

Influence of polymers on the grinding and rheology of ultrafine Egyptian calcium carbonate suspension

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Abstract: The investigation of surface modification of Egyptian calcium carbonate via polymers was achieved with simultaneous ultra-fine grinding. Attrition mill and planetary mill were used for wet and dry grinding, respectively. The parameters affecting the grinding were studied such as ball number, speed and grinding time. The rheological characteristics of the aqueous calcium carbonate suspensions were studied in the presence of different types of polymers. The results indicated that the mechanical force could clearly affect the modification characteristics of calcium carbonate due to its mechano-chemical effects. The viscosity of calcium carbonate suspension depends on the volume percentage or weight percentage. The dispersing agent increases the solid concentration for a given particle fineness.

Keywords: fillers, calcium carbonate, ultra-fine grinding, surface modifications, Mechano-chemical activation, polymers

1. Introduction

The most common filler in the polymer industry is calcium carbonate (CaCO_3). It saved and increased the mechanical characteristics of the polymers therefore it is used as filler in pigments, paper, coating, plastics and ceramic. In nature, calcium carbonate exists in limestone, marble and dolomite minerals. Its characteristics are varied depending on the origin, formation history, and associated impurities, Table 1.

The main processing of the calcium carbonate filler includes milling, precipitation, and coating. Milling is achieved via dry or wet processes to produce ultra-fine product (Li et al., 2021; Alomari et al., 2019). Ultra-fine grinding is considered as an energy intensive process. The wet grinding performance using vertical stirred mill is investigated through testing the most affecting factors such as stirring speed, feed size, solid concentration and grinding time. The milling performance was evaluated with achieving fine sizes while using less energy (Santosh et al., 2020). A slight increase in milling performance may result in a high impact in the process economics. The product fineness as well as energy consumption is the tool to evaluate grinding performance. The grinding time and stirring speed are also important factors (Eswaraiah et al., 2015).

Ultrafine grinding increased the accessible surface area by decreasing the particle size. Grinding is regarded to be an energy-intensive process; hence additives are commonly used in fragmentation operations. Additives of chemical compounds were added to the suspension that is ground to obtain finer particles. The increasing of specific surface area could reach up to twenty times that of the particles milled without any additives (Ippolito et al., 2020). Ultra-fine wet grinding methods are used in a variety of the industrial applications. However, it is still challenging to anticipate and regulate the characteristics of ultrafine grinded product (Selim and Abd El-Rahiem, 2014).

Coated fillers are substantially more hydrophobic than uncoated fillers. This led to reduction of water pick-up and has also been demonstrated to affect polymer morphology, and resulting in polymer characteristics modification (Toraman et al., 2019; Selim et al., 2020).

During the treatment of fillers and pigments, traditional surface modification procedures such as heating mix and packing modification methods have been widely used. Traditional approaches have some shortcomings, such as poor stirring capabilities, low materials mixing degrees, uneven agent and material dispersion, and also a lack of reaction foundation. Furthermore, when employing traditional methods, the modification effect is weak and the product quality is unstable. As a result, the products mechanical performance has not improved significantly (Hancock and Rothon, 2003).

Nowadays, dry coating is considered as an alternative tool to wet coating and it has taken much attention. It could be applied with high mixers, vibrating mills, planetary ball mills as well as jet mills (Ding et al., 2007; Jeong et al., 2009; Lefebvre et al., 2010; Sato et al., 2012; Hait and Chen, 2014).

Ding et al used sodium stearate (SDS) merged with the wet ultra-fine grinding simultaneously, and then filled into polyethylene (PE) for calcium carbonate modification. The wet ultra-fine grinding displayed a significant effect on the modification as the active rate reached up to 98% which is three times that of non-ground particles. Also, SDS dosage was much lower than the conventional surface modification method (Ding et al., 2007). Similar results were obtained in GCC modification with poly(acrylic acid, sodium salt), which revealed that mechanochemical modification was helpful to prevent the agglomeration of particles and promote the dispersion of GCC particles in the polymer (Cho et al., 2009).

Deepika et al used Stearic acid (SA) to modify CaCO_3 powder via the ball milling method. The CaCO_3 hydrophobicity was greatly improved due to the contact angle of water on the modified CaCO_3 was nearly 100° compared to 59° for unmodified CaCO_3 (Deepika et al., 2014). The investigation of the effects of various modifiers such as stearic acid, oleic acid, palmitic acid, salicylic acid, and oleyl amine were employed (Deepika et al., 2013). The results displayed that the maximum thickness of coating on CaCO_3 particles was 16.3 nm obtained by ODSA (octadecenyl succinic anhydride) modification, followed by stearic acid with a value of 3.35 nm. However, there was no coating on the CaCO_3 particles modified by salicylic acid because of the weak reactivity between salicylic acid and CaCO_3 .

Sodium oleate was demonstrated to be chemically adsorbed on the surface of CaCO_3 particles and form the calcium oleate coating (Yoğurtcuoğlu and Uçurum, 2011).

Mechanochemical modification via milling technology is necessary for gaining better modification effect toward CaCO_3 powder in comparison with traditional modification. Various polymer modifiers are needed to be employed for CaCO_3 surface modification, and different molecular weights of polymer modifiers are required to be evaluated for the better modification effects (Li et al., 2021).

In this work, the effect of two milling methods on obtaining ultrafine calcium carbonate in the presence of modifying agents (polymers with different molecular weights) was investigated.

2. Materials and methods

2.1. Materials

A pure calcium carbonate sample (99.3%) was supplied by El-Minya, Egypt. Dry and wet grinding was carried out using planetary and attrition mill, respectively to get a suitable size for coating process. The polyacrylic acid and polyamide from Aldrich Company were used as dispersants. Analytical grade sodium hydroxide and hydrochloric acid solutions were used as pH regulators.

2.2. Methods

2.2.1. Ultrafine Grinding of Calcium Carbonate Sample

2.2.1.1. Dry Milling

Dry milling was carried out using a planetary mill. 50g of sample was primarily ground by high impact of grinding ball and in part by friction between the balls and the wall of grinding bowl. The grinding bowl with feed and balls rotate around their own is in counter-rotating planetary disc. The grinding was performed at 200 rpm during 2 hours for all experiments. The centrifugal forces are caused by rotation of grinding bowl and supporting discs. The force resulting from rotation of grinding bowl when mill at starting is causing rub the balls against the inside wall of the bowl. Thus, the grinding material and the influencing factors such as mill speed and ball size were studied (Mourad et al., 2019).

Table 1. Variation of calcium carbonate characteristics

Typical Properties of Calcium Carbonate	
Density	2.7-2.9 g/cm ³
Specific surface area	5-24 m ² /g
Particle size	0.2-30 μm
Water suspension pH	9.0
Oil absorption	13-21 g/100 g

2.2.1.1. Wet Milling

Grinding time plays an essential role in achieving ultra-fine grinding; therefore, it was the most important studied factor (Mourad et al., 2019). The wet grinding of calcium carbonate was carried out using a vertical laboratory attrition mill, "Union process attrition mill model 1S". It consists of a stainless-steel vessel of 9.5 liters capacity, lining with special rubber. It accompanied with a stainless-steel shaft fitted with five arms of stainless-steel. The shaft is belt driven by a motor of 3HP. The tank is water jacketed for cooling and it includes a bottom discharge valve, and bar grid. The grinding process was carried out by mixing 2.5 kg of the sample with 4 liters of water and 5 kg of 4 mm alumina balls. The latter was subjected to grind for different time to reach a particle size of less than 50 microns as a desired size. The product was dried, weighted and loss of ignition was determined. Grinding time plays an essential role in achieving ultra-fine grinding; therefore, it was the most important studied factor (Mourad et al., 2019).

2.2.2. Surface Coating of Calcium Carbonate

The rheological and physical properties of aqueous suspensions of calcium carbonate particles were investigated using different types and concentration of polyelectrolyte such as polyacrylic acid and polyamide. 50 ml of calcium carbonate suspension was added with 50 ml of different polymer concentrates during 20, 30, 60, 120 and 180 minutes. Suspensions with different volume% were carried out at many shear rates and shear times. The effect of conditioning time on the polyacrylic acid adsorption and zeta potential of the calcium carbonate were studied.

2.2.3. Characterization of untreated and treated Samples

- The morphology of the samples, before and after chemical treatment with polymers, was examined using scanning electron microscope (JSM-6400 type) (Abdel-Khalek et al., 2015; Mourad et al., 2019; Selim et al., 2020).
- The particle size distribution of the sample was determined using a laser particle size analyzer (Fritsch model Analysette) (Somasundaran et al., 2000; Abdel-Khalek et al., 2015).
- FTIR spectra "Model FTIR 6300" was carried out for calcium carbonate before and after treatment. The washed dry sample was analyzed using KBr pellet method (Somasundaran et al., 2000; Abdel-Khalek et al., 2015).
- Routine chemical analysis of samples was conducted using standard methods. Loss on ignition was determined by gravimetric method (Abdel-Khalek et al., 2020). Meanwhile, X-ray fluorescence (XRF), Philips model, was used for complete chemical analysis of the samples.
- Adsorption tests were conducted by addition of a 0.5gram sample to 50 ml of double distilled water and a required concentration of dispersing agent or polymer. After conditioning the pulp for the equilibrium time, the samples were centrifuged at 15,000 rpm during fifteen minutes to separate the supernatant from the settled fraction. The total organic carbon analyzer, Phoenix 8000, was used to measure the residual concentration of TOC content in 40 ml of the supernatant (Somasundaran et al., 2000; Abdel-Khalek et al., 2014; Abdel-Khalek et al., 2015; Selim at al., 2020; Abdel-Khalek et al., 2020; Hassan et al., 2020).

- The viscosity measurement of aqueous calcium carbonate suspensions was carried out by slow addition of the needed amount of the dry powder to an aqueous polymer solution under controlled stirring. Then, the suspension was transferred to a viscometer (Model DV-3P) for measurement. Temperature of slurry was kept constant in all tests at 25°C (Somasundaran et al., 2000; Abdel-Khalek et al., 2015).
- A laser Zeta Meter 'Malvern Instrument Model 2000' was employed for zeta potential measurements. A 0.01g of grinded sample was placed in 50 ml double distilled water with certain suspension concentration at definite ionic strength (2×10^{-2} M NaCl). A 0.1 M solution of sodium hydroxide and hydrochloric acid were utilized as pH modifiers. The suspension was conditioned for 30 min under pH control. The final pH was recorded after shaking. The supernatant was allowed to settle for 3 min, and then a 10 ml of it was transferred into the standard cuvette of the zeta potential measurement. Solution temperature was kept at ($25^\circ\text{C} \pm 2$). Three measurements were taken and the average was reported as the measured zeta potential (Abdel-Khalek et al., 2020).
- The optical properties include brightness and whiteness was determined by using "UV whiteness and color-meter model JY 9800". About 10 g of the dried sample for two hours at 105°C was compressed in a powder mold. The smooth surface of compressed sample disc exposed to UV lamp in the measuring port. The equipment is connected to the computer and printer for out put the results.

3. Results and discussion

3.1. Characterization of Calcium Carbonate Sample

XRD of the representative sample showed that the ore sample is mainly composed of calcite mineral, Fig.1. It was confirmed by XRF analysis which indicates that the sample contains more than 99.3% CaCO_3 with about 97% whiteness, Tables 2 and 3.

Table 2. Chemical analysis of calcium carbonate ore

Item	%
CaO	57.5012
SiO ₂	0.2791
Al ₂ O ₃	0.0885
Fe ₂ O ₃	0.0357
MgO	0.0858
Cl	0.0075
P ₂ O ₅	0.0877
SO ₃	0.0203
SrO	0.0277
L.O.I.	41.8665
Total	100

Table 3. Optical properties of calcium carbonate

Whiteness (%)	96.93
Brightness (%)	91.49

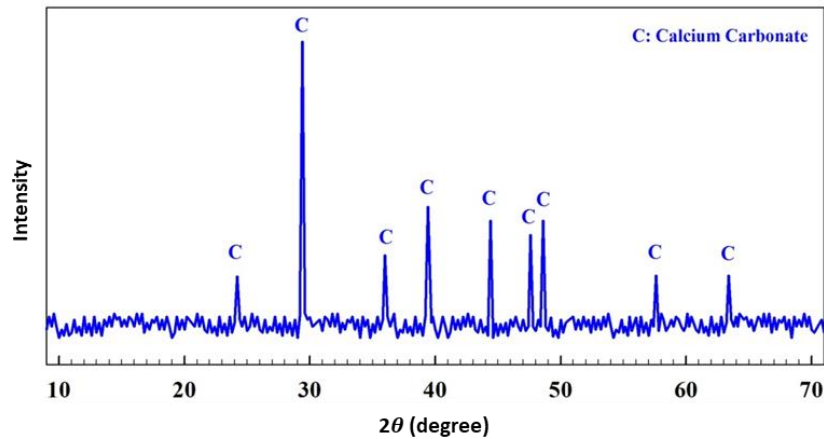


Fig. 1. XRD pattern of calcium carbonate sample

3.2. Ultrafine Grinding of Calcium Carbonate Sample

3.2.1. Parameters of the Planetary Mill

3.2.1.1. Effect of Balls Number

The grinding process was carried out using a planetary mill at speed of 100 rpm for 30 min in the presences of different number of balls. The increasing of balls number increases the ultrafine ground product. There was no significant effect on grinding efficiency in case of 2 balls while the ultra-fines were detected in the presence of three and four balls, Fig.2. This due to increasing of ball-ball contact as milling media. Thus, the intensity of collision became the determining factor. The two balls, are no sufficient to provide the necessary number of ball-ball collisions to achieve efficient grinding (Kolcsár and György, 2022).

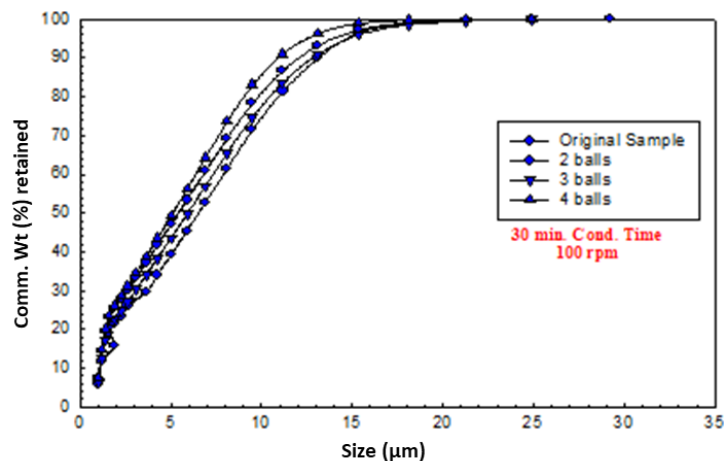


Fig. 2. Effect of number of balls on size distribution of calcium carbonate at 100 rpm

3.2.1.2. Effect of Speed

Increasing of the mill speed, increased the grinding leads to less particle size and the ultrafine grinding of calcium carbonate would be achieved. At speed of 150 rpm with 4 balls, the ultrafine ground product was achieved, Fig.3. The mill speed affect the contact force, thus the collision intensity increases with the mill speed. This confirms our interpretation of the results presented in Fig.3. that the low speed provideslower collision intensity, whichcan be compensated by the number of collisions. The higher speed produced more heat by friction and collision, thus the system might warmup at a higher rate, which expecte slightly lower grinding (Gitau et al., 2019). This may lead to the conclusion that the activation of the reaction highly depends on the energy generated by the collision number of the grinding media (Plessis et al., 2008).

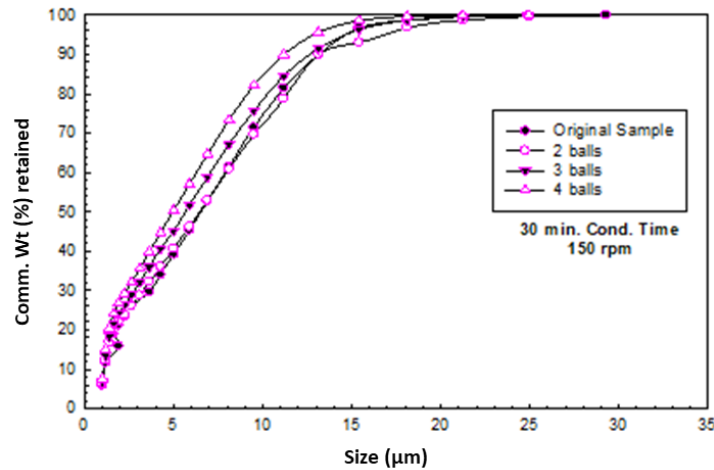


Fig. 3. Effect of number of balls on size distribution of calcium carbonate at 150 rpm

3.2.1.3. Effect of Grinding Time

The grinding process was carried out for different time range from 15 to 60 min at 150 rpm in the presence of 2 balls. Fig.4 shows the size distribution of calcium carbonate at different time. The milling process is expected to decrease particle size with time. However, the particle size decreases until a stationary point is reached, where further milling does not result in a decrease in particle size. A similar scenario was reported (Ikumapayi et al., 2019). However, consideration should be given to the milling time to preserve the microstructure as well as the particle size of the calcium carbonate.

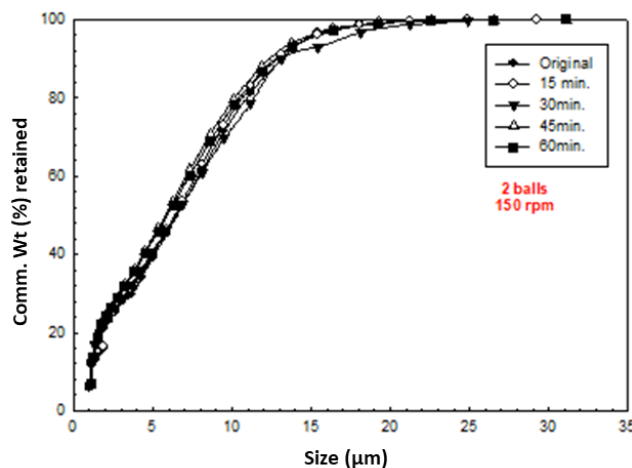


Fig.4. Effect of grinding time on size distribution.

3.2.2. Parameters of the Attrition Mill

3.2.2.1. Effect of Grinding Time

The grinding in the attrition mill was carried out for different time range from 1 to 4h. Fig.5 represents the results of size distribution of grinding products at different time. After 1 hr, the product of [D50: 3.04 μm , D90: 6.37 μm]. After 2 hrs product [D50: 2.92 μm , D90: 6.18 μm]. After 3 hours Product of [D50: 2.76 μm , D90: 5.36 μm]. After 4 hrs Product of [D50: 2.54 μm , D90: 4.80 μm]. It has been seen that with increasing grinding time leads to decreasing size of calcium carbonate but product results after 1h meets the specifications of coating process.

The effect of milling time is essential in determining the final particle size. The particle size distribution controls the effect of water demand and workability, which in turn affects its activity. Milling changes both the particulate nature as well as the microstructure of substances, which affects the coagulate characteristic. A significant number of studies reported that the physical and surface properties were modified by chemical additives (Ikumapayi et al., 2019).

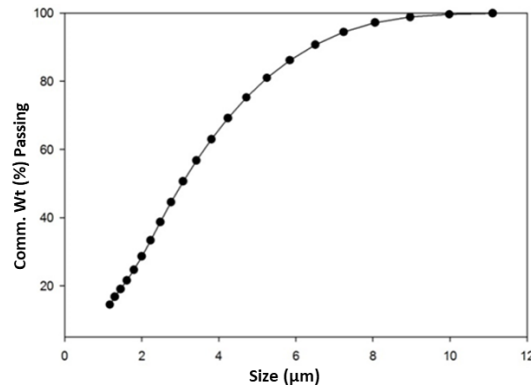


Fig. 5. Effect of grinding on size distribution of calcium carbonate for 1hr

3.3. Surface Coating of Calcium Carbonate

3.3.1. Effect of Polymers on Surface Properties

The effect of polyelectrolyte as PAA (Polyacrylic Acid) on the rheological characteristics of calcium carbonate aqueous suspensions was investigated. The adsorption kinetics explain fast adsorption as equilibrium could be reached in 60 min as shown in Fig.6(a). It is obvious that the PAA molecules adsorb extensively on calcium carbonate surface which reverse the surface charge to negative, Fig. 6(b). The minimum value of zeta potential is occurred at about 50 ppm PAA, after which subsequent PAA additions lead to a slight decrease in zeta potential. The surface charge of calcium carbonate is almost zero in the presence of 5 ppm PPA, regardless of ionic strength, Fig. 6(b).

The effect of polymer addition on the size distribution of calcium carbonate is shown in Fig. 6(c); which confirmed that there is a change in size of calcium carbonate on addition different concentrations of PAA. For different types and concentrations of polymers and all of these experiments confirmed that there is a change in the mean particle size of calcium carbonate and in turn confirmed the success of coating process as shown in Figs. 7 and 8.

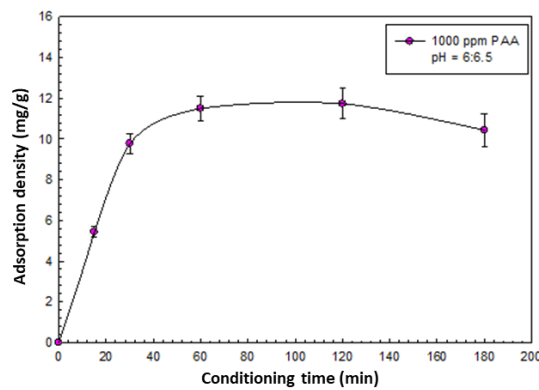


Fig. 6(a). Effect of conditioning time on adsorption of PAA (MWt 1800) onto calcium carbonate

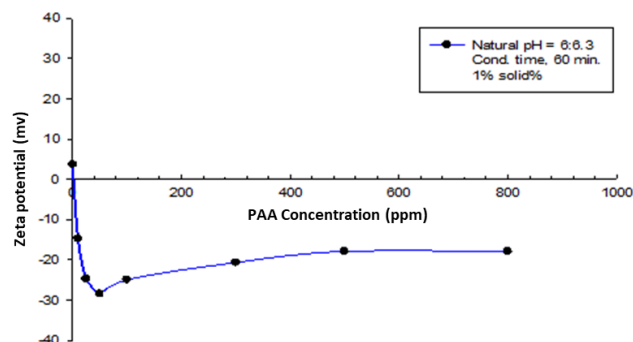


Fig.6(b). Zeta potential of calcium carbonate in the presence of PAA

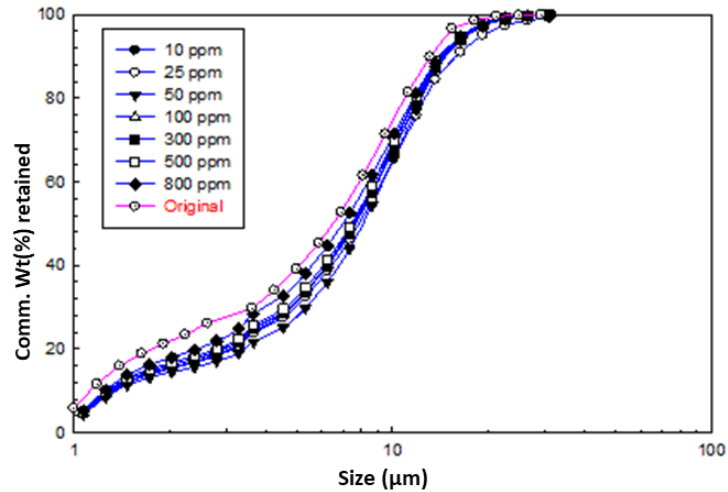


Fig. 6(c). Effect of PAA concentration on size distribution of calcium carbonate

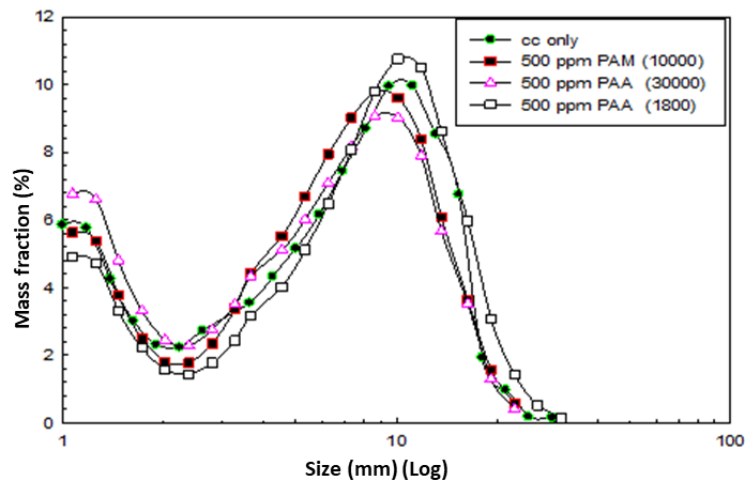


Fig. 7. Effect of polymer type on size distribution of calcium carbonate in the presence 500 ppm polymer.

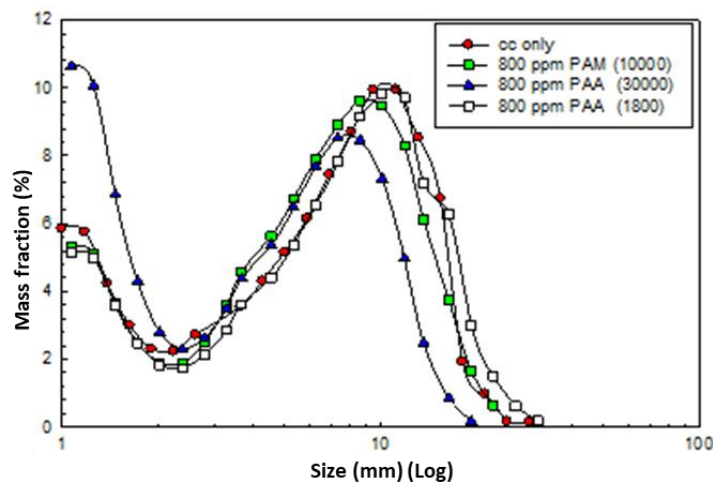


Fig. 8. Effect of polymer type on size distribution of calcium carbonate in the presence of 800 ppm polymer

3.3.2. Effect of Polymers on the Physical Properties

Suspensions with different volume % were carried out at many shear rates and shear times. Fig. 9 shows the viscosity of calcium carbonate suspensions without additives increases on increasing the volume

percentage or weight percentage of CC. These results are confirmed through study of the adsorption behavior of polymers onto calcium carbonate particles. The shear flow characteristics of aqueous calcium carbonate suspensions were performed in the absence and presence of polyelectrolyte. Fig.10 displays the stability of calcium carbonate suspensions' viscosity at different concentrations of polymer after 12 min where there is a continuous increase in the viscosity upon increasing the polymer concentration.

The relationship between the apparent viscosity at low shear rate (30.59 S^{-1}) and polymer concentration in the suspensions with PAA at volume fraction of 21.43% shows that the viscosity decreased drastically with increasing polymer concentration. It was minimal when the polymer was added at concentration of 0.26-0.67 Wt% as shown in Fig.11. This confirmed that all suspensions show shear thinning. Also, the absolute value of the zeta potential increased as the polymer concentration was increased and reached an equilibrium value where the change in zeta potential corresponded to the adsorption behavior. Therefore, it can be considered that the particles in PAA suspensions are electrostatically stabilized by the anionic charge of PAA.

On the other hand, it may be due to the lack of additional hydrogen bonds between the hetero atom and groups of the polymer, which may promote faster hydrogen transfer and improvement in the stereoselectivity. The decrease in the enantioselectivity of the mechano-chemical may be due to the increase of the temperature at the collision points. These results may be interpreted analogously, considering the same steric and electronic effects of the substituents. However, the benefit of using mechano-chemistry resides in the much more efficient energy transmission to the catalyst-hydrogen donor-reactant system, which results in the decrease of the reaction time (Kolcsár and György, 2022).

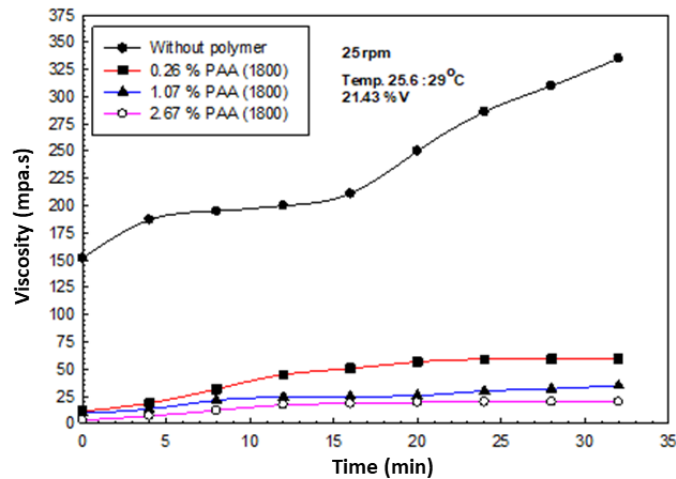


Fig. 9. Effect of shear time on the viscosity of calcium carbonate suspension as a function of PAA concentration

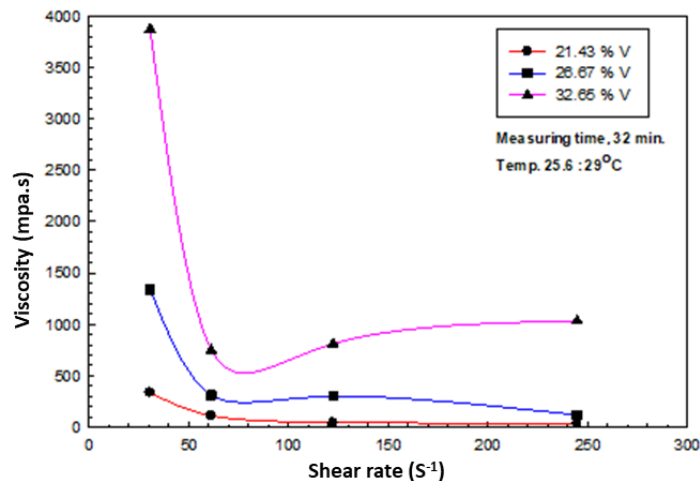


Fig. 10. Effect of shear force on the viscosity of calcium carbonate suspension at different volume

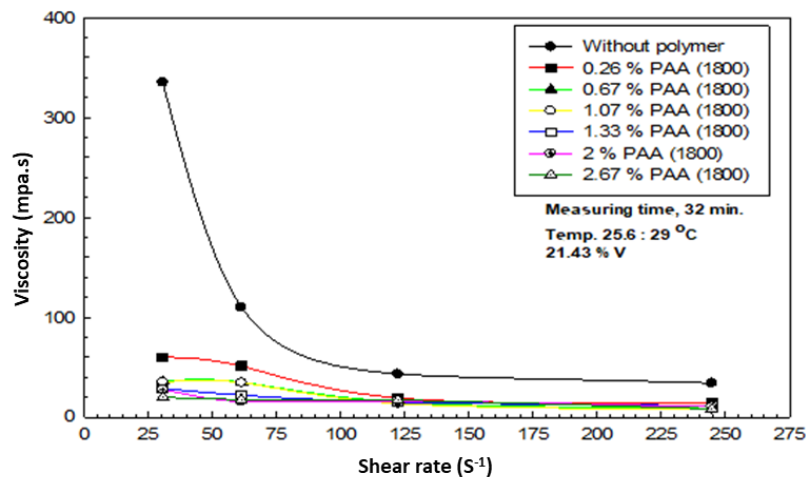


Fig. 11. Effect of shear force on the viscosity of calcium carbonate suspension as a function of PAA concentration

4. Conclusions

Calcium carbonate grinding process was carried out using planetary and attrition mills. During milling, the intensity of collision was considered as the determining factor and also increasing of the mill speed, increased the grinding leads to less particle size and the ultrafine grinding would be achieved.

Polyacrylic Acid 1800, Polyacrylic Acid 30000 and polyacrylamide 10000 were used as additives to prevent the aggregation of the particles during grinding process. The application of polymers with different molecular weights was studied to evaluate the effect of the molecular weight on the behavior of dispersion. The mean particle size of calcium carbonate was changed on addition of polymers which in turn confirmed the success of coating process.

The additives reduce the suspension viscosity and maintaining the particles in a dispersed state. The additive amount depends on the required of the product fineness and the desired dispersion state. The dispersing agent increases the solid concentration for a given particle fineness.

Shear flow properties of concentrated calcium carbonate suspensions could be explained by the repulsive forces conferred by the polymer adsorbed to the particle surface. The effect of PAA on the dispersibility is more pronounced by the steric hindrance behavior rather than the electrostatic behavior.

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