



Effect of Ball Milling Time on the Physical, Thermal and Fracture Behaviour of $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ Precursors

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Received: 9 April 2019 / Accepted: 8 July 2019
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Abstract

In this study, an evaluation has been made into the influence of milling time on the thermo-physical and fracture properties of a $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system. The powdery and compacted formulation of the raw materials was studied using scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), Brunauer-Emmett-Teller (BET), thermogravimetric analysis (TGA), particle size distribution (PSD), Fourier Transform Infrared (FTIR), and acoustic emission technique (AE). The milling mechanism comprised of essentially three stages of milling time viz.; 120, 240, and 360 min respectively, with no milling (0 min) serving as the control batch. During the first stage of milling (120 min), it was observed that the greatest deformation occurred for the powdery formulation with increasing surface area, control batch inclusive, from 26.4 to $41.1 \text{ m}^2 \text{ g}^{-1}$. It was also noticed that the density of the samples increased with progressive ball milling time. The mean crystallite sizes of un-milled and milled powders were calculated as 36.61, 48.82, 34.27 and $52.13 \mu\text{m}$ for control batch and powders milled at 120, 240, and 360 min, and denoted as MT0, MT120, MT240, and MT360, respectively. The mean crystallite sizes further reduced with increasing milling time up to 240 min and increased with milling time up to 360 min. These results were in line with the SEM findings. The acoustic emission (AE) intensity increased reaching a maximum at MT240, and a noticeable decline in the case of MT360 was observed. This indicated a gradual crack growth behavior because of the highly stressed powders used for the compacts.

Keywords Milling · Crack growth · Acoustic emission · Cordierite · Particle size

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1 Introduction

It has been widely reported that cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) has huge relevance as a ceramic material by reason of its low fractional change in size due to changes in temperature, improved resistance to shock when subjected to thermal treatment among other interesting properties. This has made it widely used in applications such as, catalytic converters, diesel particulate filters etc. [1]. The properties of cordierite hugely depend on the batch formulation and most inherently, the nature of the precursors which includes the presence of some impurities as well as the manner of preparation. A whole lot of formulations have been successfully used to prepare cordierite and the very popular choice amongst researchers and the ceramic industry is a mixture of kaolin, talc and alumina and in some cases silica is added [2, 3].

Over the years, several preparation methods for cordierite have been developed which includes solid state

sintering (mechanical treatment) and chemical methods [4–6]. Assessing these methods, the solid state sintering method has been largely adopted due to simplicity and low cost. Nonetheless, this method is largely successful when subjected to very high temperatures which inadvertently results in the appearance of cracks and reduction in mechanical properties. To prepare the cordierite through milling, it can be through the inclusion of sintering temperature reduction additives and the grinding or milling of precursors. The combination of these two methods has given room to the significant reduction in the temperature for cordierite preparation by approximately 300 °C [2].

The temperature of heating is greatly influenced by the sizes of particles. It has been reported that particles that are finer in texture can improve heating conditions [7]. The most cost effective way of reducing particle sizes is through milling. A whole lot of researchers have turned their attention towards milling or mechanical treatment of clay based materials [8–15]. The differences noticed in the crystal sizes of the materials after milling depends on parameters which include the milling action and time. Yang et al. [16] in their study reported that if illite is milled, it enhances the sizes of its pores, and consequently reduces the surface area and the volume of pores in its totality. Furthermore, the findings claim that the illite crystals peaked in terms of size after 2 h of milling. Csaki et al. [17] studied the DC electrical conductivity for milled illitic samples up to a maximum temperature of 1100 °C. It was observed that the conductivity was enhanced with the increased duration of milling. The main contention of, arguably, most of the investigations have been on the change in the structure, topography and mechanical properties caused by milling. Specifically, variations in mechanical properties are influenced by fracture during the heat treatment dwelling time. Thus, the study of crack growth is quite essential in understanding the synergistic effects of homogenous microstructures and mechanical properties of materials. This kind of investigation was performed by Knapek et al. [18] to understand the behaviour of illitic clay subjected to heating to various temperatures using the AE technique and viscoelastic analysis. They reported that cracks were noticed in the process of cooling when the temperature rose higher than 900 °C.

Here, we report the preparation of a mixture of kaolin, gibbsite, talc, and silica according to sub-stoichiometric composition of cordierite. The evaluation of the influence of milling on the physical and chemical properties of precursor powders was investigated. Since the milling and cracks during mechanical and thermal treatment have an influence on mechanical strength, the crack response during cooling, which is important for the ceramic industry, was also evaluated.

2 Materials and Methods

2.1 Materials

The starting materials used in this study were: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (kaolin), $\text{Al}_2\text{O}_3(\text{OH})$ (gibbsite), $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (talc), and SiO_2 (silicon dioxide). All of these starting materials were analytical grade reagents except kaolin which was mined from a local deposit in Kankara, Katsina State, Nigeria and beneficiated. The chemical compositions of the raw materials are shown in Table 2.

2.2 Method of Sample Preparation

The compounds were mixed in relative sub-stoichiometric weight contents of 21.74, 39.24, 28.31, and 9.99 wt% of kaolin, talc, gibbsite, and silica respectively. The as-prepared powders were milled using a ball mill (NETSCH PM100) with porcelain jar and alumina balls for milling times up to a maximum of 360 min. Samples made from the as-prepared powders are labelled MT0, MT120, MT240, and MT360 representing un-milled, milled for 120, 240, and 360 min, respectively (see Table 1). The milling of 100 g of powder was conducted in a porcelain jar at a speed of 400 rpm. Samples for acoustic emission measurements (see sub-section 2.37) were prepared using rectangular wooden moulds with dimensions of 20 × 10 × 10 mm and holes of Ø 3 mm were drilled in the green compacts to enable the insertion of a wave guide during acoustic emission testing.

2.3 Materials Characterization

2.3.1 X-Ray Fluorescence (XRF)

The chemical compositions of the samples (raw materials, milled, and un-milled powders) were determined using a Model-PW2400 Phillips X-ray fluorescence machine. For trace elemental analyses, the samples were mixed with a PVA binder and pressed into a pellet.

Table 1 Sample code details for mechanical treatment of samples

Sample code	Raw materials	Milling time (min)
MT0	Kaolin, Talc, Silica & Gibbsite	0
MT120	Kaolin, Talc, Silica & Gibbsite	120
MT240	Kaolin, Talc, Silica & Gibbsite	240
MT360	Kaolin, Talc, Silica & Gibbsite	360

2.3.2 Powder X-Ray Diffraction (pXRD) and Crystallinity Index

Powder x-ray diffraction (pXRD) patterns of the samples were collected on an Empyrean diffractometer (PANalytical BV, Netherlands) with theta/theta geometry, operating a Cu K α radiation tube ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 45 mA. The diffraction patterns were matched against the ICSD's PDF database and qualitative phase analysis was performed using the X'Pert High score plus software, PAN analytical, Netherlands. The estimated average crystallite sizes of the milled and unmilled samples were also calculated using the Scherrer broadening method [19].

2.3.3 Scanning Electron Microscopy

The observation of the surface morphology for the samples were carried out on the ultra-high vacuum and high resolution FEI XI-30 scanning electron microscope (SEM) equipped with an EVEX EDS and operated at 15 kV.

2.3.4 Thermogravimetry

The thermal behavior of the samples were determined by simultaneous thermogravimetric analysis (TGA) and derivative of thermogravimetric (TG-DTA) using a NETZSCH, STA 449 C Jupiter TG/DSC instrument in the temperature range between room temperature (RT) and 1200 °C under the air flow of 20 ml min⁻¹.

2.3.5 Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FT-IR) spectroscopy data for the samples were collected on a PerkinElmer Spectrum Two FT-IR spectrometer equipped with UATR sampling accessory in the 4000–500 cm⁻¹ range with a resolution of 2 cm⁻¹.

2.3.6 Particle Size Distribution and Surface Area Analyses

Particle size distribution of raw materials, milled, and unmilled powders was investigated using a laser diffraction particle size analyzer (PSA), covering the particle size range of 0.02–2000 μm (Mastersizer S. Malvern, UK). The mean size distribution was obtained as an average of 3 measurements. In addition, the average particle size of the milled and un-milled samples (assuming that the particle is spherical and non-porous) was obtained using Brunauer-Emmett-Teller (BET) from the relation (Eq. 1):

$$\text{SSA (BET)} = 6/\rho D \quad (1)$$

where SSA is the specific surface area in [m²/g] measured by BET, ρ is density of particle, and D is the particle diameter. Samples were analyzed using the

Micrometrics TriStar 3000 gas adsorption instrument. The surface area of samples was measured by nitrogen adsorption at -196.15 °C [20]. Prior to analyses, the samples were degassed in vacuum at 105 °C for 12 h.

2.3.7 Acoustic Emission Tests

The DAKEL-XEDO-3 acoustic emission system was used to investigate the modes of crack propagation in the ceramic bodies (using the milled and un-milled powders) during the cooling stage of firing. An alumina rod ($\varnothing$ 3 mm) was inserted into the sample and served as a waveguide. Afterwards, a piezoelectric sensor ($\varnothing$ 3 mm) was glued to the other end of the rod. The heat treatment was conducted at a heating rate of 10 °C/min up to 1200 °C with a soaking time of 4 h and then the furnace was cooled at the rate of 5 °C/min in air atmosphere. Figure 1 provides a summary of the material preparation and characterization techniques.

3 Results and Discussion

3.1 Chemical Compositions of Raw Materials

The major mineral phases as observed after XRF analysis as shown in Table 2 in talc are MgO and silica; other oxides are present in small amounts. Kaolin contains silica and alumina as significant phases whereas other oxides are present in trace amounts. The chemical analysis of the gibbsite shows 92.040% of Al₂O₃, 6.396% of SiO₂ and 0.016% of Fe₂O₃ content. The mixed precursors reveal relative amounts of all mixed raw materials.

3.2 XRD Analysis of Raw Materials

Structurally, gibbsite crystals were revealed as monoclinic gibbsite (JCPDS 74–1775) (Fig. 2a). A distinct diffraction peak at the 2θ of 18.3 was assigned to (002) diffraction. The powder diffraction reflection (Fig. 2b) is characteristic of pure talc. In Fig. 2c, the reflections of kaolin within the 2θ range of 5–50° exhibits two sharp reflections at $2\theta = 12^\circ$ and 25° . These peaks correspond to the (001) and (002) reflections typical of kaolinite [21]. The distinct reflections of kaolinite (Fig. 2c) were at $2\theta = 12.36^\circ, 19.94^\circ, 24.90^\circ, 35.98^\circ, 38.46^\circ, 45.66^\circ, 55.12^\circ, \text{ and } 62.34^\circ$ and buttressed by reports elsewhere [15, 22–27]. The reflection having a wide span between 20°–28° indicates a non-crystalline structure which is characteristic of SiO₂ as revealed in (Fig. 2d).

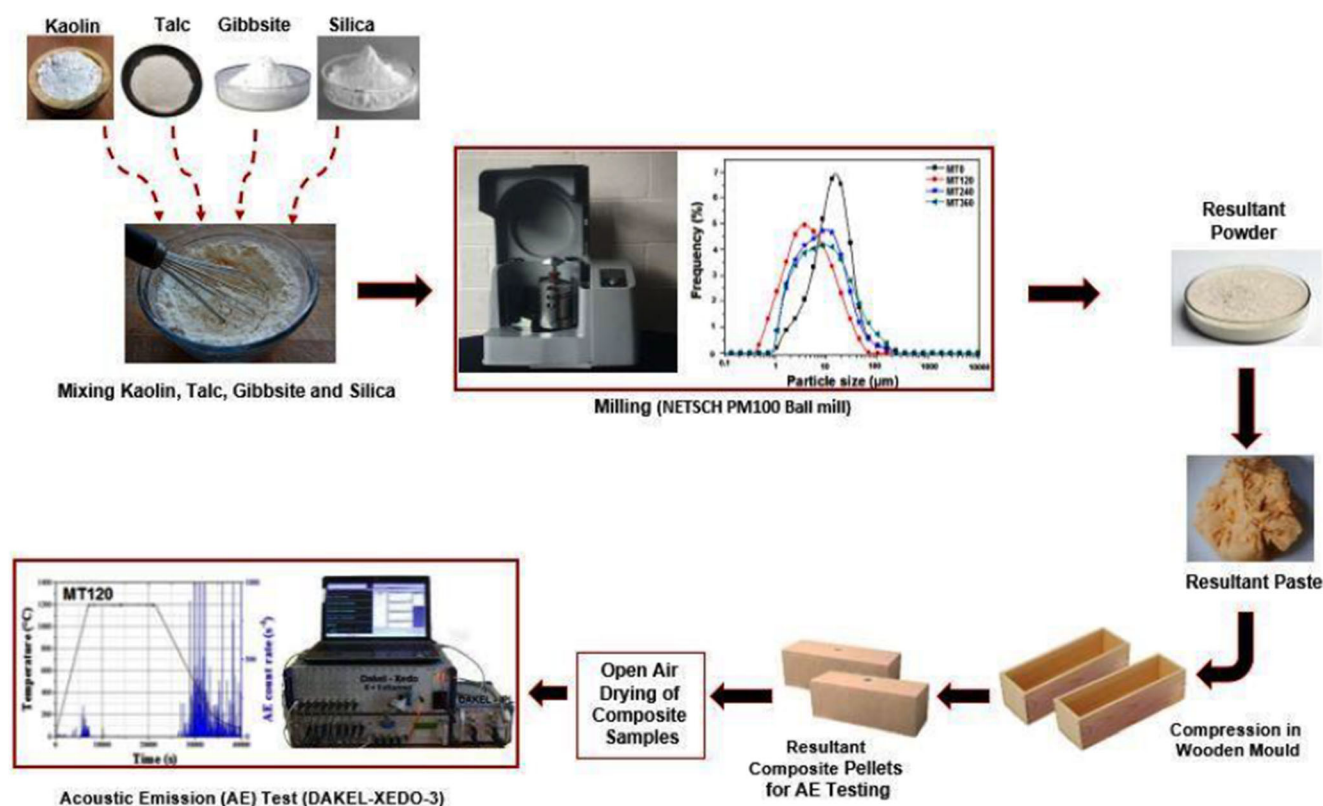


Fig. 1 Schematic of material preparation and characterization techniques

3.3 FT-IR Analysis of Raw Materials

Grauby et al. [28], describes the vibrations of talc as follows (Fig. 3): 1) Si-O stretching vibrations at 687

and 1040 cm^{-1} , respectively, 2) Si-O-Si stretching vibrations at 1014 cm^{-1} , and 3) δOH for OH vibrations at 669 cm^{-1} (other bands were not captured because ATR was used for IR sampling). The IR of the kaolin (Fig. 3) shows different absorption peaks at 750, 795, 800, 912, 1100, 1634, 3443, 3650 3443, and 3650 cm^{-1} . The appearance of the absorption peaks at 750, 795, 912, and 1634 cm^{-1} specified the clay materials, while the peak at 1634 cm^{-1} could be ascribed to bending vibration mode of the retained water on the surface of the silica and the peaks at 750, 795, and 912 cm^{-1} can be assigned to the Al-Al-OH, Al-Mg-OH and Si-O-Al vibration of the clay structural orientation [29]. In addition, reflections at 795 and 1019 cm^{-1} correspond to O-H bending and Al-O vibrations of gibbsite, respectively.

3.4 Morphological Study of Raw Materials

As shown in Fig. 4a, kaolin observations revealed a well-crystallized kaolinite. The flaky shaped crystals exhibit orderly layered arrangement. The microstructure of talc samples as shown in Fig. 4b, indicates that the talc particles are of platelets form with particle sizes in the micrometer region. The size of talc in the SEM image is consistent with the results of particle size distribution (see section PSD of raw materials). Figure 4c shows gibbsite particles that have a hexagonal and/or pseudo-

Table 2 Chemical composition of raw materials

Concentration (Wt%)					
Element	Talc	Gibbsite	Kaolin	Silica	Mixed Precursors
Na ₂ O	0.156	0.507	0.610	0.528	0.274
MgO	42.329	0.774	0.47	0.113	19.180
Al ₂ O ₃	1.569	92.024	28.20	1.613	27.073
SiO ₂	52.525	6.396	51.50	96.523	51.301
P ₂ O ₅	0.000	0.000	0.000	0.091	0.000
SO ₃	0.277	0.195	0.000	0.727	0.282
Cl	0.140	0.005	0.000	0.285	0.074
K ₂ O	0.062	0.018	1.80	0.023	0.503
CaO	2.644	0.028	1.21	0.043	1.015
TiO ₂	0.002	0.010	0.12	0.010	0.032
Cr ₂ O ₃	0.000	0.000	0.00	0.000	0.000
Mn ₂ O ₃	0.019	0.002	0.000	0.000	0.022
Fe ₂ O ₃	0.278	0.016	0.91	0.039	0.219
ZnO	0.000	0.024	0.000	0.004	0.022
SrO	0.000	0.001	0.000	0.000	0.002

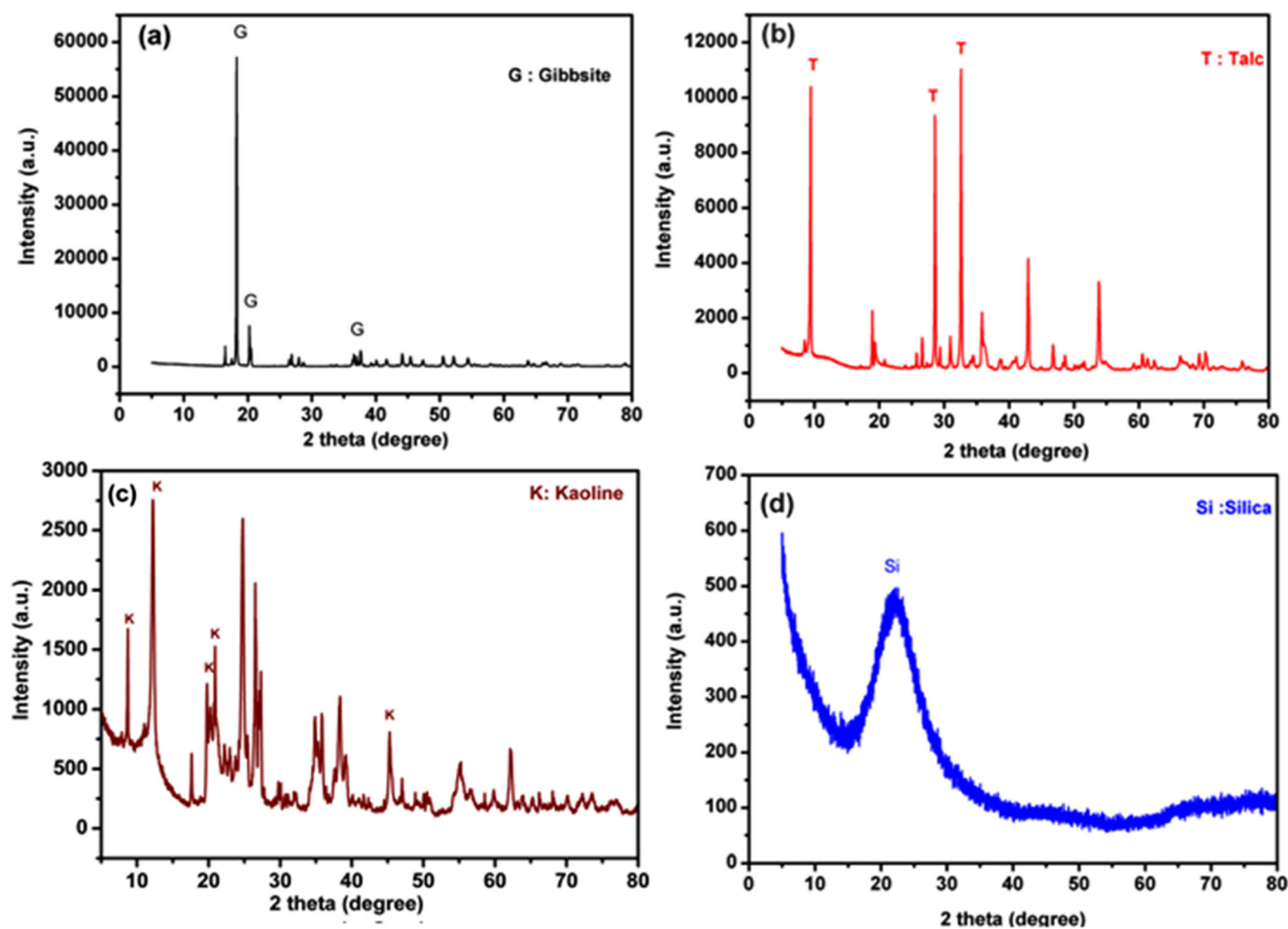


Fig. 2 X-ray diffraction pattern of patterns of raw materials (a) Gibbsite; (b) Talc (c) Kaolin (d) Silica

hexagonal shape with some irregular contours [30]. The morphology of SiO_2 as shown in Fig. 4d reveals

spherical images which are almost uniformly distributed with considerable amount of porosity.

Fig. 3 Fourier Transform Infrared (FT-IR) spectroscopy of Gibbsite, Kaolin, and Talc

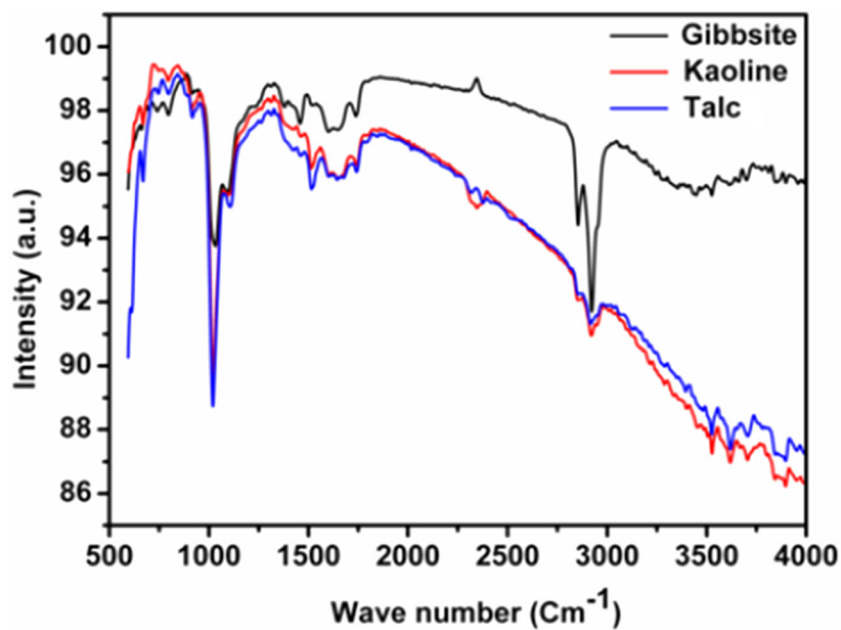
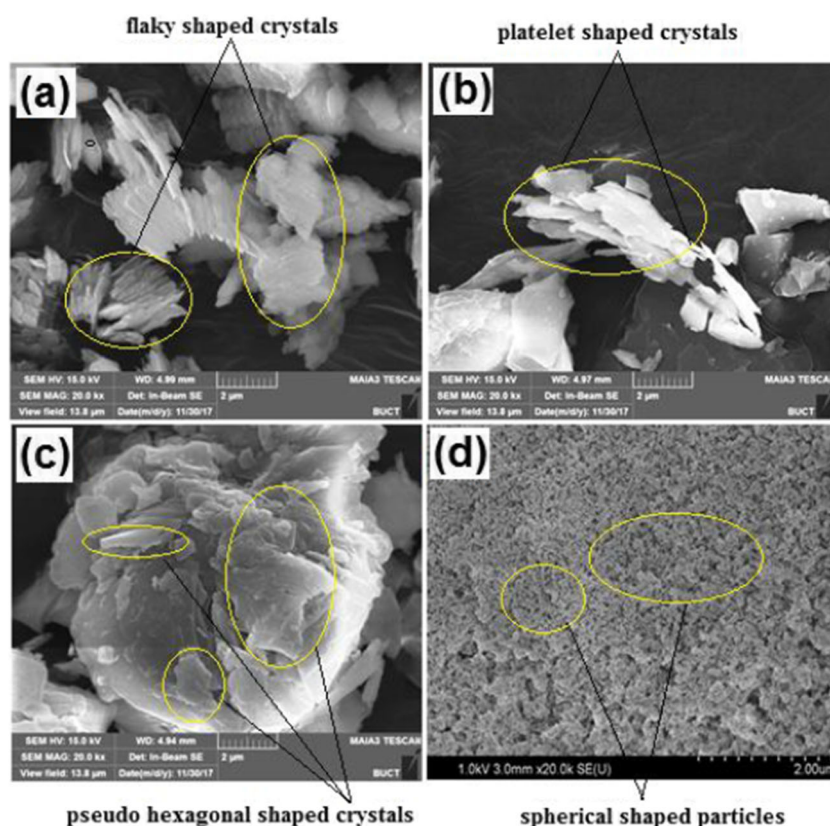


Fig. 4 SEM images of the raw material (a) Kaolin; (b) Talc; (c) Gibbsite (d) Silica



3.5 Particle Size Distribution of Raw Materials

The particle size analysis shown in Fig. 5 reveals that d_{50} and d_{90} (particle size at 50% and 90% cumulative) of talc, kaolin, gibbsite, and silica are 12.24 μm and 30.77 μm ; 13.04 μm and

63.31 μm ; 10.46 μm and 25.08 μm ; and 12.61 μm and 25.99 μm , respectively. These results show that the sizes of talc, gibbsite, and silica particles can be considered to be relatively fine as compared to the kaolin particles. A one mode particle size variation was observed for all the raw materials.

Fig. 5 Particle size analysis of raw materials

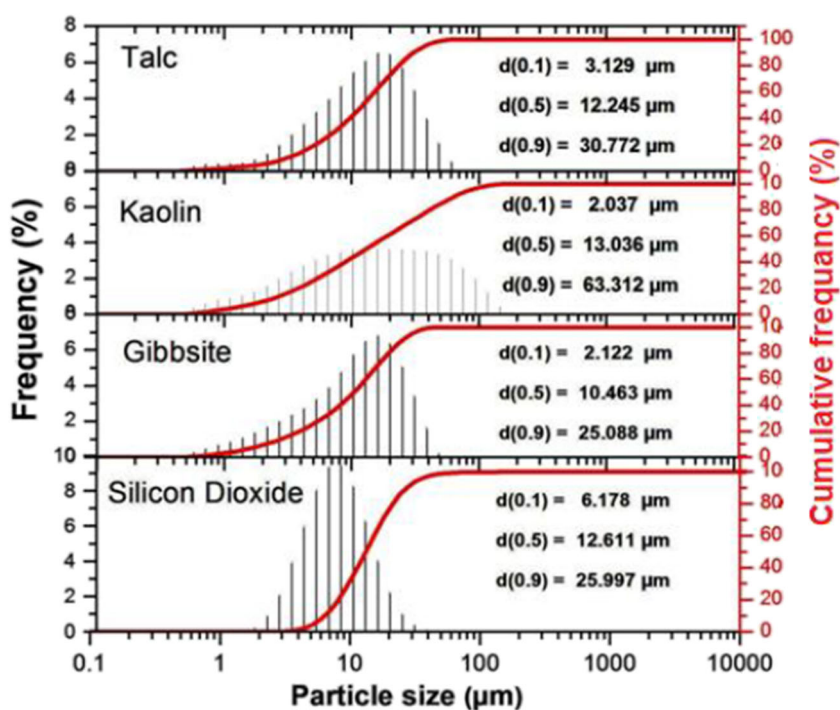


Table 3 Crystallite sizes after mechanical treatment of powders

Sample Code	JCPDS Number	Crystallite Size (μm)	Compound Name	Chemical Formula
MT-0	00-001-0527	36.61	Aluminum Silicate Hydrate	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
	96-901-0227		Magnesite	$\text{Mg}_6\text{C}_6\text{O}_{18}$
MT-120	96-900-7693	48.82	Magnesite	$\text{Mg}_6\text{C}_6\text{O}_{18}$
	00-001-0527		Aluminum Silicate Hydrate	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
MT-240	00-001-0527	34.27	Aluminum Silicate Hydrate	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
	96-901-0227		Magnesite	$\text{Mg}_6\text{C}_6\text{O}_{18}$
MT-360	96-901-0227	52.13	Magnesite	$\text{Mg}_6\text{C}_6\text{O}_{18}$
	00-001-0527		Aluminum Silicate Hydrate	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

3.6 Structural Confirmation of Un-Milled and Milled Samples

Table 3 describes the crystalline structure and size of the milled and un-milled samples. The observations revealed that the mean crystallite size of MT-0 was 36.61 μm . As the milling time progressed up to 120 min, the presence of aluminum silicate ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) besides the gibbsite, kaolinite, and magnesite phases, was observed, which indicated the start of a mechano-chemical reaction in the system. The mean crystallite size further reduced with increasing milling time up to 240 min. With further increase in milling time up to 360 min, the mean crystallite size increased to 52.13 μm . A trend of increase and decrease in crystal sizes is observed and these results are consistent with SEM findings (see section 3.8 on SEM studies of milled and un-milled samples).

The X-ray diffraction patterns for the samples are presented in Fig. 6. During milling, the force induced by ball impacting can bring about heavy mechanical deformation in the powder. This has the tendency to introduce large stress accumulation in

the powders. Likewise, the grain size gradually reduces and these factors induce the reduction of XRD reflections and its broadening. The initial powder mixture MT0 exhibits sharp reflections of SiO_2 around Bragg's angle of 19° (JCPDS PDF 65-0466) and MgO around Bragg's angle of 30° and 32° (JCPDS PDF 87-0651), while the intensities of reflections of all starting phases in the samples that were milled are lower. It is also observed that there are small increments in peak broadening which indicates that defects are relatively introduced during milling. The peak broadening is noticed due to micro strain introduced in the powders and heat evolution during milling. The intensities of the reflections at characteristic Bragg's angles are altered for the milled samples indicating that defects were introduced.

3.7 FT-IR Analysis of Un-Milled and Milled Powders

The IR bands noticed for the milled and unmilled powders as shown in Fig. 7 are quite identical which indicates that ball milling doesn't have significant effects on the functional

Fig. 6 XRD patterns of unmilled (a) MT0; and milled powders (b): MT120; (c) MT240 and (d) MT360

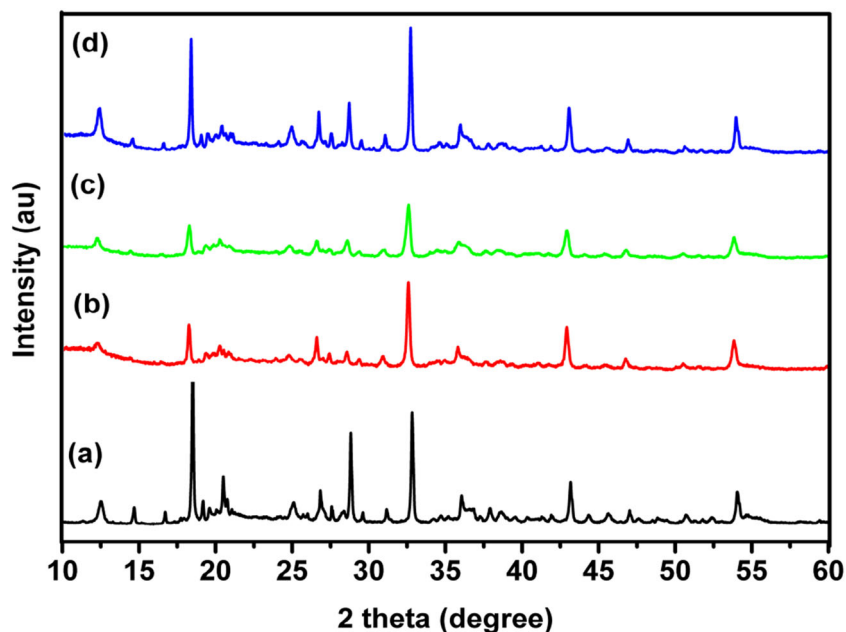
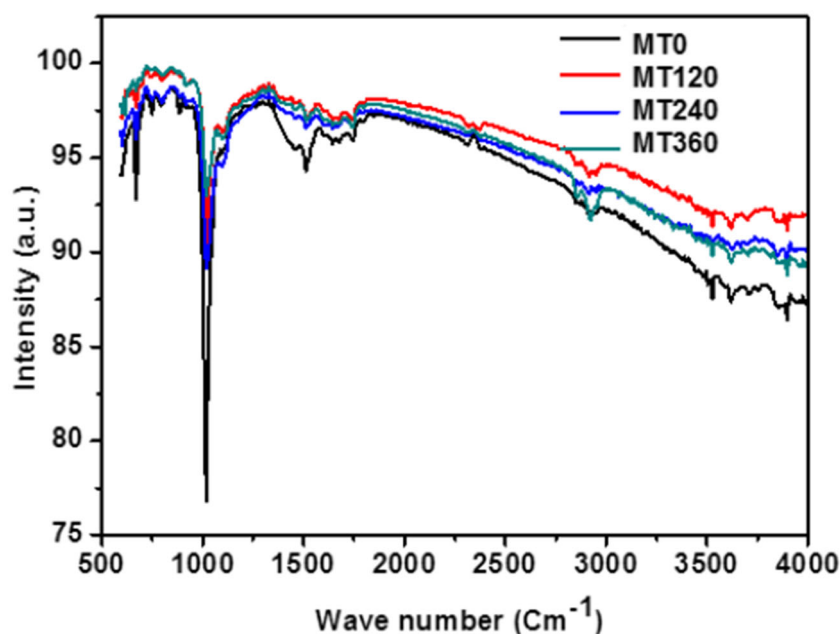


Fig. 7 FT-IR Spectra of un-milled (a) MT0; and milled powders (b): MT120; (c) MT240 and (d) MT360



group of the milled powders. For instance, the bands which depict the functional group of kaolinite had no noticeable shift but changes only in terms of intensity [31]. This obvious change in intensity correlates with the absorption band in 1000 cm^{-1} which is by reason of the energy of Si-O-Si in terms of stretching in the tetrahedral silicon sheet.

3.8 Morphology of Un-Milled and Milled Powders

The SEM micrographs for the samples are revealed in Fig. 8. The crystal morphology by milling the sub-stoichiometric precursors was reshaped, and some of the compact lamellar crystals are completely removed to form a single sheet. The micrograph of MT0 (Fig. 8a) shows particles that can be termed to be irregularly shaped. Powder particles are disconnected as the mixture was not milled. It should be noted that at 120 min there was a significant attrition of the powders which consequently caused uniform blending and a great deal of connectivity (Fig. 8b). These resulted in increase in their specific surface area (see section BET of powders) and in line with this, a supposed increase in the reactivity. The aggregates seen in the background of the SEM micrograph of MT360 (Fig. 8d) were reduced by further milling. Prolonged grinding at 240 min, sample MT240, (Fig. 8c) produced powder particles with the aggregates observed. The impact of continuous milling has the tendency of significantly enhancing the reactivity of powder particles [32]. Initially, the particles become reactive and with continuous milling could form aggregates which are quite disadvantageous during heat treatment. The reduced aggregates observed for MT120 could significantly favour better outcome during the sintering process. These results also

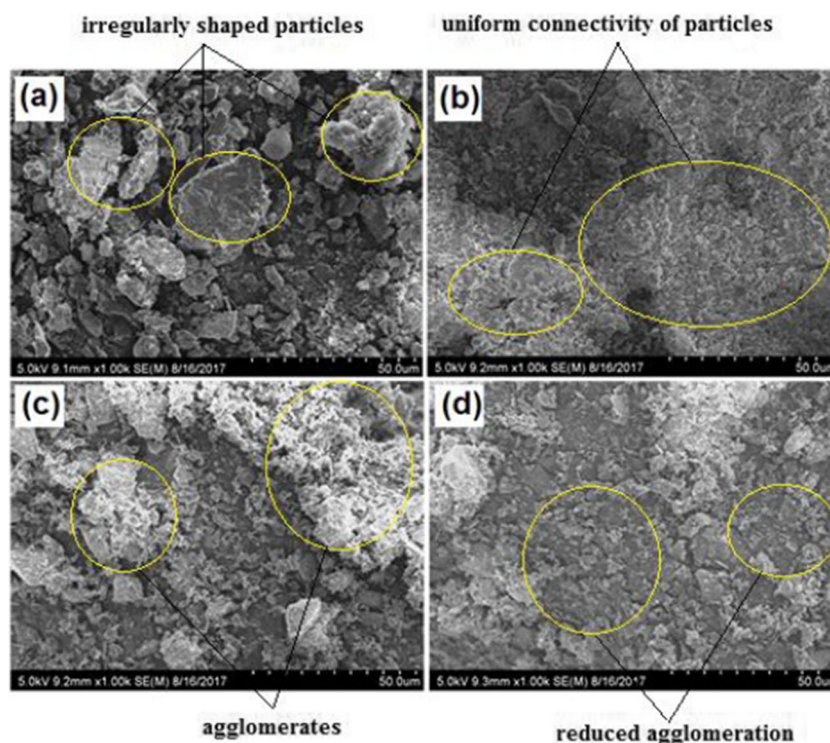
show the bonding of small particles, confirming the remarks by Palaniandy et al. [33] that particles bond because of high surface energy. Suraj et al. [34] suggested that the larger aggregates behave as large particles which are independent, therefore decreasing the surface area of the samples (see section 3.11: BET of milled and un-milled samples).

3.9 Thermogravimetric Analysis (TGA) of Unmilled and Milled Powders

Thermogravimetric analysis of the unmilled and milled samples was performed to evaluate the thermal stability of the powder composites (Fig. 9). The TG curves signify thermal stability showing three steps associated with weight loss. Two clearly defined weight loss steps are between room temperature to $180\text{ }^{\circ}\text{C}$ and between 500 and $850\text{ }^{\circ}\text{C}$. The first weight loss is linked with a weak endothermic effect. The weight loss initiates around $450\text{ }^{\circ}\text{C}$ and ends at around $750\text{ }^{\circ}\text{C}$ due to kaolinite and talc dehydroxylation.

The differential mass loss was measured and reported from the DTG signals (Fig. 9b). The DTG peaks help in the quantification of the mass percentage of a given segment or section. Two mass loss steps are described by the samples and these steps are not distinct at 200 and $400\text{ }^{\circ}\text{C}$, which are ascribed to removal of water and the hydroxyl groups, respectively [35]. The depletion of mass of the samples tends to gradually increase because there is progressive water absorption during the synthesis and grinding processes. As the grinding time progressed, the maximum peaks for the dehydroxylation process were shifted towards lower temperature at a slow rate, which means that the milling reduced the dehydroxylation

Fig. 8 SEM images of the un-milled (a) MT0; and milled samples (b). MT-120; (c) MT240; (d) MT-360



temperatures. This can be by virtue of the decline in the energy needed to change the structure of the crystallinity of the system.

The analysis of the TG curves reiterates the behaviors observed by DTA since dehydroxylation is generally linked with the corresponding mass loss. The curves of un-milled and those milled for 120–360 min are shown in Fig. 9c. It is observed that all samples have DTA peaks that are clearly explained. The first peaks are broad endothermic peaks at around 130 °C, which can be ascribed to removal of loosely held water. MT120 samples show a more pronounced endothermic peak as compared to the other samples which signifies much more rapid removal of water molecules. The clearly visible endothermic peak at around 320 °C corresponds to the dehydroxylation of compounds which are based on Al_2O_3 [36]. Large humps of exothermic peaks are clearly noticed for all the samples which can be by virtue of the removal of the hydroxide of Mg^{2+} at 405 °C.

3.10 Particle Size Distribution of Unmilled and Milled Powders

The effects of grinding on the particle size distribution of all batches are presented in Fig. 10. Increased milling time decreased the particle size. This obvious reduction in particle size was described by the maximum peak which is around 3 µm for MT120, 40 µm for MT240 and MT360, and around 50 µm for MT0 samples.

3.11 Surface Area Analysis of Unmilled and Milled Powders

From Table 4, the specific surface area continues to increase with progressive grinding up to 120 min. Therefore, it is consistent from this finding that aggregates are continuously generated with progressive milling which can result in the drop of surface area. But, after 120 min (MT120) of milling, the specific surface area and pore sizes have a little variation where it can be observed that surface area dropped and inconsistencies were observed in the pore sizes. This is as a result of larger aggregates being formed when there is continuous milling. Thus, it can be seen that the first stage of the milling process produces the greatest alteration with increasing specific surface area from 26.4 to 41.1 $\text{m}^2 \text{g}^{-1}$. According to Table 4, samples MT240 and MT360 show a small decrease in surface area when compared with the MT0 sample. Furthermore, the size reduction of the samples can be seen to result in an increase in pore size for all milled samples. Correlation between the grinding duration and particle size is also described according to Table 4. The particle sizes of MT0 and MT360 samples are slightly above nanometer scale, and based on the milling process, average particle sizes of MT120 are comparatively much closer to the nanometer range.

Figure 11 shows the comparison of the BET curves for the milled and unmilled powders. The straight line on BET curves indicates that the BET equation holds well (eq. 1) and measured BET surface area gave a clear picture of actual surface

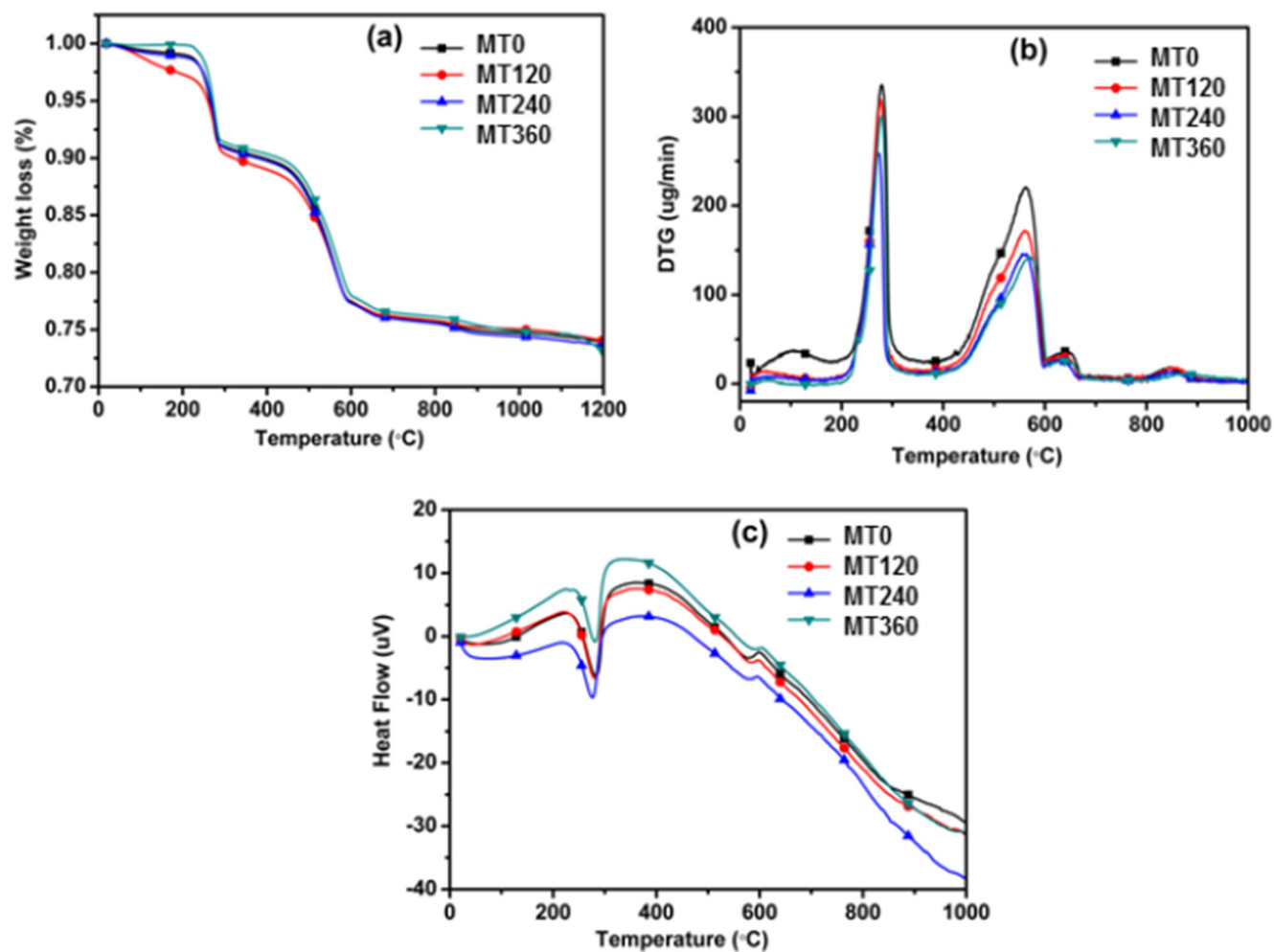


Fig. 9 Thermogravimetric curves of the unmilled and milled powders. (a) TG; (b) DTG and (c) DTA

Fig. 10 Particle size distribution graphs of milled and un-milled samples

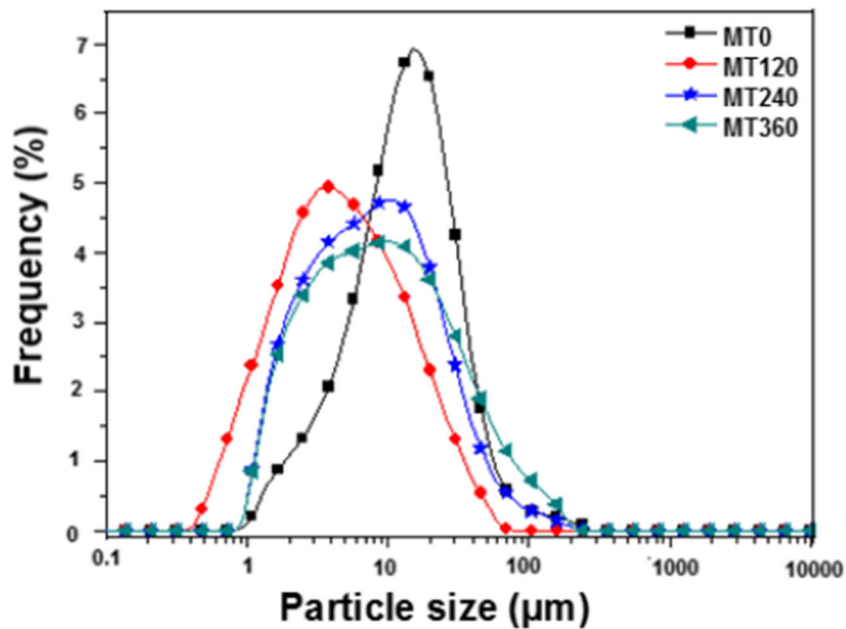


Table 4 Surface characteristics of raw materials

Sample Code	Average Particle Size (nm)	BET Surface Area (m ² /g)	Pore Size (nm)
MT-0	227.1961	26.4089	2.1508
MT120	145.9355	41.1140	2.1542
MT240	151.6089	39.5755	2.1547
MT360	161.2872	37.2007	2.1516

area of powders. The plot describes the adsorption of gas molecules on the solid surfaces which depicts the pore sizes of the powders vis-à-vis milling action, and serves as the basis for an important correlation with the specific surface area of the materials. In this way, simply put, there is an inverse relationship between the least gas absorbing solid and the surface area of the same. It should be noted that MT120 powders absorbed the least amount of gas molecules. This is an indication of lower porosity in line with the compactness provided by the milling action of the powders and thus an enhancement of the surface area. It has been noticed that the larger aggregates observed by SEM on MT360 behaved as individual large particles, and this is a possible reason for the reduced surface area of the sample. In this way, in comparison, MT360 adsorbed more gas molecules compared to other milled powders, but our assertion that this generated an inverse relationship with surface area remains valid.

3.12 Particle Size Analysis of Unmilled and Milled Powders

The particle size analysis of the powders which corresponds to D_{50} is illustrated in Fig. 12. It can be noticed that progressive

milling time not only produces particles that are finer but also streamlines the distribution of particle size by altering the sizes of coarse particles in a reduced manner. The median particle size (0.5) for the ungrounded mixture (MT0) is around 12.5 μm , and the size declines with progressive milling time, i.e. for MT120 (4.25 μm), increases slightly for MT240 (8.16 μm) which can be ascribed to particles aggregating during progressive milling. Similar trend was observed by SEM observations of the powders for MT360 as the particle size at the 50% point (7.25 μm) reduced in comparison with MT240. It should be noted that comparatively, MT120 produced the finest particles at every point of measurement (D_{10} , D_{50} , and D_{90}). Essentially, the outcomes of particle size analysis, described in Fig. 12, are in line with microstructure analysis (see section 3.8 on SEM analysis).

3.13 Crack Propagation Intensity of Milled and Un-Milled Compacts

Figure 13 presents the crack propagation observed for the milled and un-milled powder compacts. The initial signals appeared during cooling at 840 $^{\circ}\text{C}$ (for MT0), when the compressive stresses led to a formation of micro cracks. The AE

Fig. 11 BET linear plots of milled and un-milled samples

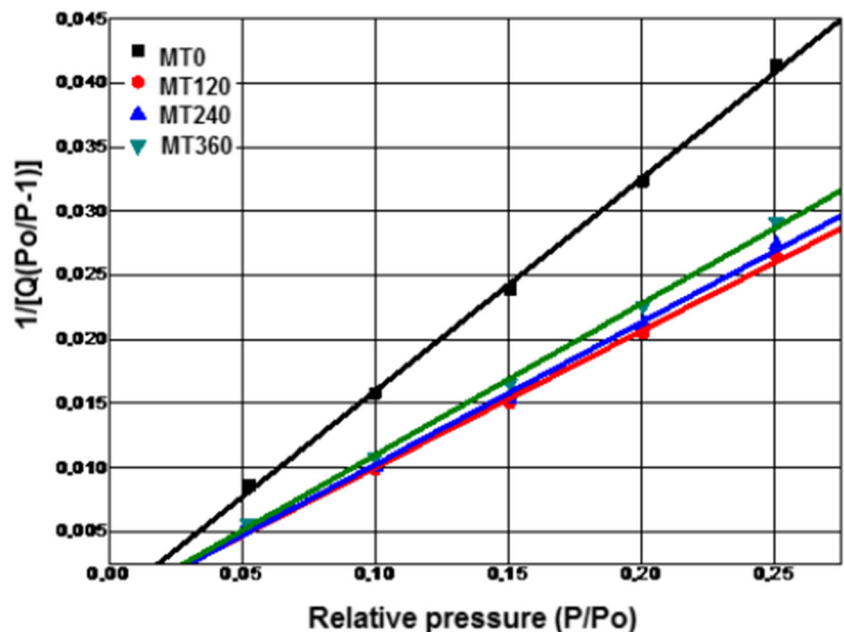
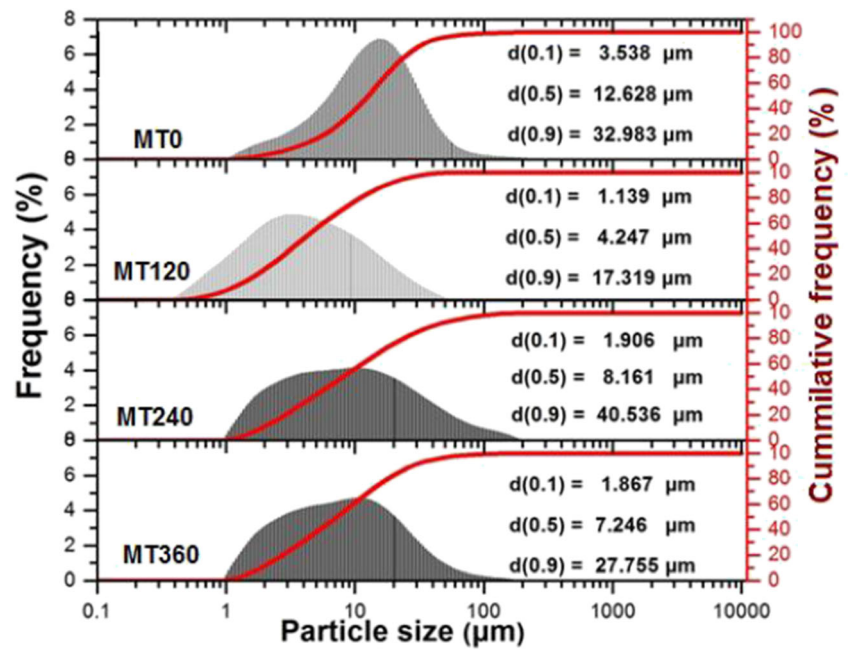


Fig. 12 Particle size analysis of non-activated and activated powder mixtures



activity increased step-wise by the prolongation of the milling time. Samples prepared from powders milled for 240 and

360 min exhibited the highest AE activity, thus an intense crack growth was expected in these samples. This can be

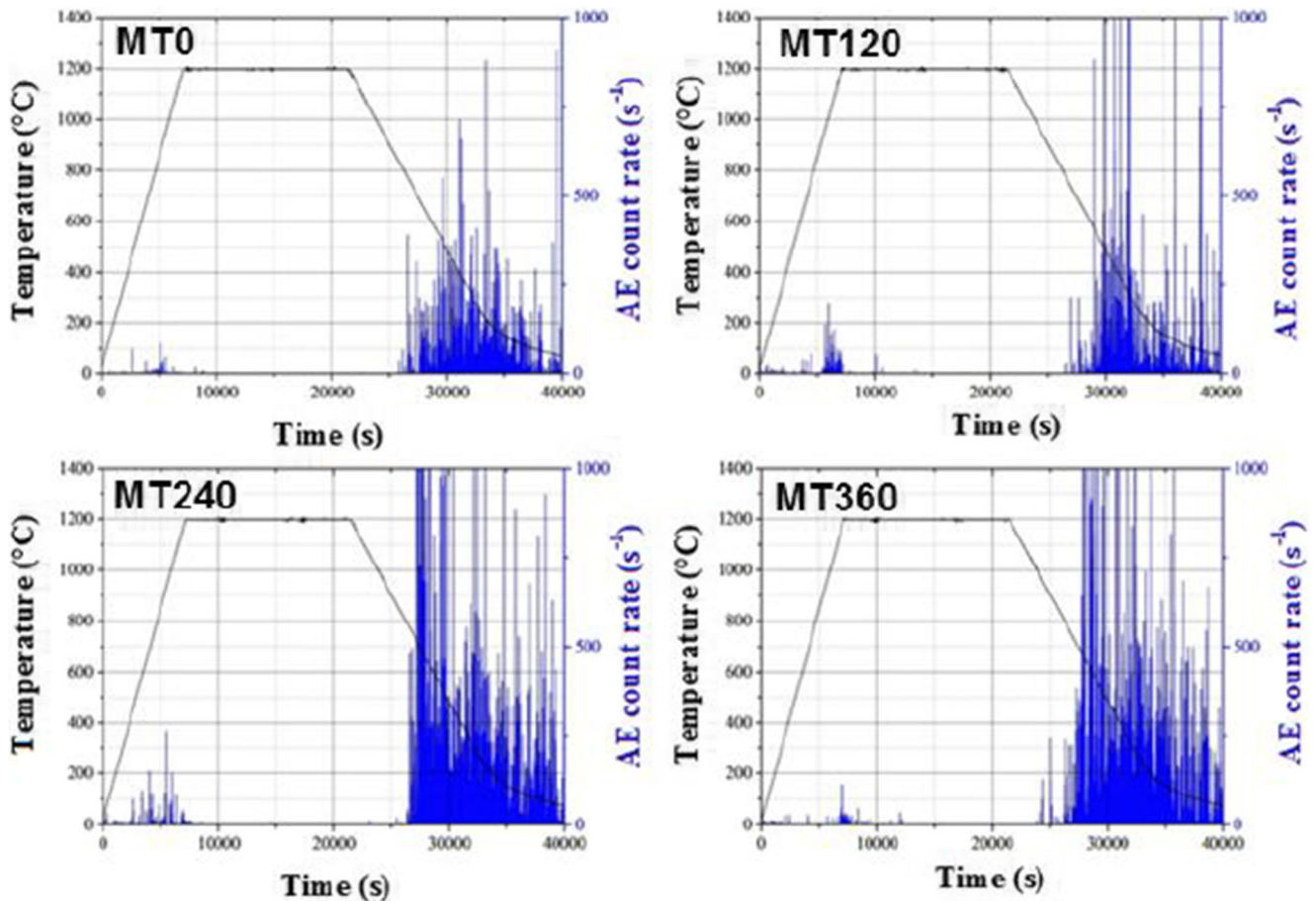


Fig. 13 AE signal intensity of unmilled and milled powder mixture

ascribed to the presence of small quartz grains, around which circumferential cracks appear. The lower AE activity of the samples MT0 and MT120 can be explained through the bigger quartz grains, which are present in smaller amounts. Another possible explanation is that some minor mineral phases with different coefficient of linear thermal expansion than that of the matrix are still present in the structure. In all cases, the most intense crack growth was observed at temperatures above 400 °C. Authors of [18] reported crack healing at lower temperatures, which may explain the absence of cracks on the SEM images. However, from practical point of view, the sample MT120 is the most purposeful milled mixture, considering the low intensity of AE signals.

4 Conclusions

A sub-stoichiometric formulation of cordierite was milled for 0, 120, 240, and 360 min in order to examine the influence of various milling times on thermo-physical processes of the mixture for the production of cordierite powders. The samples were subjected to thermal analyses, particle size measurements and structural observations. To monitor the crack formation during cooling, AE measurement was carried out. The results can be summarized as follows:

1. Relatively, the minutest of particles are formed after 120 min of milling. Longer milling time promotes the formation of aggregates which may significantly retard reactivity of materials during heat treatment
2. With respect to the BET results, there is an inverse relationship between the least gas absorbing solid (powders) and the surface area of the solid. MT120 powders absorbed the least amount of gas molecules which is in conformity with SEM results and implies a more uniform microstructure and slightest defects in the MT120 sample.
3. The major dehydroxylation peak is shifted to lower temperatures with increasing milling time as a result of the particle size reduction and mechanical activation
4. From AE measurements, progressive milling duration promotes cracking during cooling. The AE intensity increases firstly, reaching a maximum at MT240, and a noticeable slight decline in the case of MT360. This generally depicts a gradual crack growth behavior because of the highly stressed powders used for the compacts

Acknowledgements Authors acknowledge the Department of Mechanical Engineering and Materials and Metallurgical Engineering, Ahmadu Bello University, Zaria, Nigeria for providing facilities to carry out this study. The research support received by one of the authors BAA from SRS with grant ID G2017031593437655 is greatly appreciated. In addition, DDA acknowledges the support of the University of Ghana BANGA-Africa programme.

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