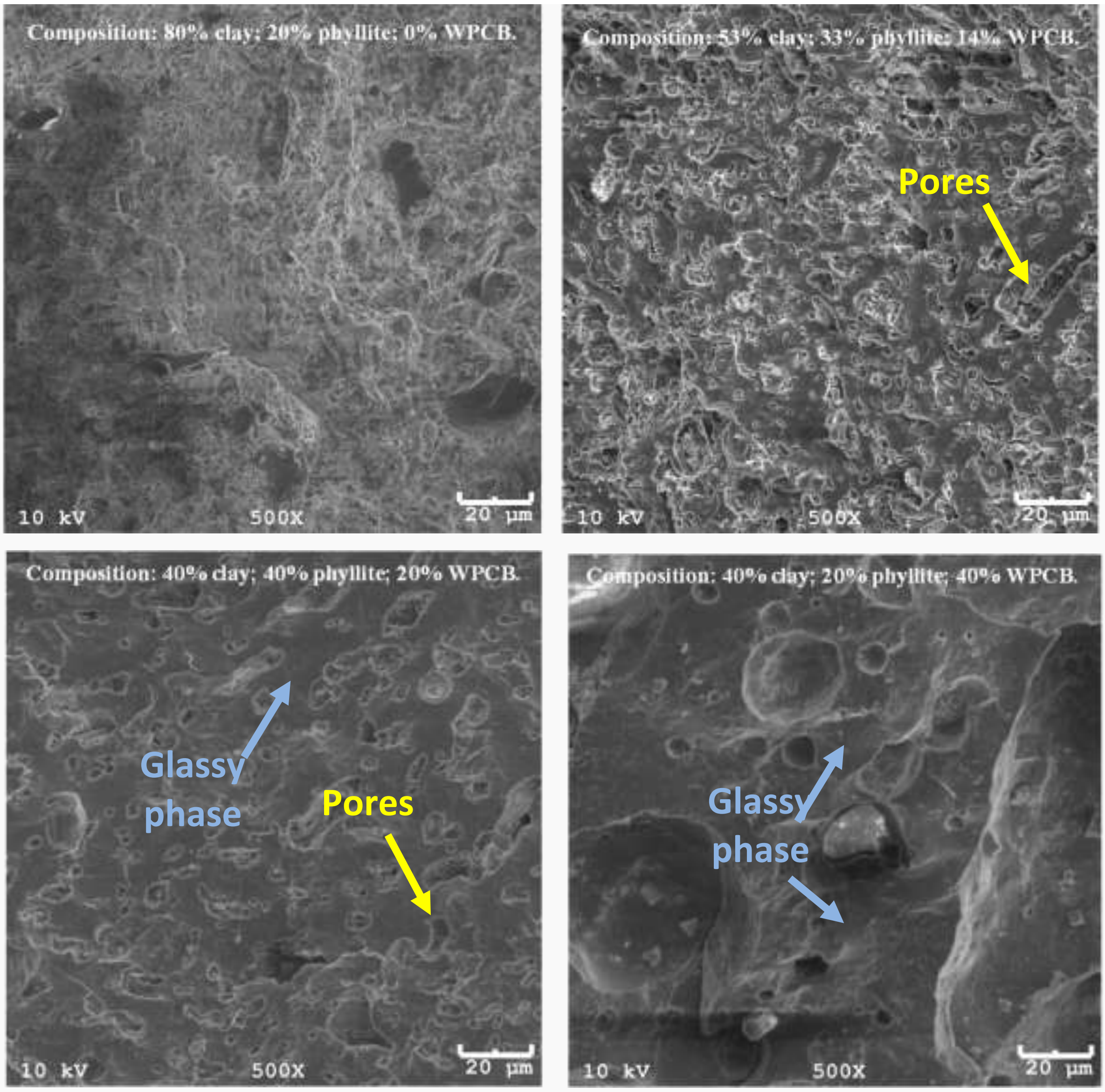

Figure 3: SEM micrographs of fractured samples containing (a) 0%; (b) 14%; (c) 20% e 40% WPCB.

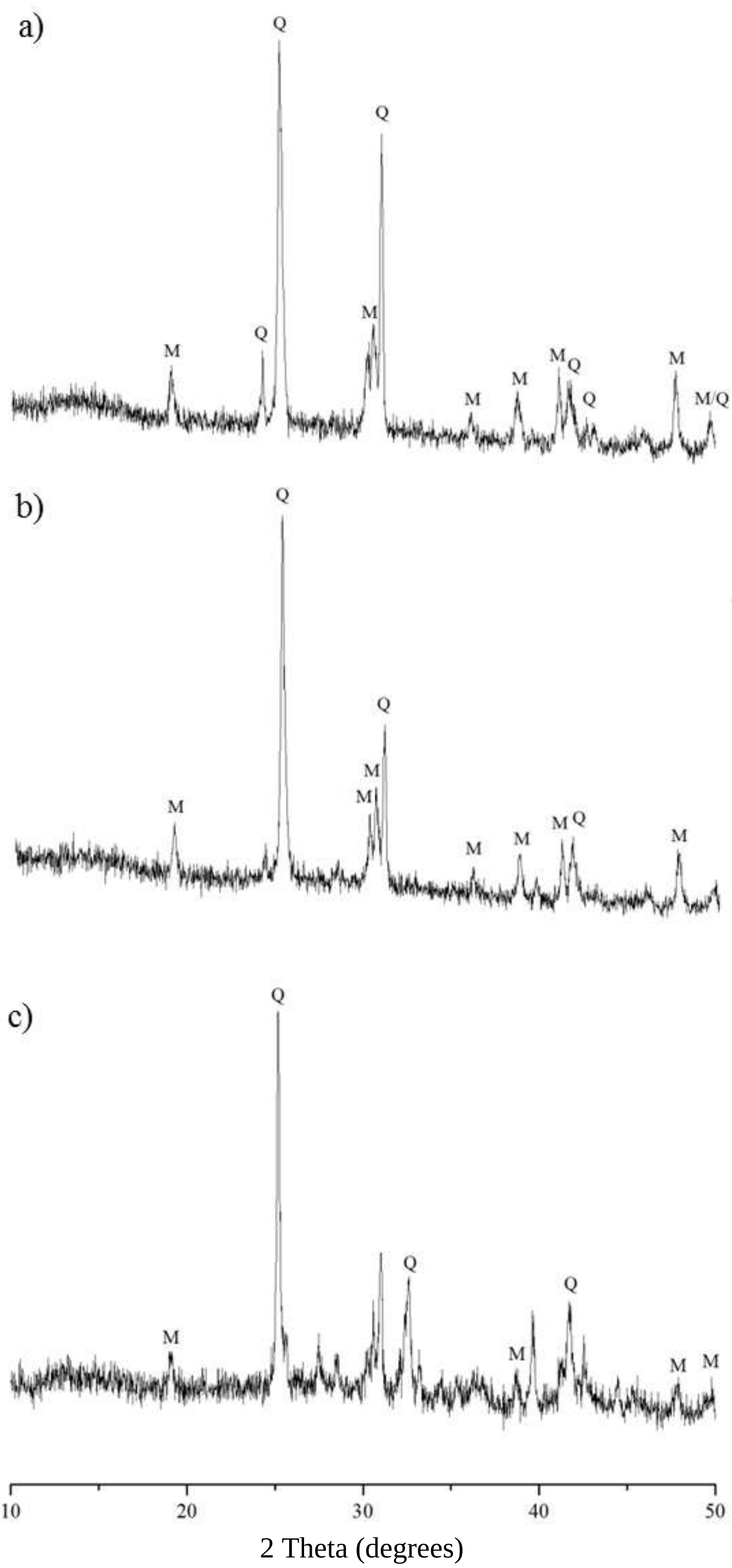

Figure 4: XRD patterns of sintered samples. (a) 7, (b) 6 (c) 3, with 14, 20 and 40% residue.

CONCLUSIONS

The samples with 14 and 20% WPCB showed FMoR higher than those observed for the samples without residue. This event is related to decrease in WA. Samples containing 40% WPCB were very weak due to formation of amorphous content in excess. The addition of WPCB also not hindered the development of mullite, ceramic phase of great interest, because it is related to the strength of sintered pieces.

Thus, the material properties FMoR and WA are improved, and the samples developed can be classified as stoneware or semi-stoneware according the standard NBR 13.818:1997.

Finally, it may be concluded that up to 7% residue can be added to the ceramic mass without significant decrease of the properties studied. In the case of FMoR, even better results were obtained with added waste.

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