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Review paper

Sintering characteristics of kaolin in the presence of phosphoric acid binder

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Abstract

The kaolin–phosphoric acid mixtures with various percentages of phosphoric acid (5 wt%; 10 wt% and 15 wt%) have been investigated at room temperature. During the maturation and the sintering processes, acid reacts with aluminium of kaolin to give a new phase of aluminophosphate. This new phase's appearance has been confirmed by the thermal analysis, infrared spectroscopy, X-ray diffraction and scanning electron microscopy measurements before and after the sintering processes at different temperatures (800 °C, 1100 °C and 1250 °C). The rupture strength of the body-shaped samples made with the kaolin–phosphoric acid mixtures is higher than that of those made with only kaolin. The porosity decreases with both the sintering temperature rise and the addition of phosphoric acid in the mixture. The addition of 10 wt% of phosphoric acid to the kaolin decreases its calcined temperature by 200 °C.

Keywords: A. Calcination; B. Porosity; C. Mechanical properties; C. Thermal properties; Chemically bonded ceramics; Energy savings

Contents

1. Introduction

The requirement for the sintering of green bodies of ceramics at high temperatures to obtain desired characteristics, makes the ceramic manufacturing industry a highly intensive-energy [1–4]. In this respect, the use of bonding materials reacting chemically with the matrix particles at low temperatures is attractive for relevant applications [5,6].

The literature indicates that phosphoric acid and certain phosphates offer good prospects as bonding agents [7–9]. Some phosphates [10–18] are widely used as bonding agent for the production of high strength refractories, refractory cements and motors [8,15].

Kaolin is a major raw material used for the fabrication of conventional ceramics. It is obtained from the alteration of granitoid rocks. It consists mostly of kaolinite and a small amount of impurities such as quartz, micas and other phyllosilicates.

Kaolin has the advantage to be easily accessible and not expensive [19–25]. Kaolinite firing induces a numerous complex structural and microstructural transformations leading

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to the formation of mullite and silica phase [26,27]. Mullite phase is characterized by some advantageous properties [28] such as good corrosion resistance, low-dilatation coefficient, good creep and thermal shock resistances, thermal stability and high strength. These advantages confer to this phase different applications [29–31].

The phosphate bonding of ceramic bodies involves reaction of the aluminium with the phosphatic content of the phosphate binders. This reaction leads to the formation of different forms of aluminium phosphate at a significantly lower temperature compared to conventional silicate bonding of ceramic manufacturing [15,32–34].

The objective of this paperwork is to study the impact of the phosphoric acid binder added at different percentages (5 wt%; 10 wt% and 15 wt%) to the kaolin. The structural transformations taking place during maturation at room temperature and sintering at different temperatures (800 °C, 1100 °C and 1250 °C) have been studied. In addition, this study aims to characterize the resulting bodies with thermal analysis, mechanical resistance, infrared spectroscopy, X-ray diffraction and scanning electron microscopy before and after the sintering process.

2. Materials and methods

2.1. Starting materials

The raw material powder of kaolin was supplied by BWW Minerals, with the chemical compositions listed in Table 1. The kaolin was ground to pass through a 60 μm diameter sieve before use.

Orthophosphoric acid (H_3PO_4, 85%; 1.75 g cm^{-3}) supplied from FLUKA was used as binder.

2.2. Preparation of powder and ceramic specimens

The effects of phosphate treatment of kaolin in the final proprieties of crude and fired kaolin products are investigated in relation to the amount of phosphoric acid and the sintering temperature. For this purpose, some kaolin mixes are prepared by using different experimental conditions. Solutions of orthophosphoric acid are prepared using deionised distilled water, mixed in predetermined proportions to adjust the weight % of the bulk solution to the desired levels. The clay is treated with a fixed volume of phosphate solution. This volume, which imparts good homogenization to a kaolin mix, is predetermined from blank trials (100 g of air-dried kaolin required 100 mL of orthophosphoric acid solution). The weight percentage of the phosphoric acid in kaolin mixes is adjusted within a range between 5 and 15 wt% (5, 10 and 15 wt% PA). A dry and disaggregated weighed sample of kaolin is milled with a required volume of orthophosphoric solution and treated by ultrasound for 15 min. The kaolin mix is then covered and matured at room temperature for 48 h to allow the additive dispersion and to initiate reactions. The kaolin mixes are air-dried and then oven dried for 24 h at 110 °C. Powder mixtures are moulded in a metal mould and uniaxially pressed at 150 MPa to form cylindrical compacts with a diameter of 20 mm and a thickness of about 6 mm. The green compacts are then heated in a laboratory electric muffle furnace in air at temperatures from 800 °C to 1250 °C. The heating and cooling rates are 10 °C and 20 °C, respectively, with a soaking period of 2 h at the peak temperature of all firing.

Table 1
Chemical composition (percentage weight: wt%) of kaolin.

Element	SiO_2	Fe_2O_3	Al_2O_3	MgO	K_2O	SO_3	CaO
wt%	52.41	3.48	29.83	0.81	0.73	0.07	0.36

2.3. Experimental methods

Standard methods of wet chemical analysis were used for the determination of silica [35]. The content of the other elements was determined by using atomic absorption spectrometry (Perkin-Elmer 5000).

The X-ray diffraction pattern of crude and sintered samples was obtained by a Seifert XRD 3000 TT diffractometer (monochromatized Cu Kα radiation). The crystalline phases were identified from the powder diffraction files (PDF) of the International Center for Diffraction Data (ICDD).

Thermal analyses (DTA and TG) were carried out using about 30 mg of powder (DTA-TG, Seteram Model). The heating rate was of 10 °C min^{-1}.

Linear shrinkage was determined by dilatometry (Setearam TMA 92 dilatometer). The heating and cooling rates were 10 and 20 °C min^{-1}, respectively.

The IR spectra of the samples were recorded in the wave number range of 400–4000 cm^{-1} using a Perkin-Elmer 783 infra red spectrophotometer in KBr.

The microstructure of the sintered compacts was investigated by a scanning electron microscope (SEM Philips XL 30) on fractured sample surfaces.

The porosity of the as-sintered kaolin ceramics is determined by mercury porosimetry (Micrometric). Four specimens are selected to determine porosity with an error of less than 1% of the measured porosity value.

Mechanical properties of the compacts were measured by Brazilian test. The optimum rupture strengths σ_r was offered by the following equation [36–38]:

$$\sigma_r = \frac{2P}{\pi De}$$

where σ_r is the tensile strength, D and e are the diameter and the thickness of the sample and P is the maximum applied load.

The experiments were realized by using a ''LLOYD EZ50'' device on cylindrical samples of approximately 6 mm in thickness and 20 mm in diameter. At least six specimens were tested for each test condition. An average of the values was then calculated.

3. Results and discussion

3.1. Characterization of the crude powder

It is important to note that the samples are annealed at 110 °C for 24 h before analysis.

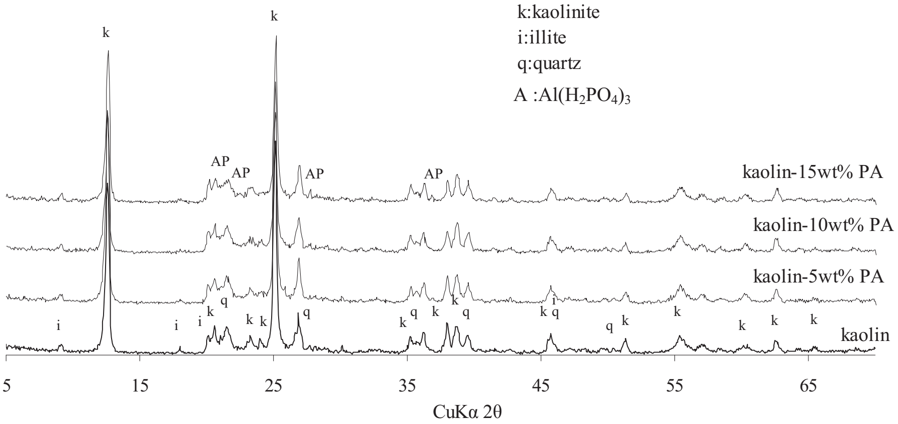

Fig. 1. X-ray diffraction spectra (Cu Kα) of kaolin and kaolin mixes (kaolin–5 wt% PA, kaolin–10 wt% PA and kaolin–15 wt% PA).

The XRD pattern of the original kaolin is given in Fig. 1. This spectrum shows that the kaolin contains kaolinite (k) as major clay minerals and quartz (q) as non-clay mineral [39]. Kaolin includes illite (i) in trace amounts.

The XRD patterns obtained from kaolin mixed with phosphoric acid (Fig. 1) exhibits some changes. According to Fig. 1 some characteristic XRD peaks for the kaolinite (k) and illite (i) disappear after 48 h as maturing time. However, four additional reflections appear, especially, for mixture with 15 wt% PA. Those reflections are attributed to aluminium phosphate hydrate $Al(H_2PO_4)_3$ [40].

Fig. 2 illustrates the changes in the SiO (at around 426, 466, 696, 1004, and 1110 cm^{-1}), SiOAl (at around 534, 754, and 786 cm^{-1}), AlOH (at around 910 and 928 cm^{-1}) and OH (at around 3692, 3668, 3650, and 3618 cm^{-1}) infrared vibration bands after treatment of kaolin with phosphoric acid [41]. The mixing with acid induces broadening and weakness in terms of intensity of the SiO, SiOAl and AlOH bands. This fact indicates the distortion of tetrahedral and octahedral layers [41,42]. This is further evidence that the kaolinite phase is a less ordered after the acid treatment. The most visible changes are noted in the range of 1250–1000 cm^{-1}. This change is also due to the existence of a new vibration band of PO at around 1150 cm^{-1} [43].

Fig. 3 illustrates the DTA curves of kaolin, kaolin–5 wt% PA, kaolin–10 wt% PA and kaolin–15 wt% PA. Indeed, the DTA thermogram of raw kaolin shows two endothermic peaks at 150 °C and 520 °C and an exothermic peak at 975 °C. The first endothermic peak is relative to the deshydratation of the clay. The TG curve of raw kaolin (Fig. 4) shows a great weight loss of 12.5% correlating with, the dehydroxylation of the kaolin at 520 °C. The exothermic peak, at 975 °C corresponds to the metakaolin–mullite transformation. The DTA thermograms of the mixes kaolin–PA show the appearance of a new peak around 630 °C. This peak may be due to the decomposition of the hydrated alumino-phosphate phase formed from a reaction between kaolin and phosphoric acid [5].

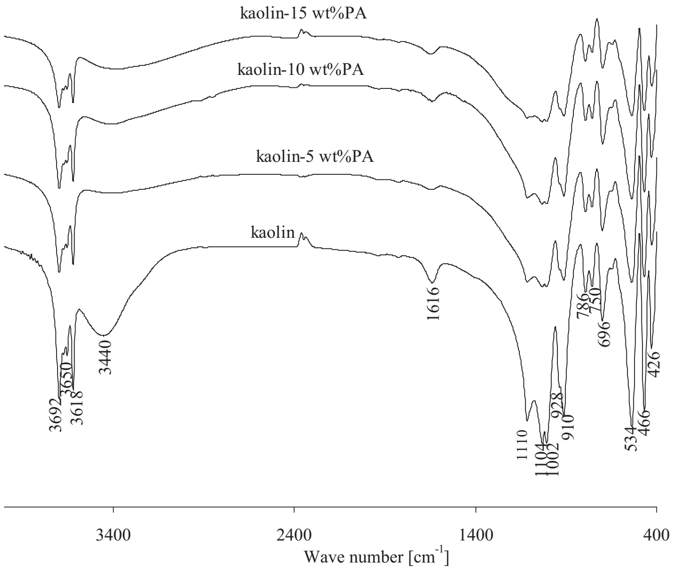

Fig. 2. IR spectra of kaolin and kaolin mixes (kaolin–5 wt% PA, kaolin–10 wt% PA and kaolin–15 wt% PA).

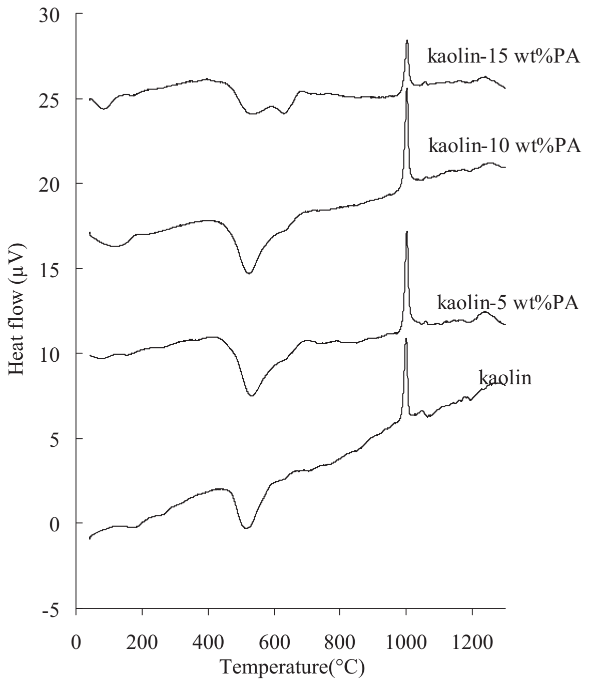

Fig. 3. DTA curves of kaolin and kaolin mixes (kaolin–5 wt% PA, kaolin–10 wt% PA and kaolin–15 wt% PA).

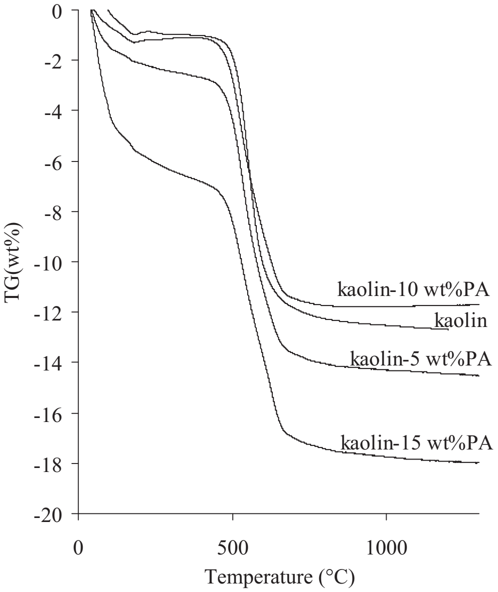

Fig. 4. TG curves of kaolin and kaolin mixes (kaolin–5 wt% PA, kaolin–10 wt% PA and kaolin–15 wt% PA).

Observing the TG curves in Fig. 4, we notice two weight losses:

- The first weight loss is related to dehydration. The dependency of this weight loss with the amount of phosphoric acid can be interpreted in terms of the relative abundance of OH groups. In the case of kaolin–PA blends, these hydroxyl groups are generated from both original hydratation and those released during the reaction of the acid with aluminium. The maximum weight loss, achieved in the case of kaolin–PA 15 wt%, was attributed to the intensity of the collapse of kaolinite lattice. The latest increases with the amount of PA and the heating temperature.
- The second weight loss is caused by the dehydroxylation of the kaolinite. We noticed a slight decrease in weight loss in case of mixtures comparing to kaolin. This leads to conclude that the reaction of phosphoric acid with aluminium reduces the amount of metakaolin.

Fig. 5 shows the dilatometric measurements of the different powders used in this study (raw kaolin and kaolin–PA mixes). The sintering process begins at about 1143 °C, 1129 °C, 1125 °C and 1187 °C for raw kaolin, kaolin–5 wt% PA, kaolin–10 wt% PA and kaolin–15 wt% PA, respectively. The addition of PA, until 10 wt%, decreases the calcined temperature of the raw kaolin. Add a larger amount of phosphoric acid (15 wt%)

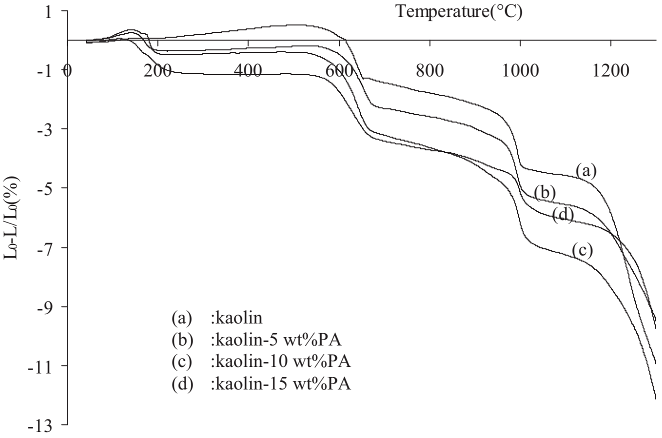

Fig. 5. Linear shrinkage versus temperature of kaolin and kaolin mixes (kaolin–5 wt% PA, kaolin–10 wt% PA and kaolin–15 wt% PA).

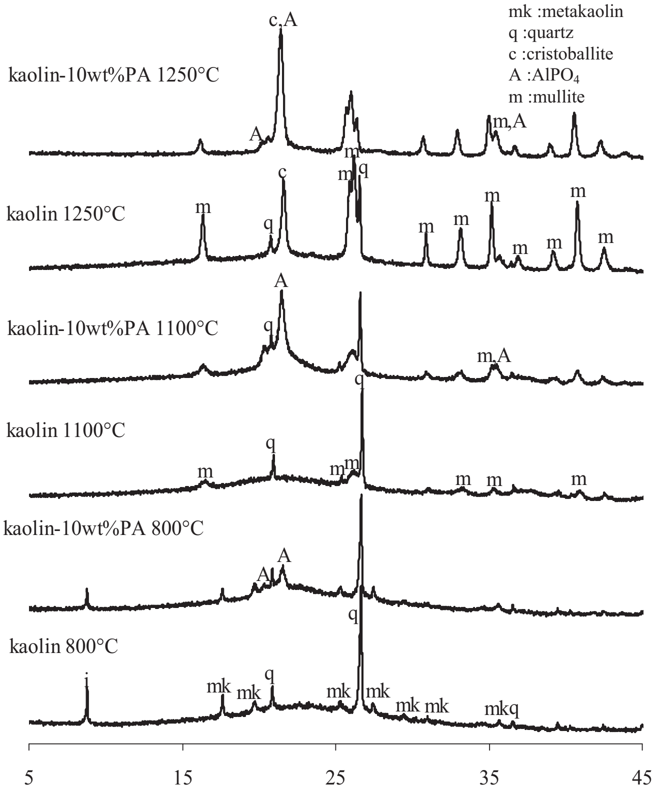

Fig. 6. X-ray diffraction spectra (Cu Kα) of kaolin and kaolin–10 wt% PA mixes sintered at different temperatures (800, 1100 and 1250 °C).

Table 2
The porosity and the mechanical strength of different kaolin-compounds sintered at various temperatures with different amounts of phosphoric acid.

	Kaolin			Kaolin–5 wt% PA			Kaolin–10 wt% PA			Kaolin–15 wt% PA		
	800 °C	1100 °C	1250 °C	800 °C	1100 °C	1250 °C	800 °C	1100 °C	1250 °C	800 °C	1100 °C	1250 °C
Porosity (%)	15.95	13.8	4.09	15.13	9.83	3.5	13.69	11.3	5.3	10.55	10.1	7.03
Mechanical strength[a] (MPa)	5.90	7.50	17.50	10.09	15.20	24.96	13.92	17.50	26.41	12.90	15.50	19.23

[a] The standard deviations for mechanical strength: 10%.

had an adverse effect on the behaviour of kaolin during sintering. It seems that the addition of the phosphoric acid modifies the slope of sintering and consequently its speed. The reduction of the sintering speed, in the case of the mixtures (kaolin–PA), minimizes defects after sintering process.

3.2. Characterization of samples after the sintering process

3.2.1. Effect of PA additive on mechanical and porosity properties of kaolin

Table 2 summarizes the porosity and mechanical strength of different kaolin-compounds sintered at various temperatures (800 °C, 1100 °C and 1250 °C) with different amounts of phosphoric acid (5 wt%, 10 wt% and 15 wt%). The rupture strength increases with sintering temperature. The maximum mechanical resistance reached 26.41 MPa at 1250 °C with the 10 wt% addition of phosphoric acid (Table 2). This study shows that small additions of phosphoric acid can significantly enhance the sinterability and strength of kaolin (with 5 wt% PA the strength pass, at 1250 °C, from 17.50 to 24.96 MPa).

These results are in agreement with those of porosity. The porosity decreases with the heating temperature and the addition of PA. Thus, in this study, we showed that the presence of the phosphoric acid until 10 wt% in the kaolin matrix improves the mechanical properties of the sintered kaolin. Moreover, the addition of 10 wt% of phosphoric acid to the kaolin reduces by 200 °C the heating temperature of the mixtures while maintaining mechanical properties similar or even better than those of the kaolin.

3.2.2. Characterization of sintered kaolin–10% mix

After sintering, two techniques characterized the samples: X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The XRD patterns of the powder compacts heat-treated at various temperatures (800, 1100 and 1250 °C) for 2 h are

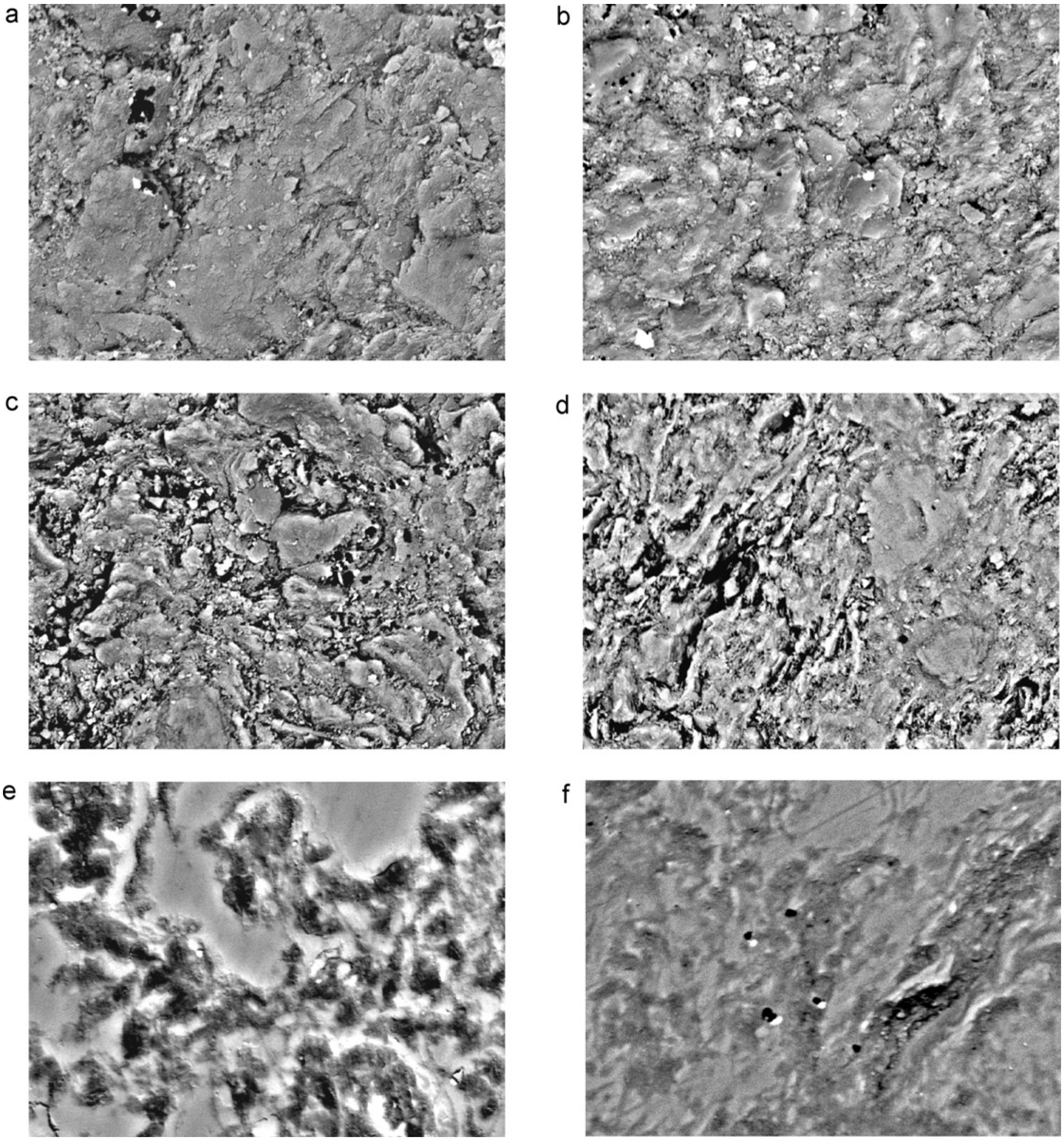

Fig. 7. SEM micrography of kaolin and kaolin–10 wt% PA mixes sintered at different temperatures ((a and b) 800 °C, (c and d) 1100 °C and (e and f) 1250 °C).

shown in Fig. 6. From the patterns, the kaolin powder compacts underwent a series of phase transformations as the temperature was raised from room temperature to 1250 °C. We note at 800 °C that the quartz and metakaolin are the major phases (Fig. 6). Mullite phase first appears at a temperature around 1100 °C, its amount increases with the increase of the temperature. The addition of phosphoric acid to kaolin leads at 800 °C the appearance of small quantity of a new phase ($AlPO_4$). The quantity of $AlPO_4$ grows with the increase in temperature as indicated by the number of characteristic peak of this phase on the XRD patterns.

The SEM examination of the fracture surface of the kaolin sintered at various temperatures (800 °C, 1100 °C and 1250 °C) is reported in Fig. 7. The fracture surfaces clearly reveal a distinct difference in the sample's microstructure, shows that at 800 °C; the kaolin–10 wt% PA sintered presents an intergranular porosity lower than the kaolin samples. The porosity of kaolin–10 wt% PA sintered subsequently is eliminated at 1250 °C in contrast to the kaolin, we observe large holes at this temperature. This is also supported by the shrinkage and strength values of sample kaolin–10 wt% PA that is higher than that of the kaolin when the sintering temperature is below 1250 °C. So, the formation of the new phase of $AlPO_4$ and the glassy phase increase the densification and mechanical properties of this sample against the kaolin.

4. Conclusions

The effect of PA additive in raw kaolin was observed in XRD, IR and thermal analysis. The PA reacts with aluminium from kaolin to provide new compounds which are $Al(H_2PO_4)_3$ at room temperature and $AlPO_4$ when heated to temperatures above 800 °C. Also, the influence of PA addition on the kaolin was detected in the mechanical properties of the sintered bodies. The mechanical properties of the kaolin and the kaolin–PA mixes were measured by the Brazilian test. The evolution of the rupture strength of samples was investigated as function of sintering temperature. The mechanical properties of sintered kaolin were increased until 10 wt% PA. However, with 10 wt% PA, the mechanical resistance reaches its maximum value at 1250 °C (26.41 MPa). Comparing to the raw material (kaolin), the addition of phosphoric acid until 10 wt% into the mixtures save 200 °C of calcined temperature and keep or even improve the mechanical proprieties of the kaolin–PA blends.

Above 10 wt% PA, the mechanical properties are hindered. The increase of the mechanical properties of kaolin after addition of the PA is due to the appearance, during the maturing and the sintering processes, of aluminophosphate compounds.

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