PREPARATION OF ALUMINA GRAFTED BY ACRYLONITRILE FOR IMPROVEMENT SOME MECHANICAL PROPERTIES [+]

Mahmood S.AbdulHussien [*] **Fawziea M.Hussien** [**]
Muna Noori Ismail[***]

Abstract :

This work involves an experimental investigation of preparing alumina compacts by using alumina adsorbed acrylic acid then grafted by acrylonitrile which was pressed under different loads (243.8 MPa. to 585.191MPa.) by using dry pressing technique. All alumina compacts were fired firstly at 1000 ^{o} C then at 1550 ^{o} C. It was found that (487.659 MPa.) the best pressing load to give the best mechanical properties.

The influence of the concentration of benzyl peroxide initiator for polymerization and the amounts of present and adsorbed polymer on all properties of alumina studied, by using washing process. Mechanical properties such as have been compression strength and scleroscope hardness, for alumina adsorbed acrylic acid and alumina grafted acrylonitrile have also been studied.

تطعيم ألالومينا باستخدام ألاكريلونايترول لتحسين بعض الخواص الميكانيكية

محمود شاكر عبد الحسين*	فوزية محمد حسين**	منى نوري اسماعيل***

المستخلص:

تم في هذا البحث تحضير العديد من مكبوسات الالومينا بعد ان تم امتزازها اولآ بحامض الاكريلك ثم اجراء البلمرة التطعيمية بواسطة الاكريلونايترل، تم تحضير تلك المكبوسات باستخدام عملية الكبس الجاف باستخدام احمال مختلفة تتراوح بين (٢٤٣,٨MPA الى.MPa ٥٨٥,١٩) ثم تلبيد تلك المكبوسات بدرجات حرارة ١٠٠٠م^{o}و ١٥٥٠ م^{o} وقد تبين ان الحمل(.MPa ٤٨٧,٨٥٩) اعطى احسن نتيجة من حيث الخواص الميكانيكية المدروسة. دُرس تأثير تركيز البادئ للبلمرة (بيرو كسيد البنزويل) وكذلك كمية البوليمر الممتز وغير الممتز على جميع الصفات للالومينا وذلك باستخدام عملية الغسل.

درست الخواص الميكانيكية مثل، مقاومة الانضغاط والصلادة للالومينا المازة لحامض الاكريلك والالومينا المطعمة بالاكريلونايترول.

General:

Ceramics are non-metallic inorganic materials with a broad range of composition. They are usually hard, brittle, wear resistant, prone to thermal shock, refractory, electrically, thermally insulative and chemically stable [1] Ceramics are usually processed by mixing the particulates of the material together with water and organic binder. The mixture is then pressed into mould to obtain the desired shape dried to evaporate the water and the binder burned out by thermal treatment [2,3]

Organic binders are essential additives for the processing of many commercial ceramics. The binders provide green strength and plasticity to clay-free ceramics so that

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[*] **Professor / Foundation of Technical Education**
[**] **Lecturer/ Technical College-Baghdad**
[***] **Assist Lecturer/ Institute of Technical/ Anbar**

bodies can be molded and retained in the desired shapes before firing. Ceramic processes that utilize organic binders include dry pressing, extrusion, tape casting, roll forming, and slip casting. All except injection molding and compression molding involve the use of binders that are dissolved or dispersed in a liquid; the binders are dissolved molecularly in water or an organic solvent or dispersed in liquid as an "emulsion", to give film-forming type. These film formers usually are long-chain polymers that possess characteristics of internal flexibility in contrast to polymers that have the substantial three dimensional linkages, which tend to be rather rigid [4]

Alumina is widely used as electrical insulators, and can withstand high voltage as well as temperature fluctuations. It is suitable for use in spark plug insulators. It is also used as lining for high temperature furnaces since its melting point is very high. Also it is used for tool tips and grinding tools since it has high compressive strength and is wear resistant [5,6]

James. L, pointed out room temperature plasticity may play an important role in the compressive failure of even the most brittle ceramics .Compressive failure at room temperature in polycrystalline alumina is shown to be strain – rate dependent, with the rate dependent mechanism being deformation twinning .This twinning which commences at between 25 % and 50% of the failure stress level initiates micro cracks at twin/grain – boundary [7]

Yint. K ,et al ,stady that poly(octadecyl methacrylate), poly(dodecyl methacrylate), and (hexyl methacrylate) are high effective as lubricating surfactants in the preparation of dense flocculated but low viscosity suspension .An effective polymeric surfactant can be a graft type copolymer whose backbone possesses site which can serve as anchors to adsorb onto the particle surfaces, and has strongly solvated chains that protrude from the particle surfaces to develop repulsive forces [8]

Barlow J.W, and Marcus H.L., investigated the affect of particle size on Selective Laser Sintering (SLS) and post processing of alumina with polymer binders .Samples were given suitable heat treatment to remove the polymer binder followed by sintering treatment at 1600 ^{o}C. [9]

Aftanas G. et. Al., studied the equilibrium and kinetics of adsorption of n-propylamine and di-n-propylamine on γ - Alumina, at several temperatures both lower than that were deamination is observable and in the region of temperatures where the reaction takes place.[10]

Hussine F.M., examined alumina compacts using graft polymerization with different alkyl monomers (methylacrylate ,n-butyl acrylate, methylmethacrylate, and ethyl methacrylate) which have been copolymerized with acrylic acid to provide strong surface attaching groups for alumina particles.[11]

Szafran M.; Rokicki G. , studied the effect the chemical structure of acrylic –styrene copolymers on the properties of ceramics tapes from alumina obtained by the tape – casting method are presented the presence of carboxylic groups as polymer pendant groups in an optimal amount which has an additional effect on the ceramic tape density , uniformity , and mechanical properties , before and after the the sintering process.[12]

Experimental work:

Adsorption Experiments:

The alumina powder was dried at 150 ^{o}C in oven for (24 hours), and then it was allowed to cool at room temperature, inside desiccators over silica gel. The alumina powder (150 g) was dispersed in (200 ml) toluene. Components were mixed by stirrer. Nitrogen gas was bubbled in the reactor then Acrylic acid (200ml) was added. The reaction was carried out at 60 ^{o}C in water bath for (12 hours). The resulting mixture was filtered and washed with

methanol, at least three times. Alumina adsorbed. Acrylic acid was dried in vacuum at 60 ^{o}C for several hours.

Alumina Grafting with Acrylonitrile:

Alumina adsorbed with Acrylic acid was dispersed in (200 ml) toluene. Benzoyl peroxide was added to stirred solution. Nitrogen gas as carrier was bubbled in the solution to which (150 ml) acrylonitrile was gradually added. The reaction vessel was placed in water bath at 60 ^{o}C. The polymerization reaction takes about (20 hours).

After the formation of polymer, the product was washed with toluene three times. Filtering, drying was carried out in vacuum at 60 ^{o}C for (10 hours) before examination by IR. Alumina grafting stage was repeated twice by using (0.1 g) and (1 g) benzoyl peroxide respectively and comparison was made.

Forming and Firing of Specimens:

The grafted Alumina powder and alumina which adsorped acrylic acid were milled then compacted by dry-pressing techniques with hydraulic press type (Hydraulic press, England, SER No. DI 393). The alumina which adsorped acrylic acid was pressed into disc (16 mm) at various loads (5, 6, 7, 8, 9, 10, 11, 12) Ton which equal to (243.8, 292.595, 341.36, 390.127, 438.89, 487.659, 536.425, 585.191) MPa, but grafted alumina powder was pressed under the pressure of (487.659 MPa).

The steps for pressing powder were:

1- The die was filled with (2 g) of grafted Alumina.
2- Grafted Alumina was pressed to the required pressure.
3- Pressure was kept for 10 sec.
4- The compact sample was pulled from die.

Then the specimens were fired in two stages. The first stage was at rate 10 ^{o}C / min, and then held at a temperature of (1000 ^{o} C) for two hours. Finally, they were fired at a rate of 10 ^{o} C /min up to 1550 ^{o} C kept at this temperature for two hours. The furnace is supplied with a temperature control type "Carolite Sheffield England" operating from (0-1700 ^{o}C).

<u>Results and discussion</u>:

Adsorption of Acrylic Acid Monomer onto Alumina

Adsorption of acrylic acid monomer was carried out onto alumina surface at 60^{o}C without using benzoyl peroxide initiator as illustrated in fig. (1).

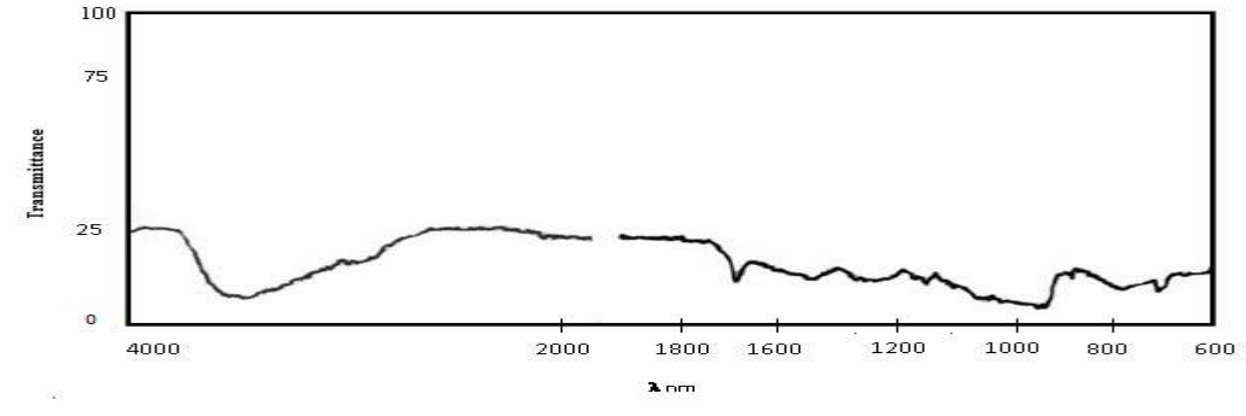

Fig. (1): IR of acrylic acid adsorption on γ-alumina surface

This figure clearly shows that good adsorption happened between the alumina and acid molecules. This comes from the formation of a new band which is a carboxylate band at the (1500 cm^{-1}) , in addition to the presence of acidic carbonyl group at (1775 cm^{-1}) and the C-H stretching aliphatic at (3050 cm^{-1}).In this stage adsorbed acrylic monomer can act as an anchor group but it does not provide a good stability or lubrication as well as densification .That means we need to establish another monomer onto product.

Alumina Grafted Poly Acrylonitrile:

The adsorped acrylic monomer was extended by polymerization of acrylonitrile monomer by using two different concentrations of benzoyl peroxide initiator. The part of resulting products was washed and examined by using IR, Fig.(2 ,3). These Figures exhibit the presence of the nitrile group. Although it was very small and different from each other, the weight differences between the original alumina adsorbed acrylic acid molecules and the grafted poly acrylonitrile should the gain in weight, this implies that a real polymerization took place on the alumina surface. Again, the two IR Figures (2-3) show clearly the disappearance of vinylic bond (C=C) assigned for acrylic monomer which confirms the polymerization of acrylonitrile standed from the acrylic acid monomer.

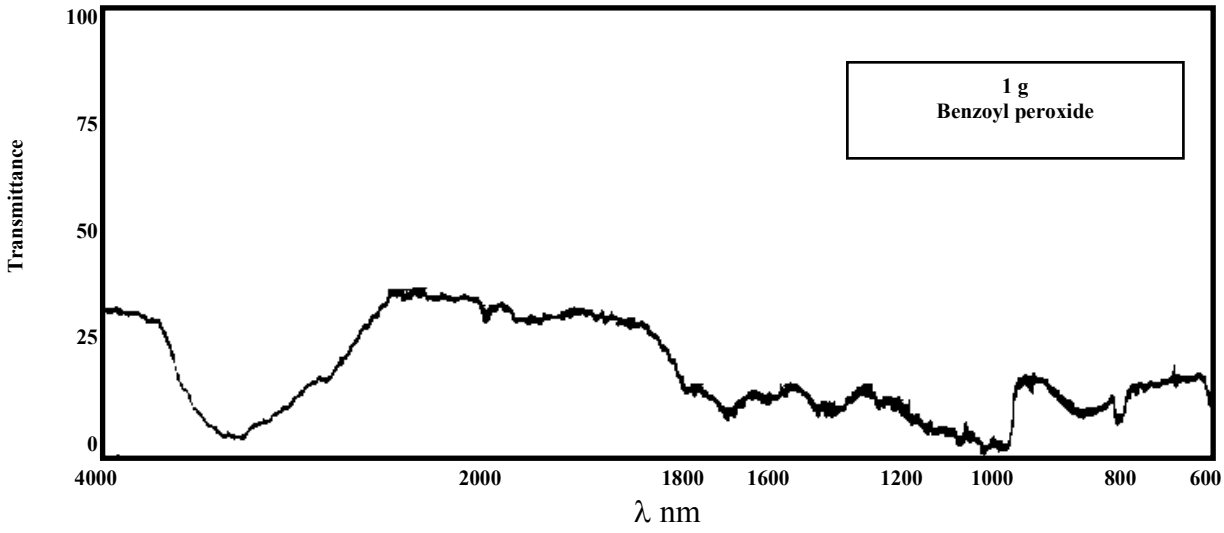

Fig. (2): IR of alumina grafted poly acrylonitrile

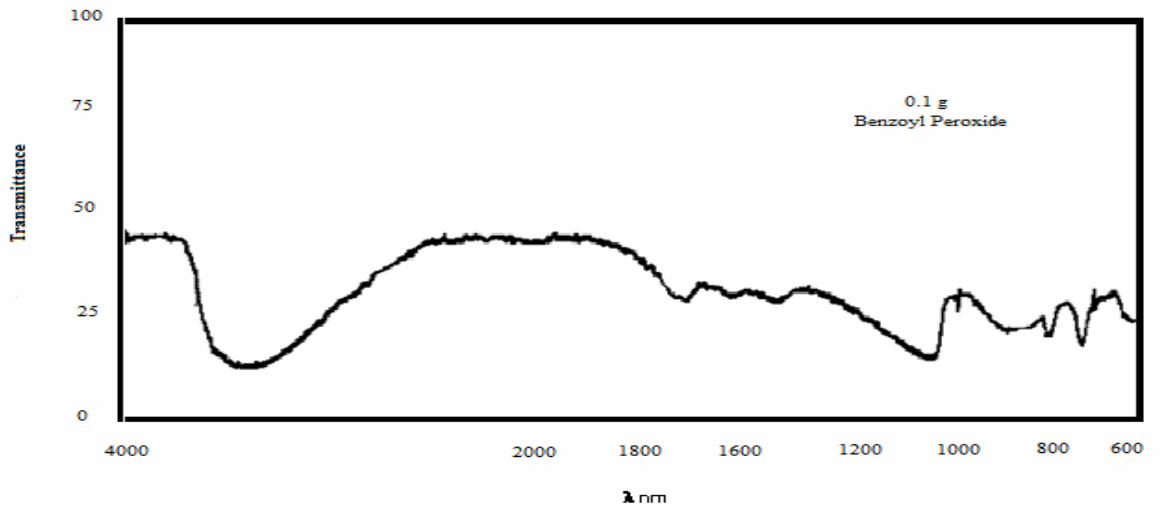

Fig. (3): IR of alumina grafted poly acrylonitrile

Mechanical properties:

Diametrical compression and Sceroscope hardness:

The results of mechanical properties (Diametrical compression and Sceroscope hardness) are shown in Tables (1),(2), and (3).

Table (1): Mechanical properties of alumina powder which adsorped acrylic acid.

Load (Mpa)	δ_f (Mpa)	Scleroscope hardness (Mpa)
243.8	31.626	685
292.595	32.96	725
341.36	33.99	740
390.127	35.732	755
438.89	39.86	780
487.659	40.47	788
536.425	39.20	770
585.191	37.56	765

Table (2): Effect of polymer on the mechanical properties of alumina grafted acrylonitrile by using (0.1 g) initiator under (487.659MPa).

Method of washing	Amount of present polymer (mg/g)	δ_f (Mpa)	Scleroscope hardness (Mpa)
U.W.S	1.124	42.950	805
1.T.W	0.929	44.682	810
4.T.W	0.810	48.662	820

Table (3): Effect of polymer on the mechanical properties of alumina grafted acrylonitrile by using (1 g) initiator under (487.659MPa).

Method of washing	Amount of present polymer (mg/g)	δ_f (Mpa)	Scleroscope hardness (Mpa)
U.W.S	2.500	53.970	840
1.T.W	2.346	60.563	855
4.T.W	1.490	65.975	875

Diametrical Compression:

This test was carried out on the alumina adsorbed acrylic acid which was pressed under different loads.

Examining the results obtained, one can conclude that the load (10 Ton) produced ceramic which had higher compression strength among other these shown in Table (1).This is attributed to the better density and lower porosity and may not have any internal crack created because of higher pressing load, Fig. (4).decreasing diametrical compression after load of (10 ton) due to the presence of some cracks.

Obvious differences can be seen between alumina grafted acrylic acid and alumina grafted acrylonitrile with each concentration of initiator. Amount of present polymer effect on a diametrical compression is shown in Fig. (5).The increase in amount of present polymer causes a decrease in the density and also a decrease in diametrical compression, this is because it gives a bad compact which leads to cracks or flaws, but only adsorbed polymer is attributed to the better diametrical compression.

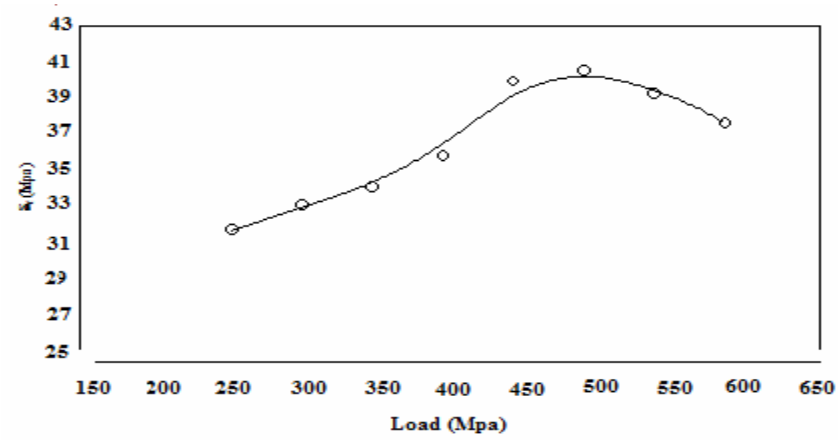

Fig. (4): Effect of pressing load on diametrical compression for alumina powder which adsorbed acrylic acid.

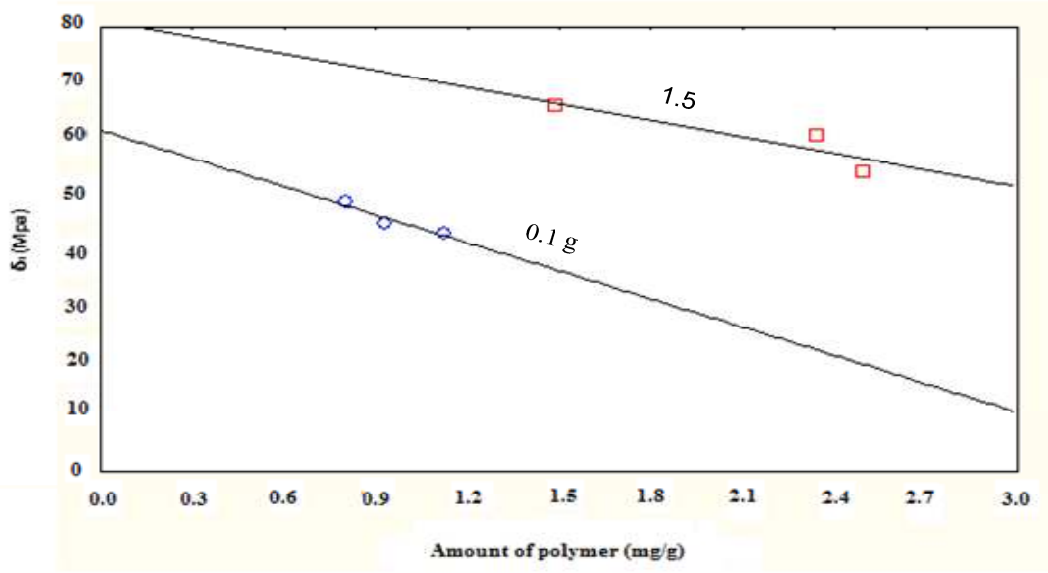

Fig. (5): Effect amount of polymer on diametrical compression for alumina grafted Acrylonitrile.

Hardness:

Scleroscope Hardness:

Hardness is one of the best indicators of the ability of the material to resist scratching, abrasion or penetration.

The effect of pressing load on Scleroscope hardness for alumina adsorped acrylic acid is shown in Fig. (6), which shows that increasing the pressing load leads to increase in Scleroscope hardness. Fig. (7) Shows that hardness of alumina grafted acrylonitrile decreases with increase in amount of polymer. This is related with porosity and density therefore, unwashed alumina grafted acrylonitrile has hardness less than washed grafted alumina. [11]

For alumina grafted acrylonitrile, the increase in the amount of present polymer causes the decrease in Scleroscope hardness because of high level of porosity and lower level of density. The amount of polymer adsorbed on alumina grafted acrylonitrile by using (1g) initiator was more than in (0.1g) initiator. This amount is reflected in scleroscope hardness value, as shown in Fig. (7).

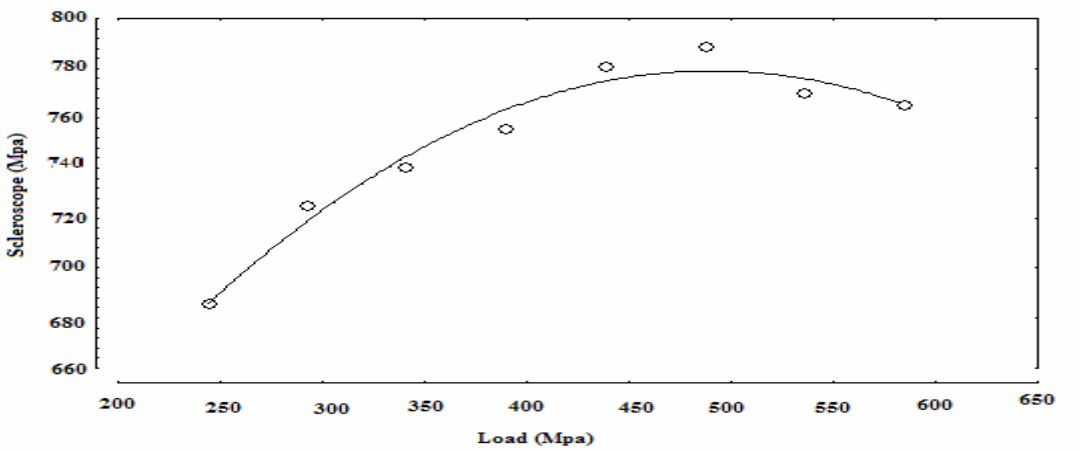

Fig. (6):Effect of pressing load on scleroscope hardness for alumina powder which adsorbed acrylic acid

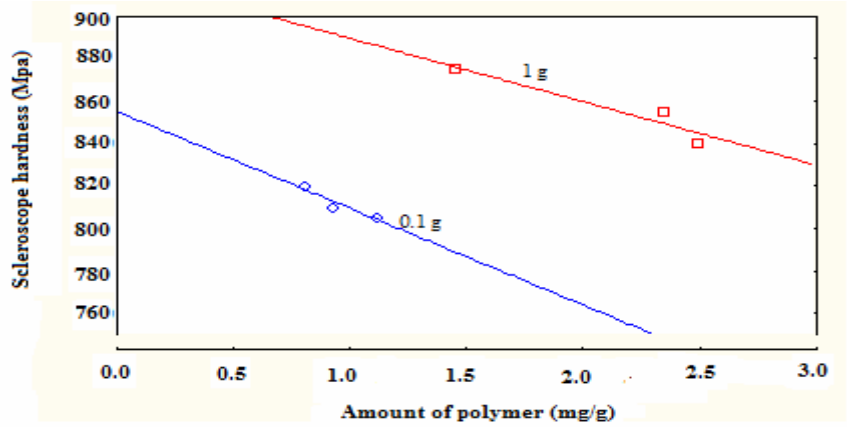

Fig. (7): Effect of amount polymer on scleroscope hardness for alumina grafted acrylonitrile.

Conclusions:

1) Grafted γ-alumina by acrylonitrile with acrylic acid using benzoylperoxide as initiator was successfully conducted at 60 ^{o}C and (18-20 hours).
2) The grafted polymers were identified by IR-spectroscopy, the characteristic absorption bands at (2270 cm^{-1}) and (1775 cm^{-1}).
3) The mechanical properties decrease with increasing the amount of polymer on alumina but increase with increasing amount of polymer adsorbed. This depends on washing process . The compression strength, hardness and increase with increasing pressing load.

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