The Study of Dielectric and Microstructure Properties for Iraqi Kaolin Under the Effects of Binder and Calcinations.

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Abstract:

The calcination treatments and a binder of poly acrylic acid PAA (1wt%) effects on kaolinite particles were investigated through dielectric properties at 1MHz ,quantitative analysis of X-ray diffraction and microstructure. The calcinated samples at 850°C/3hr and fired at 1350°C/2hr were revealed decrease in broadening (Full Width at half maximum) FWHM and increase of dielectric constant.

Keywords: Kaolin Duekhla, Poly acrylic acid (PAA) , calcinations ,microstructure.

دراسة الخواص العزلية والتركيبية للكاؤولين العراقي تحت تأثيرالمادة الرابطة وعمليات الكلسنة

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الخلاصة:

ان المعاملة تحت تأثيرعمليات الكلسنة (التحميص) والمادة الرابطة بولي أكرلك أسد (1wt%) على حبيبات الكاؤولينيت تمت دراستها من خلال الفحوصات التشخيصية للاشعة السينية والمجهرية والقياسات العزلية وتبين ان العينة المكلسنة عند 850م°لمدة 3ساعات والملبدة الى 1350 م°لمدة ساعتين امتازت بنقصان في التعريض عند منتصف الشدة (FWHM) وزيادة في ثابت العزل.

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Introduction

Cracks behind the drying process forming problems, and machining difficulties through the manufacturing of commercial insulators that have always been attributed to poor plasticity of the body .It was proposed that by adjusting dispersant addition ,the plasticity of the clay under study can be optimized [1,2].The improvement of plasticity allows for extrusion at lower water contents, which reduces shrinkage and the possibilities for cracking.Plastic ,properties of clay suspension depend affectively on particle-particle interactions.Polyelectrolytes modify this interactions, which acts as dispersants [1,3].Polyelectrolyte are often used to prepare highly concentrated dispersions of particles of heterogeneous surfaces such as kaolin of controlled viscosity and stability. Many works had done in this field , such as [4-7].In present study we examined the performance of a poly acrylic acid (PAA) as scale formation inhibitors and dispersants in such systems(kaolin).

Experimental Work

Iraqi kaolin Duekhla asensed as a raw material .The chemical composition is listed in table 1 .

Table 1- Chemical composinion of the used kaolin clay

Oxide	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	SO_3	Na_2O	K_2O	L.O.I
(wt%)	52.35	1.31	34.02	0.12	1.2	1.11	0.45	-	-	12.54

Kaolin after milling and sieving process, the selected particles size are (D)<250 µm . Calcinations process applied to temperatures of 450 ^oC ,850 ^oC for one hour each,and 850 ^oC for three hours consequently .Then ,followed by milling and sieving to select the required particle size as sown in table 2 .

Table 2- The samples and their preparation conditions.

Kaolin material treatment	Calcinations temp(°C)	Untreated	450	850	850
	Calcinations time(hr)	—	1	1	3
	Particle size(µm)	D<45	D<45	D<45	D<45
	Poly acrylic acide(wt%)	1%			
Sample No.		A1	A2	A3	A4
Sintering conditions (for all samples)	For 2hrs	1250°C 1300°C 1350°C			

Poly acrylic acid supplied by BDH Company, with high purity of 99.99% , where the FTIR spectrum is shown in figure.

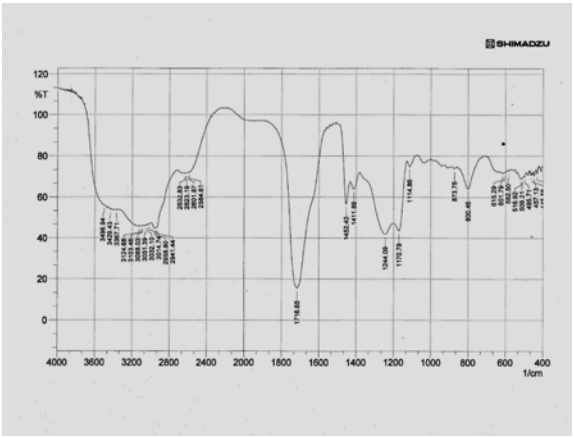

Figure 1- FTIR spectra of Poly acrylic acid **.**

The samples were prepared by wet mixing of kaolin and a poly acrylic acide (1wt%) , and then semi drying, the composition well milled to pass through a sieve of mesh size 250 µm to make them as agglomerated powder. Selected amount of powder was placed in a steel die and compacted at 100 MPa for 60 sec. The compacts samples of 25 mm in diameter and about 3mm in the thickness are obtained by

using programmable Electrical press (model, 3888,4D10A00,CARVER-Inc,USA).

The resulted green body, were dried at temperature 100^{o}C over night by using electrical oven, to remove the residual moisture. A programmable Electric Muffle Furnace (model, Nabertherm HT62Ti7 ORZ ,Germany) was used for firing process to the temperatures (1250 , 1300 and 1350) ^{o}C respectively, holding them at that temperature for two hours. When required soacking time is completed, the furnace turn off and kept them into a furnace to cool down to the room temperature.

The dielectric properties and microstructure were studied for Iraqi kaolin Duekhla under the combination effects of calcination conditions and poly acrylic acid as a binder. The parallel capacitance (C_P) and resistance(R_P) as a function of frequency were measured by using the HP-R2C unit 4274A LCR meter (Hewlett-Packard, USA) in the range of 100 KHz–10 MHz and the Agilent 4275B LCR meter (Agilent Technologies Japan, Ltd.) in the rangeof 1 KHz–100 kHz.

The dielectric constant (ε') and dielectric loss factor(ε") are calculated by using the following eq's[10]:

$$\varepsilon' = (1/\varepsilon_0)(d/A)C \quad (1)$$

$$\varepsilon'' = d/\omega\varepsilon_0 A R_p \quad (2)$$

Where ε_o the permittivity of a vacuum, d is the thickness of the samples , A is cross section area of the samples ,C the capacitance of dielectric material and ω the angular frequency. .

The structure of calcinated kaolin and fired ground powder of selection prepared samples identified by powder X-ray diffraction technique by using the diffractomete Shimadzu X-Ray Diffraction unit Model (6000) with the characteristics , target Cu ,wave length (λ) =1.5405 A , speed 5 deg/min, filter Ni ,voltage 40 (KV), current30(mA). Microstructure observations carried out on freshly fracture polished of selected samples with scanning electron microscopy SEM (Te scan Vega).

Results and discussion

Table 3 and Figure 2: revealed FWHM related with calcination temperatures**.**

Table 3- Broadening (FWHM) at calcinations temperatures and loss factor with firing temperatures.

Sample No.	FWHM (deg)	Firing temperature °C for 2hours		
		1250	1300	1350
		Loss factor ε''		
A1	0.2599	0.544	0.192	0.740
A2	0.26010	0.642	0.274	0.672
A3	0.24880	0.538	0.145	0.675
A4	0.2571	0.732	0.300	0.121

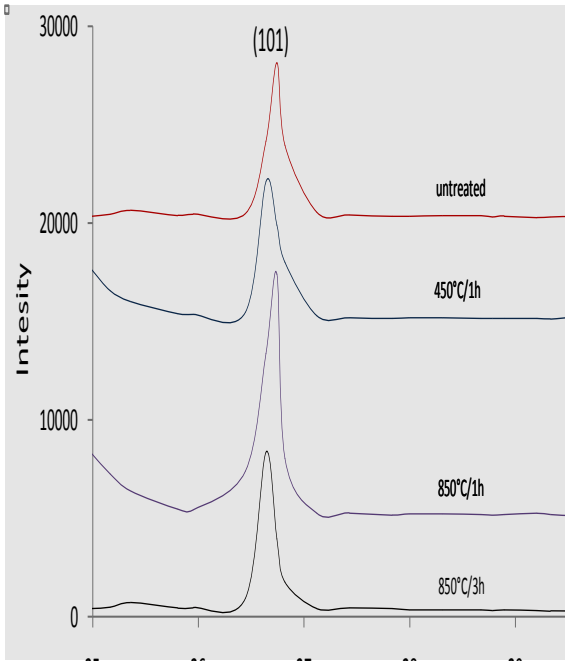

Figure 2- Illustration of X-ray line broadening for calcinated kaolin.

Which noted that raw clay (kaolin) was attacked only slightly at room temperature . The first Decomposition reactionsin kaolinitic is dehydroxylation in the region of its decomposition temperature (circa 500˚C) [8].

So that The samples A1 and A2 were showed stability of FWHM with calcinated

temperatures. On the other hand, the calcined sample at 850˚C/1h reflected strong decrease in FWHM as showed in table 3 which that due to decomposition, which is marked as 500˚C of calcined clay to the partial recrystallisation of alumina to the γ-form after exceeding decomposition temperature, i.e. 500˚C. When kaolinite was heated to about 940˚C approaching the temperature of the exotherm noted in DTA Figure 3 [9]

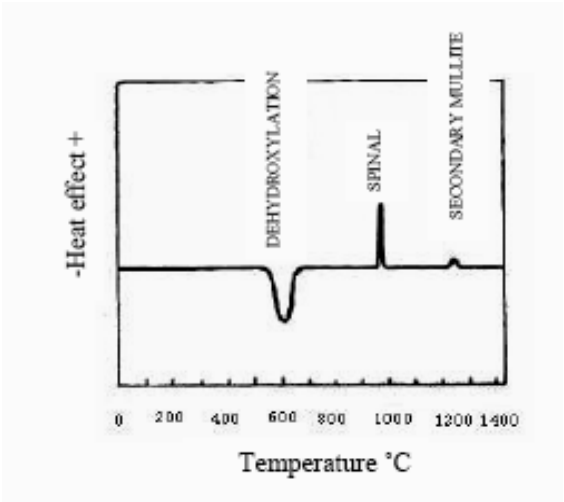

Figure 3- Differential thermal analysis curve for pure well crystallized kaolin[9].

The meta –kaolin suddenly crystallizes into a spinel structure . and its quickly breaks down into mullite as shown in Figure 3,which reflected to the disappearance of most of the chemical activity [8,10]. The sample A4 which treated at 850˚C/3h revealed increase of FWHM refer to the chemical reaction degree and progressive crystallization to mullite phase as observed by Kingery et al. [10]. Also, the presence of impurities of Halite and sintering oxides of (potassium, calcium and sodium) which have effective of chemical reaction degree, and consequently lead to changes in FWHM values[8].

FWHM corresponding to firing temperatures were plotted in Figure 4

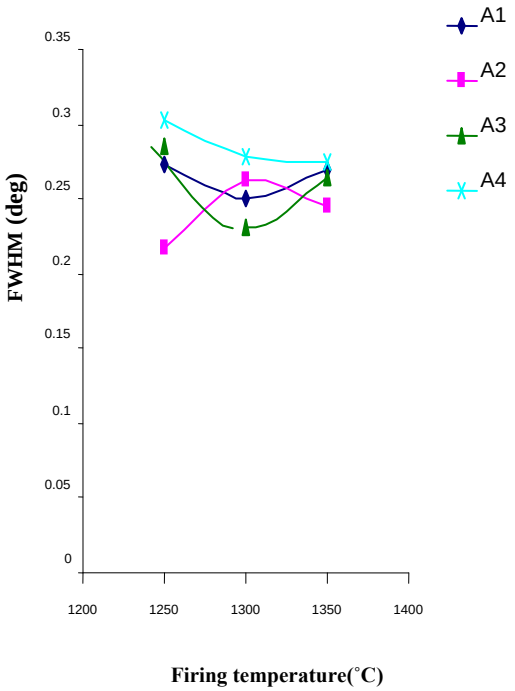

Figure 4- X-ray line broadening (FWHM) with firing temperatures.

Which exhibited the effect of firing process on compacted samples at 100 MPa, where values of FWHM at firing temperature 1250˚C were changed from 0.31 to 0.22, furthermore, at 1350˚C the broadening decrease form 0.27 to 0.25, for calcined samples A4 at 850˚C/3h and A2 at 450˚C/1h respectively, this reflect to solid state reactions which was occurred a new phase transformations as revealed by the quantitative analysis of X-ray diffraction in figure 5(a-d) ,and the microstructure using SEM for sample A4 fired at 1350˚C as shown in figure 6 Higher temperatures lead to particle coarsening and a corresponding decrease in broadening [11].

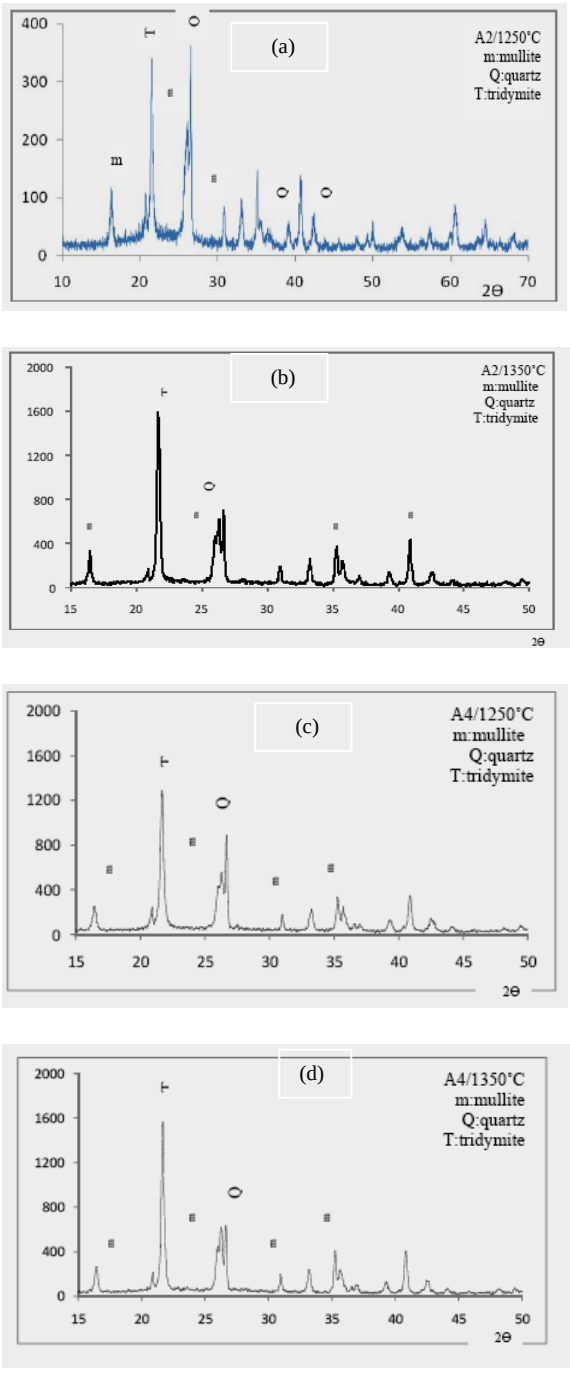

Figure 5- (a-d) XRD patterns for the fired samples A2 and A4 at 1250˚C and 1350˚C for two hours

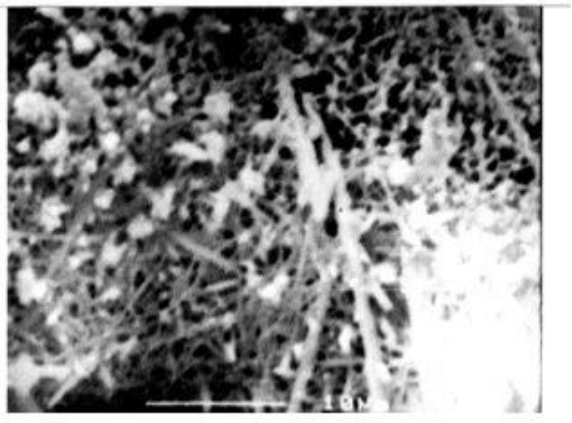

Figure 6-SEM observation on fracture of sample A4 fired at 1350˚C for two hours**.**

The outstanding feature of Poly acrylic acid (PAA) as a binder when solute in water at natural pH many of the side chains will lose their protons and acquire a negative charge. So it was deflocculates as polyelectrolyte solution [11]. The effect of electrolyte solution in clay structure is to disperse medium which implies to the homogeneous and densifiy structure [12,13].Consequently, the results of FWHM were stable with firing temperature as increased from 1250-1350˚C interval i.e 0.3035 to 0.2747 for calcined samples at 850˚C/3h (A4) .

Figure 7 shows the highest value of dielectric constant at 1MHz for sample A4 fired at 1350˚C for two hours, the reason behind this result ,poly(acrylicacid) acts as dispersant, in this case , The particles are more readily dispersed in water when (PAA) are present, through their active electrolyte behaviour on the surface of the particles (that makes them hold onto water), the repulsive forces between particles are promoted , creating a deflocculated matrix with low viscosity through preparation process of batches[1,14]**.**

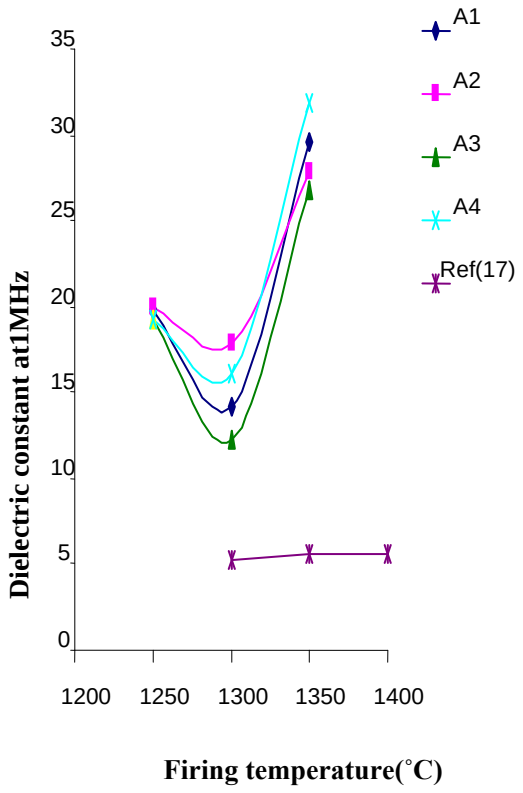

Figure 7- Dielectric constant at 1MHz corresponding to Firing temperature.

The loss factor as illustrated in table 3 reveal that for sample A4 fired at 1350˚C for two hours have highest value at frequency of 1 MHz , may be attributes to size of the mullite crystals which that growth with the heat - treatment, whereas, the boundaries between mullite crystals are considered to paths that allow dissipation of current from the sample. The number and length of such boundaries or continuous paths also called the mean free-paths control uninterrupted flow of current through the sample in a manner so that longer boundaries constitute longer mean free- paths resulting in more current and dielectric loss . Longer mean free-paths are formed by bigger mullite crystals. The loss factor of the sample, therefore, increased with the rise in mullite crystal size, as observed by Chaudhuri and Sarkar [15]. It is noticed from table.3 the results of loss factor for groups fired at 1300˚C for two hour are approximately low, compared with other conditions, refer to remain quartz crystals which consider as discrete insulating particles (defect free structure) in sample matrix [16],coincidence rearrangement of particles to give a more effective packing. Also, the results was compared with Ref.[17] which used PVA(Poly vinyl alcohol)as a binder with same raw material that is kaolin, its show present results have a higher values of dielectric constant

Conclusions

Using PAA as a binder in 1wt% with local kaolin of particle size D<45 µm calcinated sample at 850˚C/3hr and fired at 1350˚C for two hours, shows decrease in broadening (FWHM), and increase of 5 times in dielectric constant values compared with that using PVA as a binder with out calcinations.

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