Studying the effect of temperature and treating time on some physical properties of carbon black

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Abstract

Samples prepared by using carbon black as a filler material and phenolic resin as a binder. The samples were pressed in a (3) cm diameter cylindrical die to (250)MPa and treated thermally within temperature range of (600-1000)^{o}C for two and three hours. Physical properties tests were performed, like density, porosity, and X-ray tests. Moreover vicker microhardness and electric resistivity tests were done. From the results, it can be concluded that density was increased while porosity was decreased gradually with increasing temperature and treating time. In microhardness test, it found that more temperature and treating time cause more hardness. Finally the resistivity was decreased in steps with temperature and treating time. It can be concluded that these variables may increase the graphitizing degree, and minimizing in interplanar distance for samples comparing with ideal one, when these variables may increased.

Key words
Thermal fragmentation, Infusible, Heat treatment.

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دراسة تاثير درجة الحرارة وزمن المعالجة على بعض الخصائص الفيزيائية لاسود الكاربون

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الخلاصة

في هذا البحث تم تحضير عينات من أسود الكاربون و صمغ الفينول فورمالدهايد كمادة رابطة بعد كبس المزيج في قالب اسطواني بقطر (3) سم وبضغط مقداره 250(MPa)، جرت معالجة العينات حراريا بمدى من درجات الحرارة (600-1000) درجة مئوية ولفترة ساعتين وثلاثة ساعات. تم دراسة الخصائص الفيزيائية للعينات من كثافة ومسامية وفحص الاشعة السينية، اضافة الى ذلك تم فحص صلادة فيكر للعينات . كما تم بيان تأثير التغير في قيمة المقاومية الكهربائية والخصائص التركيبية بدلالة المتغيرين درجة الحرارة وزمن المعالجة . من نتائج الفحص تم استنتاج ان الكثافة تزداد يصاحبها نقصان في المسامية بزيادة درجة الحرارة وزمن المعالجة، أضافة الى زيادة صلادة العينات مع هذين المتغيرين. اما في فحص المقاومية ، فقد وجد انها تقل تدريجياً مع درجة الحرارة وزمن المعالجة. وهذا يدل على ان هذين المتغيرين تزداد بهما درجة الكرفتة ، وتناقص الفرق في المسافات البينية للعينات مقارنة بالعينات المثالية بزيادة هذين المتغيرين .

Introduction

The demand for advanced carbon fibers, or graphite increased in the recent years and it is necessary for the progress requirements and civilization development. Therefore, the focus is now on carbon black uses in structural and classical applications because it has thermal resistance, wear resistance and moreover it properties are stable with temperature increase, it has advantage over metals.

Carbon black is a pigment made of carbon formed by the pyrolysis of gaseous hydrocarbons in a minimum of oxygen. In short, they burn natural gas, crude oil residues, without enough air so it makes a lot of soot (although carbon black is created under much more controlled circumstances than soot, so it doesn't have any of the impurities of soot). It comes as a fine black powder, in the form of spheres and their fused aggregates with particle sizes below 1000 nanometers.

It is also known as lampblack. Lampblack is, however, is not "carbon black", as it is created from a different process: the sooty burning of liquid hydrocarbons, such as kerosene. Varieties include acetylene black, channel black, furnace black, and thermal black. These vary by the exact process used in their manufacture, and subsequently have differences in their particle size, structure, etc.

It is used mainly as a reinforcing agent in rubber products such as tires, tubes, conveyor belts, cables and other mechanical rubber goods; used as a black pigment in printing, lithographic, letterpress, carbon paper and typewriter ribbon inks, paints, coatings, lacquers, plastics, fibers, ceramics, enamels, paper, record discs and photocopier toner; leather finishes. It is used in manufacture of dry-cell batteries, electrodes and carbon brushes; electrical conductors; conductive and antistatic rubber and plastic products; electromagnetic interference shielding; videodiscs and tapes; UV stabilization of polyolefins; and high temperature insulating material.

The process for its manufacture was invented by Wright, a Philadelphia ink maker, in 1864, though it wasn't mass produced until the 20th century with more advanced technology making it profitable[1].

The element carbon exists in three allotropic modifications, amorphous carbon, graphite, and diamond. Graphite is soft crystalline modification of carbon. It is a fairly natural crystal, its growth in natural environments has not been well understood yet [2], but it has observed experimentally during preparation of synthetic graphite.

Novolak is normally prepared by the interaction of a molar excess of phonel with for maldehyde (commonly about 1.25: 1) under acidic catalyzed conditions [3]. The cross- linked phenol-formaldehyde resin is rigid, infusible. Phenolic resin is not attacked by most organic solvents, weak acids and bases. The mechanical properties of network polymers are shown in Table (1).

In phenolic resins, pyrolysis is found to occur by three general processes;

1-Low temperature out gassing of free phenol present in the resin material.

2-Formation of water from post - cure reaction at 150 -300°C.

3-Thermal fragmentation of the polymer structure above 530°C to yield lower molecular weight species which are evolved, with hydrogen gas as the primary product (in the absence of oxygen at 700 $^{\circ}$C and above [4, 5].

This work aims at studying the carbon black electrical and mechanical properties heat treated at different temperatures and periods. A number of experimental techniques are proposed to be utilized like X-ray diffractometry, electric conductivity measurements, and mechanical testing.

Experimental Procedures

The preparing procedure consists of mixing powders of carbon black (0.5 μm), with (10% wt) novolak resin (62 μm), in a pot, and it will be well mixed for half an hour to ensure maximum homogeneity throughout the resin. The mixture is poured or placed in a cylindrical metal mold with (10) cm height and (2.2) cm diameter. Then the sample will be pressed with (250MPa), and cured in electric furnace at (150 $^{\circ}$C) for (2 hr) in free atmosphere. After that the sample leaved in the furnace after the power be cutoff. Ten samples are prepared following the same procedure.

Five of them are heat treatment at (600-1000° C) for (2 hr) in under vacuum to avoid oxidation, using crystal tube to install the samples, and rotary pump.

Other samples are heat treatment at same temperatures but for (3 hr), and will be leaved again in the furnace for (24 hr) to be cooled.

The samples are weighted before and after sintering. it is found that the samples that sintered for two hours have loose (7-11%) approximately, while for three hours, the loosen were (9-15) %.

Preparing many specimens from the samples with dimensions (3mm height, 22 mm diameter), using suitable saw, then grinding them in four stages, using different grinding papers, then it is followed by polishing process with polishing cloth.

1-X-ray diffraction examination

Using XRD -6000 Shimadzu, Japan type, this test was carried out to find, if there were chemical reactions between the phases of (black carbon-novolak) composite at different temperatures and periods.

It can be seen that crystal growth becomes more obvious in this plane, and bragg pikes become more intensity gradually with increasing temperature. Moreover, these pikes are shifted gradually to (26)° angle proving that the amorphous black carbon converted in percentage to graphite as shown in Fig.(1,a,b), and for comparing with the standard values from the ASTM cards for graphite. The planes (002), (004), (101), for the standard specimen that treated thermally at (1000°C), for three hours as shown a in Fig. (2). It can be noticed that (d) spacing decreased to 3.584 when the samples treated for two hours, and 3.496 for three hours for the same temperature, indicating the conversion percentage to graphite.

2-Density and Porosity Tests

The density and porosity for samples was determined according to Archimedes' method as in table (3. a, b) according to heat treatment conductions. It can be noticed, that the values of density and porosity are approximately near by the graphite one, and it gives a considerable notice of the graphitization percentage, and this approximation is increased gradually by increasing temperature.

3-Mechanical test

In this work microhardness apparatus was used type (HVS-1000) hardness tester, made in Japan, according to international specifications. ISQ9001, it has a large measuring range from soft to extremely hard. Micohardness test has performed on cylindrical samples. A relationship between temperature and hardness was plotted as shown in Fig. (3).

4-Electrical test

If a known drop voltage (V) across specimen, constant current (I) is passed through it , so the conductivity of the specimen is given by Eq.(1)

$$\sigma = \frac{V.A}{I.l} \qquad (1)$$

That A: cross-sectional area of the specimen

l: thickness of the specimen.

Conductivity depends on the degree of crystal disorder and geometrical factors such as porosity and relative distribution of different conducting phases in the matrix[6].

The heat treatment conductions affected on the specimen's conductivity, that the crystallization will be increased, and the opened pores will be closed gradually with temperature. Table (4) illustrates the electric conductivity variation with temperature for two and three hours. These values can be drawn as shown in Fig. (4), it can be noticed that there is a disagreement with Ohm's Law from nonlinearity between voltage and current, due to the residual percentage of novolak remaining in the samples, and this effect is minimized with increasing the temperature as in Fig. (5) . The effect of temperature can be noticed on conductivity

(than the period), as the temperature is increased , and this can be concerned in Fig.(6), which show the difference in conductivity values ($\Delta\sigma$) in two periods at the same temperature . The drawn curve obeys exponential function as:

$$\Delta \sigma = \sigma o \exp (T)$$

That σo : the conductivity of specimen at 600° C, T: temperature (°C)

Results and Discussion

1-From X-ray diffraction test , it can be seen that crystal growth becomes more obvious in (002) plane, and bragg pikes become more intensity gradually with increasing Temperature. Moreover, these pikes are shifted gradually to 26˚ angle, proving that the amorphous black carbon converted in percentage to graphite.

2-The density was increased gradually with temperature and time of heat treatment, while the porosity was decreased in the same manner.

3-It can be noticed that microhardness increased with temperature and time according that opened pore will be decreased or closed or semi-closed due to heat treatment.

4-The conductivity was increased gradually with temperature and time due to the residual percentage of novolak remaining in the samples is minimized with increasing temperature and the material will be more bulk and dense.

5-Moreover it can notice that increasing temperature is more effective than time in varying the properties of carbon black.

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Table (1): Mechanical properties of network phenolic polymer

Specific gravity	**3.1**
Tensile strength [Kg/m^2]	**21×10^5 - 703×10^5**
Bending strength [Kg/m^2]	**4921×10^3 -10545×10^3**
Compression strength[Kg/m^2]	**703×10^4 - 2009×10^4**

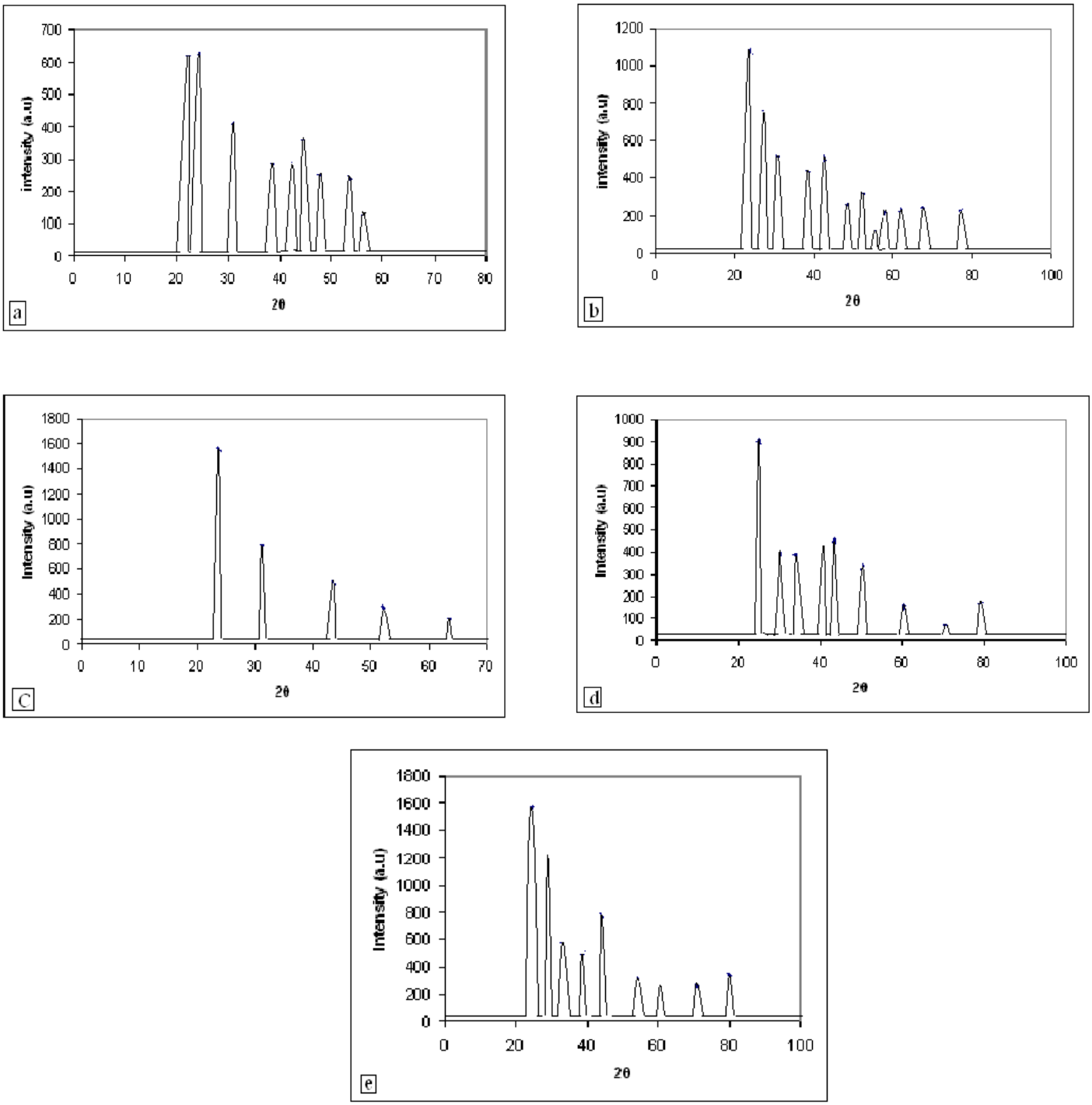

Fig.(1,a): X-Ray diffraction test for samples heat treated at (600-1000°C)for 2h.
(a) 600°C , (b) 700°C , (c) 800°C , (d) 900°C , (e) 1000°C

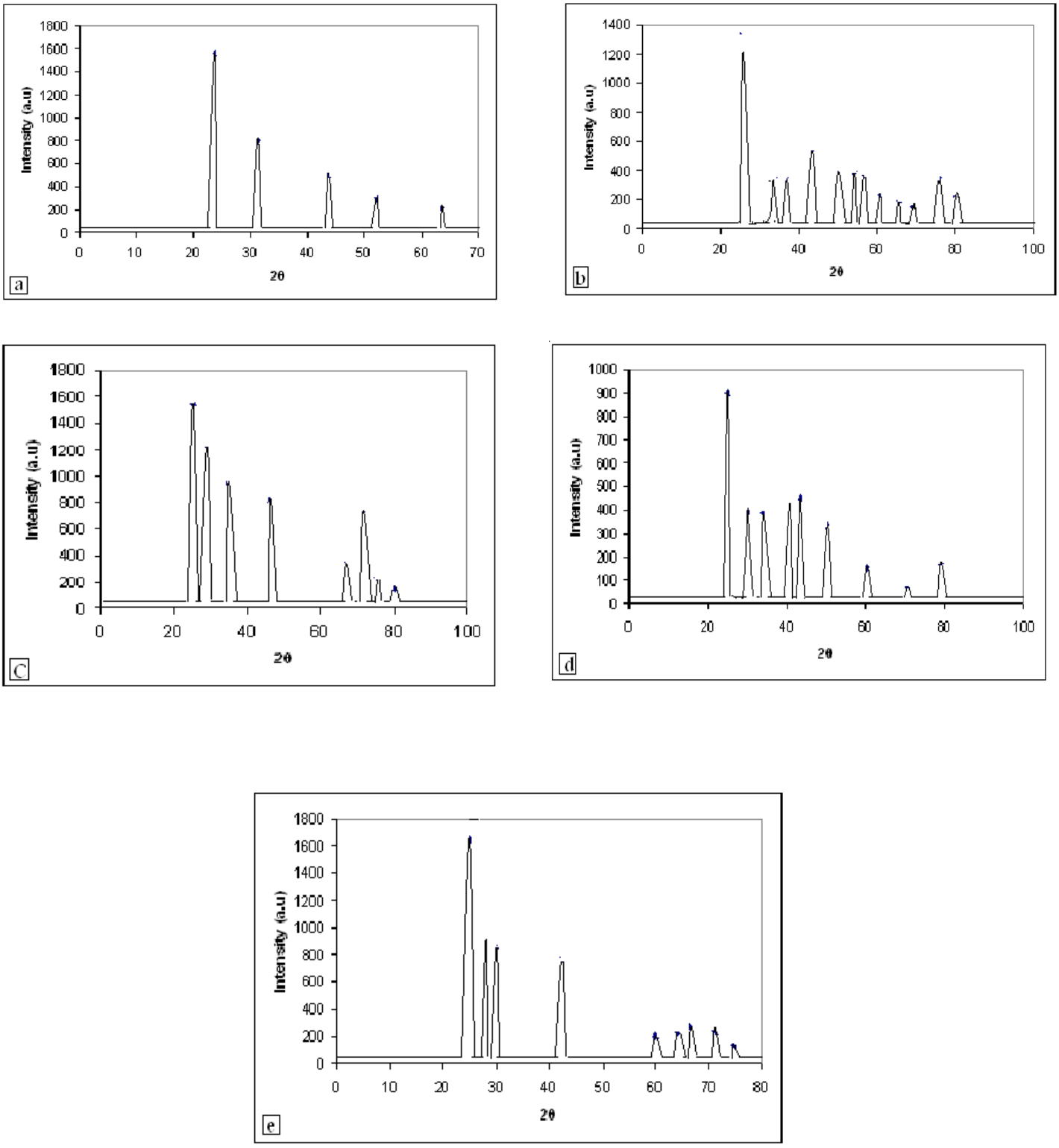

Fig. (1, b) : X-Ray diffraction test for samples heat treated at (600- 1000 °C) for 3h

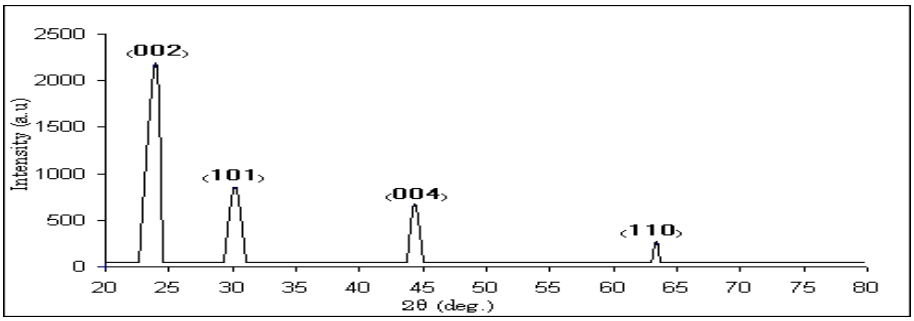

Fig.(2) : X-Ray diffraction chart for a sample sintering at (1000 C˚) for (3) hrs

Table (3,.a): Illustrate the density and porosity for samples sintered in two hours

samples	Density(gm/cm^3)	Porosity(%)
S1	**1.52**	**17.21**
S2	**1.57**	**17.47**
S3	**1.62**	**18.9**
S4	**1.65**	**18.7**
S5	**1.72**	**19.9**

Table (3, b): Illustrate the density and porosity for samples sintered in three hours

samples	Density(gm/cm^3)	Porosity (%)
S1	**1.58**	**18.2**
S2	**1.62**	**18.97**
S3	**1.72**	**18.95**
S4	**1.75**	**20.71**
S5	**1.76**	**21.93**

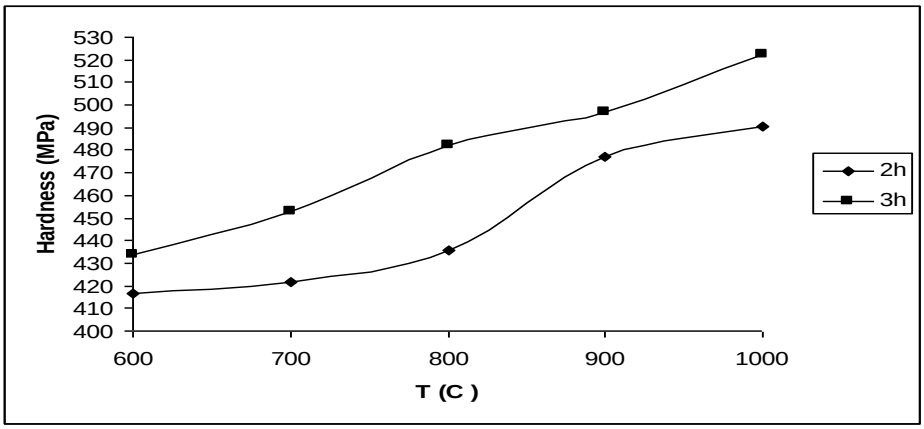

Fig.(3): The relationship between temperature and hardness

Table (4):Illustrate the relationship between conductivity against temperature for samples sintered in: (a) two hours,(b) three hours.

T (˚C)	σ at 2 (hr) (Ω. Cm) $^{-1}$	σ at 3 (hr) (Ω. Cm) $^{-1}$
006	0. 32	0.37
700	0. 38	0.56
800	0. 40	0.75
900	0. 45	0.78
1000	0. 57	1.10

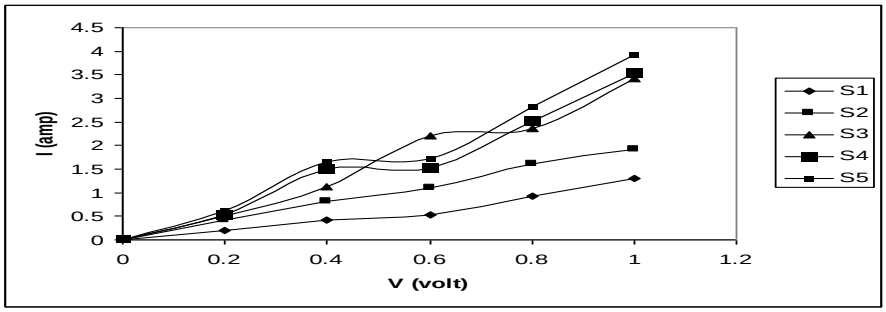

Fig.(4): Illustrate the relationship between voltage and current for samples at different sintering temperatures.

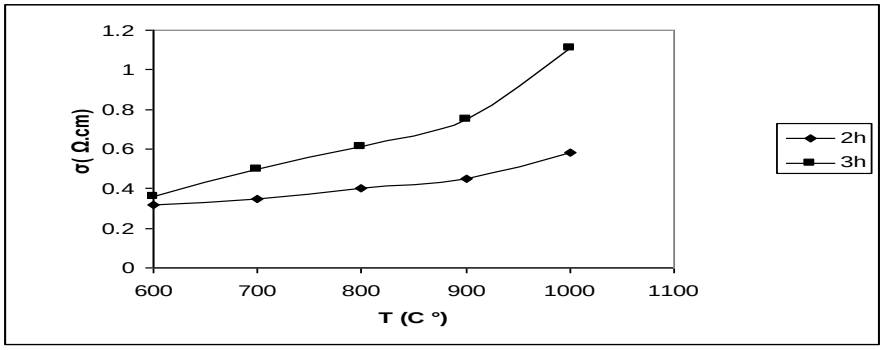

Fig. (5): Illustrate the relationship between conductivity against temperature for Samples sintered in: (a) two hours,(b) three hours.

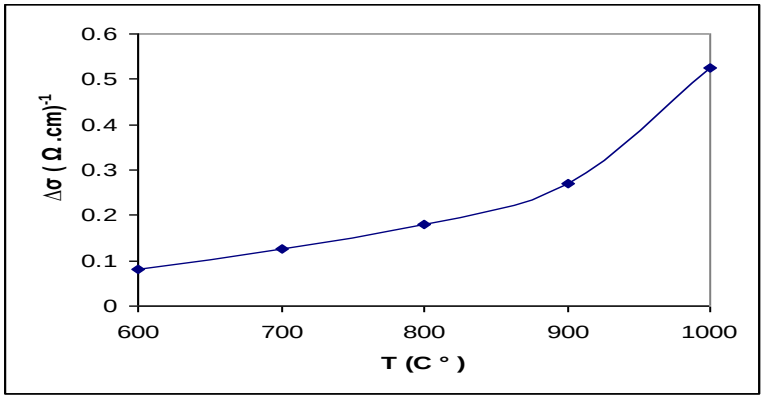

Fig. (6): Illustrate the relationship between (Δ σ) and temperature