Available online at www.sciencedirect.com

ScienceDirect

Procedia Chemistry 19 (2016) 673 – 680

Procedia Chemistry

5th International Conference on Recent Advances in Materials, Minerals and Environment (RAMM) & 2nd International Postgraduate Conference on Materials, Mineral and Polymer (MAMIP), 4-6 August 2015

Physical and Structural Transformations of Perlis Carbonate Rocks via Mechanical Activation Route

T.N.A.S. Tengku Mustafa[a], S.R.R. Munusamy[a], D.N. Uy Lan[a], N.F.M. Yunos[a]

[a]*School of Materials Engineering, Universiti Malaysia Perlis, Perlis Malaysia*

Abstract

Carbonate rocks were mechanically activated in a high energy planetary ball mill using dry grinding method. The fine grinding test works were carried out with the same ball to powder ratio (9:1) at three levels of revolution speed (250 rpm, 350 rpm and 450 rpm) and grinding time (30 min, 60 min, 90 min) respectively. The chemical composition and elemental constituents of the raw dolomite and limestone samples were determined using X-ray fluorescence (XRF) and energy dispersive X-ray spectroscopy (EDX). The structural properties such as degree of crystallinity (DOC), crystallite sizes and lattice strains of non-activated and mechanically activated carbonate rocks were analyzed using X-ray diffraction (XRD) while the morphological analysis conducted using scanning electron microscopy (SEM). Results obtained showed that high revolution speed and longer grinding duration have pronounced effect on the grindability, increase in fineness, decrease in crystallite sizes and amorphization of Perlis dolomite compared to the limestone source. This might be due to the difference in material hardness and existence of appreciable amount of quartz content in limestones.

Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

Keywords: Crystallite size; Degree of crystallinity (DOC); Lattice strain; Mechanically activated; Grindability

1. Introduction

Carbonate rocks have numerous and diversified applications as fillers in paper, paint and polymer products. These rocks are also used as aggregates, cement and lime (CaO) in building constructions, soil correctives and fertilizers in agricultural sector, source of lime in ceramics, flue gas desulfurization and metallurgical fluxes[1,2].

* Corresponding author. Tel.: +0-000-000-0000 ; fax: +0-000-000-0000 .
E-mail address: t.nurain@studentmail.edu.my

Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia
doi:10.1016/j.proche.2016.03.069

Recent studies by Mineral and Geoscience Department (JMG) Malaysia showed that the dolomite deposits ($CaMg[CO_3]_2$) of approximately 600 million metric tonnes available in Perlis are of the highest quality in Malaysia.

Mechanical milling is a convenient way of producing fine products with attrition, planetary, oscillating and vibration mills being the common types of grinding mills employed for this purpose. Mechanical treatment in a high energy mill generates a stress field within the solids. The stress relaxation occurs via several mechanisms such as heat release, development of a surface area as a result of brittle fracture of the particles, structural defects and stimulation of chemical reactions within the solids[3]. The enhancement of solid reactivity prior to mechanical activation is highly interconnected with the deformation of crystal structure, structural disordering, increase in fineness, creation of new surfaces, amorphization, etc. In addition, aggregation which is the weak, reversible adhesion of particles due to van der Waals forces due to short grinding period and agglomeration prior to long duration grinding with formations of very compact, irreversible adhesion of particles are the common phenomenon in fine grinding. Eventually these increase the particle size and decrease the free surface[4, 5, 6].

Numerous works have been accomplished on various aspects of fine grinding and breakage mechanisms of particulates involving different type of grinding mills and environments. Uniqueness of planetary ball milling is the rotation of the milling jar around its own axis while orbiting around a central axis and the collisional mechanisms involve multiple possible contacts, i.e. ball-ball, ball-wall, ball-powder, powder-powder and powder-wall. For performing a crushing process, the work that needs to be imparted on the powder is proportional to the average impact energy and the total number of impacts with a minimum energy transfer during each collisions[7]. The efficiency of collision depends on several factors such as the collision velocity and the frequency of collisions with higher collision velocity and frequency can be obtained by increasing the rotational speed of planetary mill at optimum ball to powder filling ratio.

The current study focuses on the physical and structural transformations of high quality dolomites ($CaMg[CO_3]_2$) and limestone ($CaCO_3$) with appreciable amount of quartz (SiO_2) abundantly available in Perlis. Both the non-activated and activated samples were analyzed for mineralogical composition, structural disordering (lattice distortions, amorphization, etc.), physical alterations (size, shape and texture) and grindability due to the mineral hardness and quartz contents. In particularly, this work is aimed at developing the in depth fundamental knowledge on the physico-chemical and mechano-chemical properties of the mechanically activated Perlis carbonate rocks for end applications.

2. Experimental

2.1. Raw material

Dolomites and limestone used in this experimental work were supplied by quarries in Chuping, Perlis and Sungai Batu Pahat, Perlis. The coarser bulk samples were crushed using jaw crusher for size reduction purpose. Sampling and sample preparation techniques were used to obtain representative and homogenous samples for fine grinding test works. The mineral constituents, phases and crystallite properties of the raw samples were identified using XRD method while the morphological and elemental analyses were carried out using SEM and EDX techniques. The chemical composition of the raw samples determined using XRF analysis is given in Table 1.

Table 1.The chemical composition of raw limestone and raw dolomite.

Type of composition	CaO	SiO_2	Fe_2O_3	Al_2O_3	K_2O	MgO	TiO_2	SrO	Traces
Limestone (weight percent, %)	62.78	21.63	4.36	7.42	2.53	0.21	0.57	0.11	0.02
Dolomite (weight percent, %)	83.50	1.90	1.14	1.80	-	10.0	0.22	-	1.16

2.2. Mechanical Activation

Mechanical milling of Perlis carbonate rocks has been carried out in a batch type planetary ball mill (Pulverisette P6, Fritsch GmbH, Germany) having one milling chamber. The grinding bowl rotates around its own axis while orbiting around a central axis. As a result, forces are exerted on grinding balls and materials which constantly changing directions. The grinding bowl and the milling medium (balls) are made of stainless steel. All the experiment uses 10 mm diameter milling medium (balls). The grinding time and revolution speed are varied while the ball to powder ratio and media are kept unchanged. At a constant ball to powder ratio of 9:1 (by weight), 22.2 g of Perlis carbonate rocks is grounded at different revolution speeds and grinding time as shown in Table 2.

Table 2. Grinding speed (rpm) and time (min) used in experiments.

Revolution speed (rpm)	Grinding time (min)		
	First batch	Second batch	Third batch
250	30	60	90
350	30	60	90
450	30	60	90

2.3. Characterization

X-ray fluorescence (XRF) was used to determine the chemical composition of initial samples. The mineral composition was analyzed using X-ray diffractometer (Bruker Co.). Each sample was scanned continuously at 1°/min in the range $2\theta = 5°$ to 60° at 10 kV and 30 mA in 0.04° steps. Peak positions (2θ) and the full-width at half maximum (FWHM) area under peak (A) were obtained from the XRD spectra to characterize the microstructure such as crystallite size, Dv using Scherrer equation, lattice strain, and degree of crystallinity (DOC), as shown in Eqs. (1) - (3) respectively [9, 10, 11].

$$Dv = (K\lambda/FWHM) \cos\theta \quad (1)$$

Where Dv is the volume weight mean of the crystallite size, K is a constant, θ is the bragg angle of (h,k,l) reflection, and λ is the wavelength of X-ray used (λ=1.542 Å).

$$\varepsilon = \beta / 4 \tan\theta \quad (2)$$

Where ε is the lattice strain and β is the integral breadth profile.

$$DOC = (A_t / A_0) \times 100 \quad (3)$$

Where, DOC is the degree of crystallinity, A_0 and A_t are the areas under the peak for feed and ground sample. The morphology of samples was analyzed by using JSM 6460LA Scanning Electron Microscope (SEM) which produced the secondary electron images at an accelerating voltage of 10 kV.

3. Results and discussion

3.1 XRD pattern and mechanochemical effect

Structural changes and microstructure characterization were analyzed using x-ray diffraction. Figs. 1 and 2 show the XRD pattern of the raw and ground products. The prominent peaks at 29.48° and 26.67° represent calcite and quartz peaks for raw limestone. Meanwhile, the prominent peak at 30.99° occurs at raw dolomite sample. The diffraction of ground samples have lower intensity, broader peak base as well as shift of peak compared to the raw sample, mainly was due to the disordering process of limestone and dolomite crystal structure from mechanical milling process. The reduction of peak intensities implied the formation of amorphous materials in the ground powders[10,11].

The reduction of peak intensity was clearly observed when the revolution speed was increased from 250 rpm to 450 rpm and grinding time from 30 min to 90 min. The broadening of the diffraction peaks continued to increase with increasing revolution speed and grinding times for all ground samples. The collision between grinding media and samples is vigorous at higher revolution speed, higher grinding time and impact breakage mechanism is more pronounced, which leads to tremendous stress energy being imparted on the particles resulting in massive strain in the crystal lattice. More plastic deformation and disordering of the limestone and dolomite lattice occur under intensive revolution speed and grinding time[11]. This trend provides the evidence supporting the idea that the larger the value of the full width at half maximum (FWHM), the lower the crystalline degree which indicated the crystal planes was distorted[5].

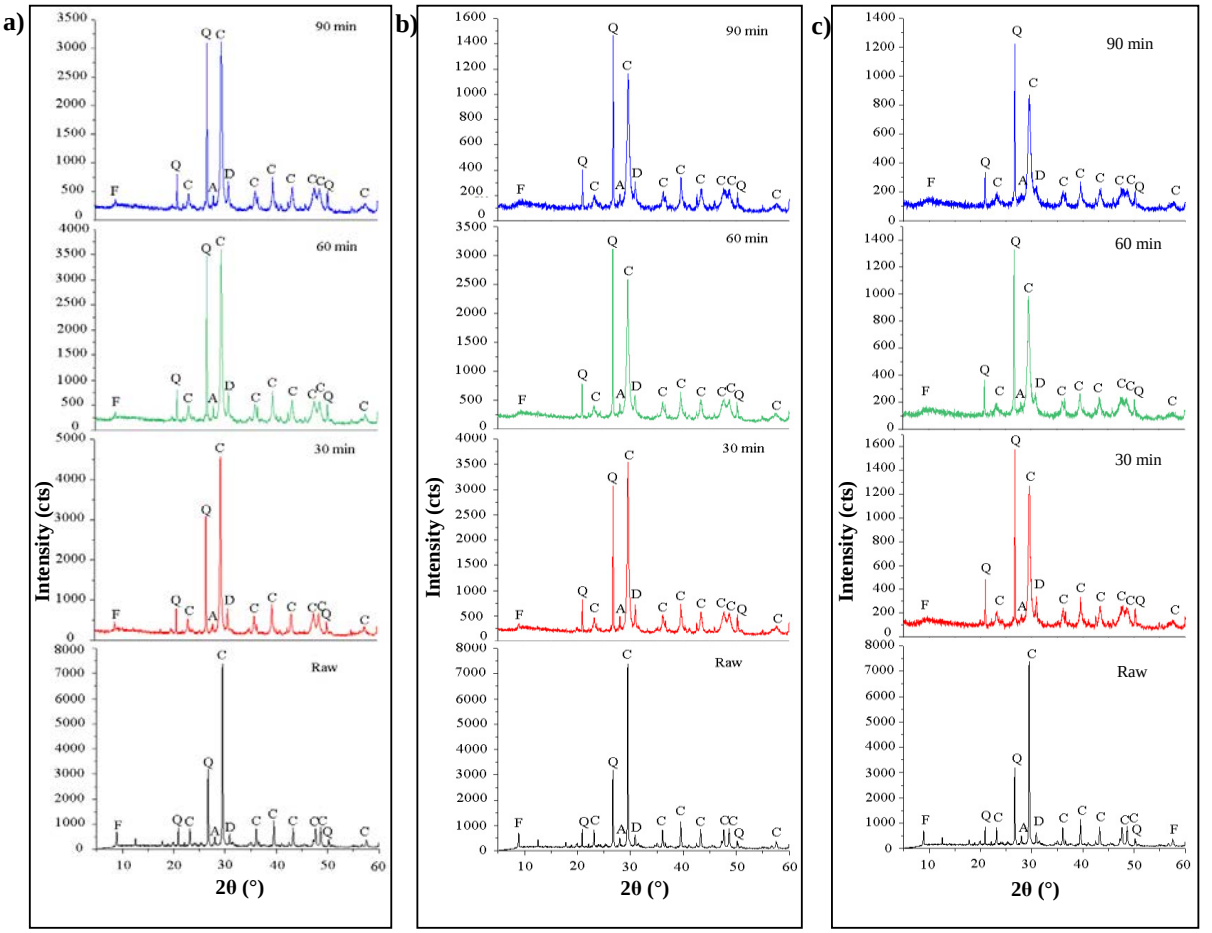

Fig. 1. XRD pattern for the feed and ground limestone products at (a) 250 rpm; (b) 350 rpm; (c) 450 rpm.
(F: fluorophlogopite ; Q: quartz ; C: calcite ; A: anorthite ; D: dolomite)

3.2 Degree of crystallinity (DOC), crystallite size and lattice strain.

Fig. 3 shows the quantification of amorphism during high intensity milling in the planetary mill in terms of degree of crystallinity. Generally, the degree of crystallinity decreases as the revolution speed and grinding time increases. The degree of crystallinity ranges from 31.69 % to 97.17 % for limestone and, 36.55 % to 54.17 % for dolomite. As the revolution speed increases, the degree of crystallinity decreases but reaches saturation at 350 rpm at respective grinding time. This result proved that the particles fall into ductile range during grinding process and at the same time it undergo plastic deformation[11,15]. Besides that, the diffraction pattern also shows that the initial stage of grinding at

lower revolution speed produces a gradual reduction in the degree of crystallinity for limestone and drastic reduction in the degree of crystallinity for dolomite at 250 rpm due to the different concentration of quartz (SiO_2) within the sample. In addition, the existence of silicone dioxide (SiO_2) within the limestone which shows the peak broadening of quartz and reduction in intensity is almost not altered revealed of high in mechanical strength [12,13]. Therefore, limestone need prolonged grinding or increase in the revolution speed to reach equilibrium in degree of crystallinity.

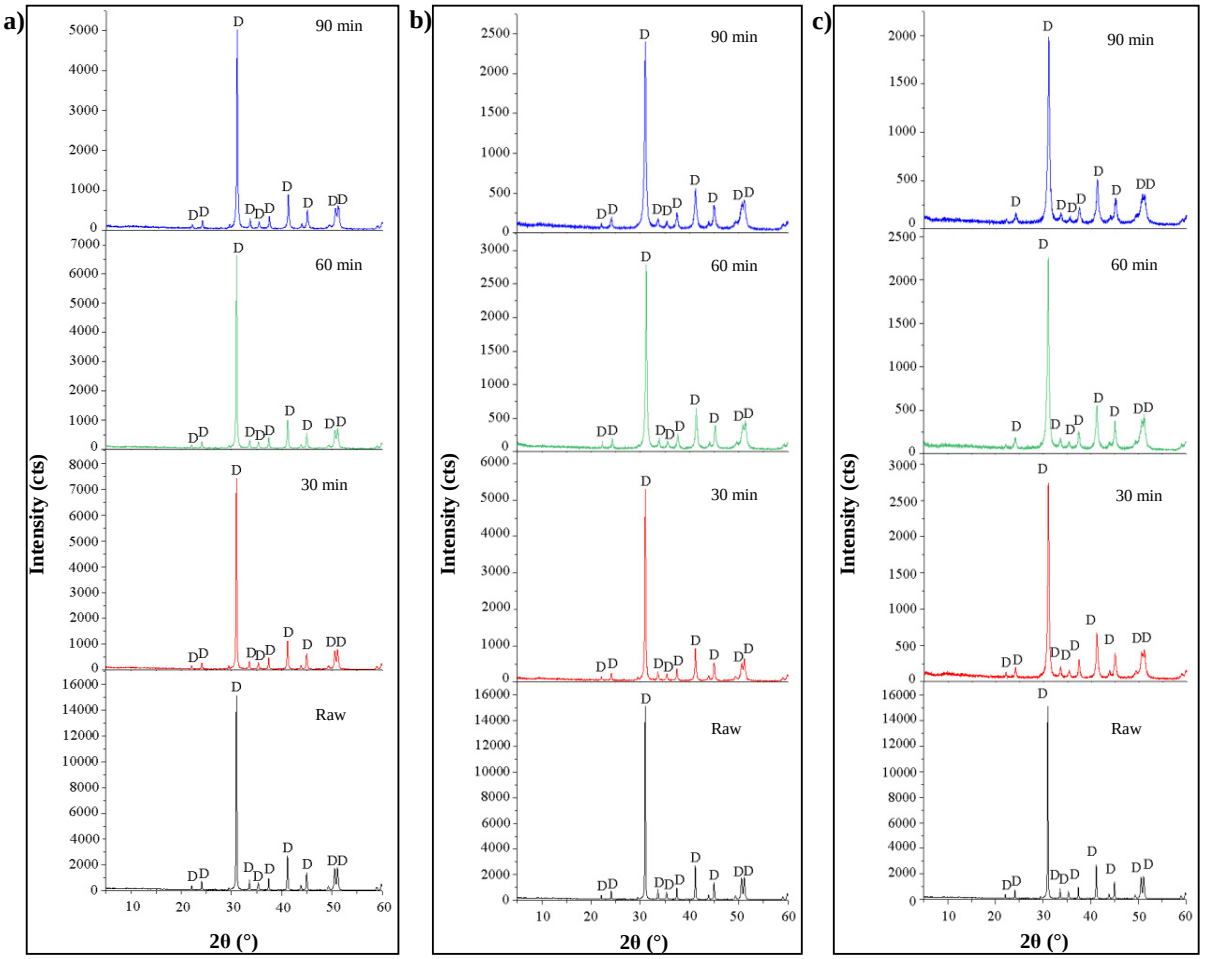

Fig. 2. XRD pattern for the feed and ground dolomite products at (a) 250 rpm; (b) 350 rpm; (c) 450 rpm. (D: dolomite)

During high energy milling of non-metallic minerals, part of applied energy is stored in the material during the mechanical stressing of finely divided solids. Nevertheless, there is a limitation in terms of the energy stored. Part of stored energy will be released during prolonged grinding, and this energy is used to bend or break the crystalline solid, which leads to several phenomena, such as amorphization, formation of active surface and increase in reactivity[11]. Major part of the energy stored were in the form of strain energy, structural disorder and point and line defect[14].

Figs. 4 and 5 show reduction in crystallite size and increase in lattice strain for limestone and dolomite as the revolution speed and grinding time increases. The crystallite size in limestone gradually decreases to a minimum value of 26.15 nm while, for dolomite sharply decrease at 60 and 90 minutes to a minimum value of 22.07 nm. Apparently, the lattice strains show a gradual increase to a maximum value of 0.54 for limestone and 0.63 for dolomite after grinding at 450 rpm revolution speed and 90 min of grinding time. The findings which proved that smaller lattice

strains corresponds to a larger crystallite size while larger lattice strain corresponds to a smaller crystallite size are in accordance to the findings by D. Chaira et al., (2009) and R. Arbain et al., (2011).

The minimum value of reduction in crystallite size of limestone for 450 rpm at 90 min was bigger compared to dolomite at the same parameter due to the different material hardness[10]. Therefore, limestone can stand high impact energy and shear stress that implied between the grinding media and the mineral surface compared to dolomite.

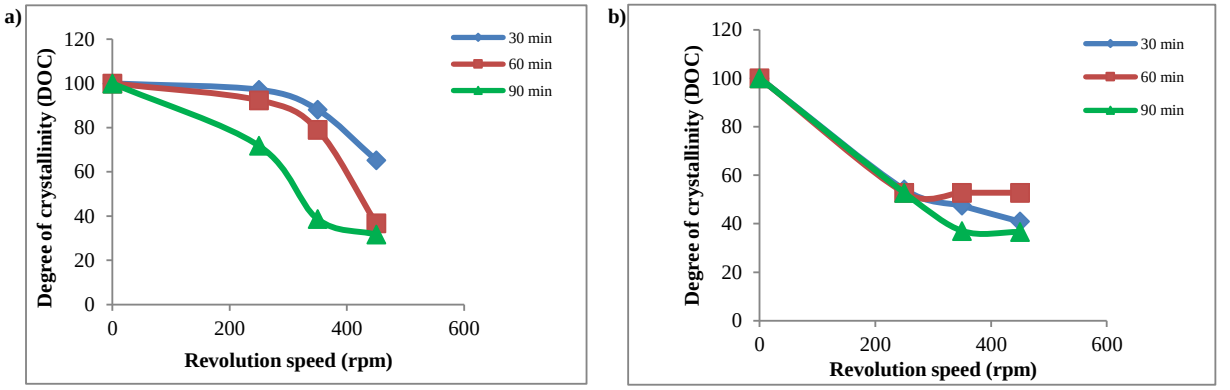

Fig. 3. Degree of crystallinity of ground sample as a function of revolution speed of (a) limestone; (b) dolomite.

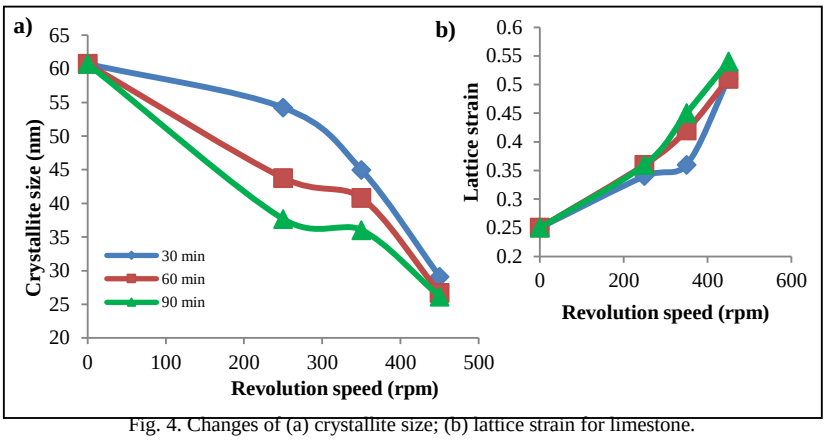

Fig. 4. Changes of (a) crystallite size; (b) lattice strain for limestone.

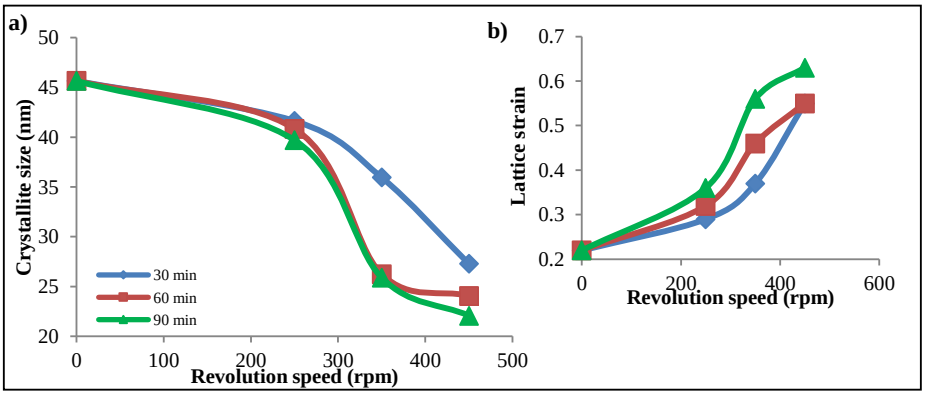

Fig. 5. Changes of (a) crystallite size; (b) lattice strain for dolomite.

3.3 Particles size and morphology analysis

Photomicrographs of feed, limestone and dolomite products are shown in Figs. 6(a) to (f). Small, intermediate and large particles with irregular shape are widely distributed in the feed limestone and dolomite samples in Figs. 6(a) and 6(d). As shown in Table 3, the existence of Ca and Mg elements in dolomite and Ca for limestone strongly proves the type and quality of the carbonate rocks. Photomicrographs of ground products in Figs. 6(b) and 6(e) indicate the size reduction during grinding might be possible by rupture of joints, cleavage and massive breakage of the constituting particles[17, 18]. It is noticed that the particles were considerably reduced in size and their shape became less defined with the increase of the revolution speed and grinding time. The morphological characteristics of the ground limestone and dolomite products can be seen in Figs. 6(c) and 6(f) at 10,000x and 40,000x magnifications. The fine particles can be seen sticking on the coarse particle [Fig. 6(f)] and formation of coarser agglomerate with the fines interaction [Fig. 6(c)]. With the increase in revolution speed and grinding time, the sharp edges and corner of the particles were trimmed off into more rounded or even edges. The morphology resulting from the prolonged grinding exposure may explain an intense agglomeration and aggregation between fines and partially broken particles for grinding ≥350 rpm. Such aggregation is a result of interactions among the fine particles through Van der Waals forces, leading to particles size increase[18].

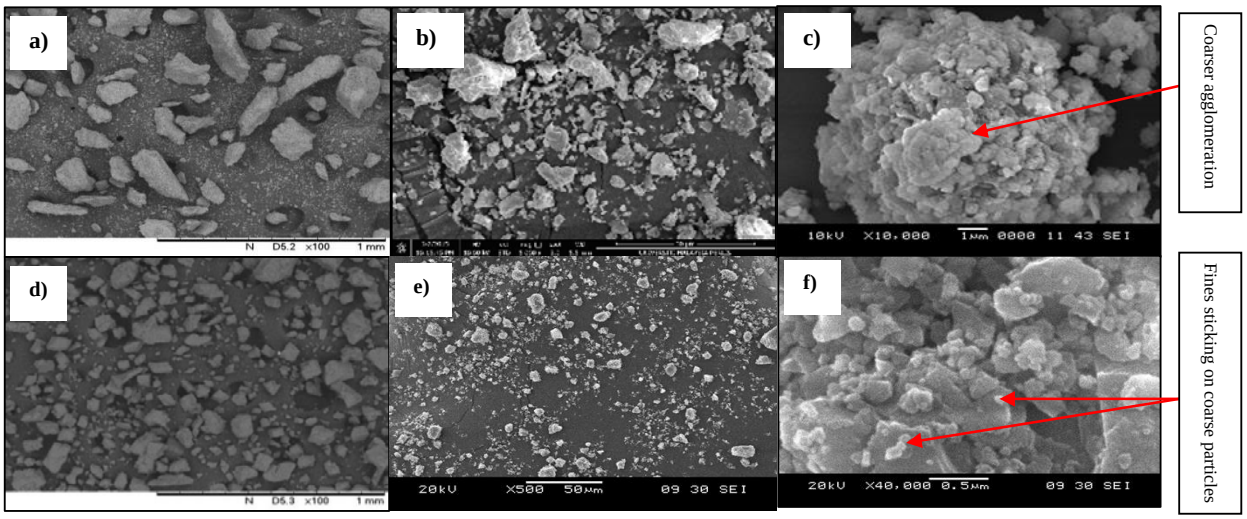

Fig. 6. SEM micrographs of (a) feed limestone; (b) limestone product at 350 rpm and 60 min at magnification x500; (c) limestone product at 350 rpm and 60 min at magnification x10,000; (d) feed dolomite; (e) dolomite product at 350 rpm and 60 min at magnification x500; (f) dolomite product at 350 rpm and 60 min at magnification x40,000.

Table 3. EDX of raw limestone and raw dolomite.

Element	O	Ca	Si	K	Al	C	Mg
Limestone (mass percent, %)	45.8	38.1	8.5	4.1	3.5	-	-
Dolomite (mass percent, %)	54.0	17.8	4.2	-	4.1	10.0	9.9

4. Conclusion

The effect of dry grinding on the physicochemical properties of carbonate rock prepared from planetary ball mill has been studied. The phase structure, degree of crystallinity, crystallite size and lattice strain were considerably

changed upon fine grinding. The broadening of the peak base prior to grinding proved amorphization with the degree of crystallinity to be decreased to a minimum value of 31.69% for limestone and 36.55% for dolomite. During the early stage of grinding process at 250 rpm and 30 min, phase structure, degree of crystallinity and crystallite size gradually decreased but lattice strain gradually increased for both materials. After 60 min of grinding, the results show gradual decrease for limestone and drastic decrease for dolomite at 350 rpm. It can be concluded that, the existence of SiO_2 within the limestone makes it to be harder compared to dolomite. Besides that, minimum lattice strain of limestone is higher compared to dolomite and this showed that limestone is harder compared to dolomite. The hardness of the materials make the bonding between the particles is stronger and difficult to break during grinding. SEM images also indicate that agglomeration tends to occurs as the grinding time and revolution speed exceeds 60 min and 350 rpm for mechanically activated dolomite and limestone samples.

Acknowledgements

The authors wish to gratefully acknowledge School of Materials Engineering and Research & Innovation department under Universiti Malaysia Perlis for supporting this research project.

References

1. Guzzo PL, Santos JB, David RC. Particle size distribution and structural changes in limestone ground in planetary mill. *International Journal of Mineral Processing* 2014; **126**:41-48.
2. M. Shui. Polymer surface modification and characterization of particulate calcium carbonate fillers. *Applied Surface Science* 2003; **220**: 359-366.
3. Elmas E, Yildiz K, Toplan N. Effect of mechanical activation of mullite formation in an Alumina-Quartz ceramics system. *Materials and technology* 2013; **47**: 413-416.
4. Chen Y, Lian X, Li Z, Zheng S, Z. Wang. Effect of rotation speed and media density on particle size distribution and structure of ground calcium carbonate in a planetary ball mill. *Advanced Powder Technology* 2015; **26**: 505-510.
5. Tiantian Li, Fengfeng Sui, Fuchun Li, Yuanfeng Cai, Zhangdong Jin. Effect of dry grinding on the structure and granularity of calcite and its polymorphic transformation into aragonite. *Powder Technology* 2014; **254**: 338-343.
6. Ludmilla Opockzky. Fine grinding & agglomeration of silicates. *Powder Technology* 1997; **17**: 1-7.
7. Hossein Ashrafizadeh and Mahmud Ashrafizaadeh. Influence of processing parameter on grinding mechanism in planetary mill by employing discrete element method. *Advanced Powder* 2012;**23**: 708-716.
8. Liang Hao, Yun Lu, Hiromasa Sato, Hiroshi Asanuma, Jie Guo. Analysis of energy transfer during mechanical coating and ball milling-supported by electric power measurement in planetary ball mill. *International Journal of Mineral Processing* 2013;**121**: 51-58.
9. P. Pourghahramani and E. Frossberg. Changes in the structure of hematite by extended dry grinding in relation to imposed stress energy. *Powder Technology* 2007;**178**: 30-39.
10. S. Palaniandy and N. H. Jamil. Influence of milling conditions on the mechanochemical synthesis of $CaTiO_3$ nanoparticles. *J Alloy Compd*, 2009: 894-902.
11. R. Arbain, M. Othman and S. Palaniandy. Preparation of iron oxide nanoparticles by mechanical milling. *Minerals Engineering* 2011; 1-9.
12. Mako, E. The effect of quartz content on the mechanical activation of dolomite. *Journal of the European Ceramic Society* 2007; **27:** 535-540.
13. Aidong Tang, Linna Su and Chuanchang Li. Effect of grinding on the physicochemical properties of silica materials prepared from kaolin residue. *Powder Technology* 2012; **218:** 86-89.
14. Sasikumar C, Srikanth S, Mukhopadhyay NK, Mehrotra SP. Energetics of mechanical activation-Application to ilmenite. *Minerals Engineering* 2009; **22**: 572-574.
15. Chaira D, Mishra BK, Sangal S. Efficient synthesis and characterization of iron carbide powder by reaction milling. *Powder Technology* 2009; **191**: 149-154.
16. Palaniandy S, Azizli KAM, Hussin H. Study on mechanical effect of silica for short grinding period. *International Journal of Mineral Processing* 2007; **82**: 195-202.
17. Frances C, Le Bolay N, Belaroui K, Pons MN. Particles morphology of ground gibbsite in different grinding environments. *Int. J. Miner. Process* 2001;**61**: 41-56.
18. Alex TC, Rakesg Kumar, Roy SK, Mehrotra SP. Mechanically induced reactivity of gibbsite: Part 1. Planetary milling. *Powder Technology* 2014;**264:**105-113.