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RESEARCH ARTICLE

Effect of ZrO_2 on Mechanical Strength, Antibacterial, and Anti Fungal of Epoxy Adhesive

Noor Ameer * and Seenaa Ibreheim Hussein

Department of Physics, College of Science, University of Baghdad, Iraq.

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***Address for Correspondence**
Noor Ameer
Department of Physics,
College of Science,
University of Baghdad, Iraq.
E. mail: noor_ameer94@yahoo.com

ABSTRACT

The aim of the research studying the effect of ZrO_2 additives on epoxy Use epoxy resins and added ZrO_2 by weight ratio (0,1,3,5,7, and 9)% for two methods in situ and solvent for Preparation nano composites. To make the mechanical strength (bending, hardness, andCompressive) , antibacterial , and anti fungal. The results of the mechanical tests showed that all of the above tests improved the specifications of epoxy resin with the addition of zirconium. The strength of the overlapping material was increased by increasing the percentage of zirconium to 5% and then the strength and stiffness of the material decreased by increasing the ratio (7, 9%) due to the phenomenon of aggregation of nanoparticles . whene added acetone with solvent method improves the mechanical strength of epoxy nano composites compared with in situ method .

Keywords : bending , hardness, compressive , anti bacterial , anti fungal.

INTRODUCTION

Polymer-matrix composites are very popular among the various industrial applications such as mechanical, electrical, automotive, semiconductor, and aerospace. This is because of the reason that the composite materials show a significant improvement in the properties such as chemical, electrical, mechanical, and coefficient of thermal expansion as compared to their original phase. Additives and fillers are widely used in the synthesizing process to enhanced the mechanical and thermal properties of polymers [1] Nanocomposite consist softwoor more components, one of them being matrix or continuous phase in which nanosized particles are dispersed. These nanoparticles, or nano fillers, constitute the second phase [2].Thermo setting epoxy polymers are widely used as adhesives, they are amorphous and highly cross linked, and the micro structure of these materials has many interesting properties for engineering application such as light weight, high failure strength, low creep, and interesting adhesive properties [3].

Zirconia shows good chemical resistance, excellent wear resistance and high hardness properties and also exhibits low thermal conductivity, high modulus, good strength and good fracture toughness [4].Nanoparticle uniformity and agglomeration**:** Based on their chemistry and electro-magnetic properties, nanoparticles can exist as dispersed aerosols, as suspensions/ colloids, or in an agglomerate state for example, magnetic nanoparticles tend to cluster, forming an agglomerate state, unless their surfaces are coated with a non-magnetic material. In an agglomerate state, nanoparticles may behave as larger particles, depending on the size of the agglomerate. Hence, it is evident that nanoparticle agglomeration, size and surface reactivity, along with shape and size, must be taken into account when deciding considering health and environmental regulation of new materials [5].

Preparation of polymer/Nano filler

Various approaches are available for each of the three synthesis methods, namely solution- blending, melt-blending and in-situ polymerization. An important task in the preparation of polymer/nanocomposite is to achieve a uniform dispersion of nanomaterial in the polymer matrix. The solution-blending technique often yields favorable dispersion in the polymer matrix, in comparison with melt blending, due to its low viscosity and high agitation power. On the other hand, melt blending is considered industrially viable and ecofriendly, with high economic potential [6].

Melt blending

Compared with other methods, melt blending is more attractive for the preparation of commercial products because it is convenient and environmentally friendly without using organic solvents [7]. For this method, researchers can mix polymer and nanocomposite directly. Polymers, such as polyurethane, polypropylene, poly (ethylene terephthalate), polystyrene, poly (ether ketone), styrene ethylene/ butylene-styrene triblock copolymer [8].

Solution blending

is the most extensive method for preparation of polymer/nanocomposites, especially in laboratory. There are three steps in solution blending. Firstly, disperse nanomaterial in a suitable organic solvent under sonication. Secondly, mix polymer in the solvent and make it dissolved. Thirdly, remove the solvent. A variety of nanocomposites, such as polytetrafluoroethylene composites [9].

In-Situ Polymerization

The melt-blending method often leads to insufficient filler dispersion, which causes aggregation and intercalation, particularly at high filler contents [10].in-situ polymerization is more effective in the formation of composites. Moreover, in-situ polymerization allows versatile molecular designs of the polymer matrix; it deliversan effective approach to the synthesis of different polymer/ Nanomaterial with an expanded property range and enables the design of the interface between the Nano clays and the polymers byflexible tuning of the matrix composition and structure [11].

MATERIALS AND METHODS

Materials

Epoxy as a matrix (Nitofill, EPLV with Nitofill EPLV hardener from Fosroc Company). Made in Jordan . The mixingratioforresinandhardeneris 3:1.Zirconuim oxide (ZrO_2) :- zirconia nanoparticles were purchased from Sigma Aldrich Germany , density 0.5 gm/ cm^3 ..Acetone: -BHD Chemical Ltd Poole, England, the purity 98 %

Atomic force microscopy analysis

The surface morphology of ZrO_2 powder nanoparticles was observed with AFM micrographs as shown in Figures(1).It has emerged that average diameter for ZrO_2 particles is 56.9 nm

Preparation samples of epoxy and epoxy / ZrO_2 nanocomposites by situ method

The solution of epoxy and hardener was formed with a ratio of 3:1.the hardener liquid was added slowly to the epoxy resin at room temperature, this mixture was stirred manually for 5 min , and the composition was left at room temperature for 24 hours today. To prepare epoxy/ ZrO_2 nanocomposites using situ polymerization method,ZrO_2 powder of percent 1,3,5,7,9% were added to the epoxy resin, then the resulting solution was put in a glass tube on a magnetic stirrer at 60 °C for one hour. After that, the composite was left at room temperature for 24 hours after mixing with hardener for 5 minutes.

Preparation of epoxy and epoxy / ZrO_2 nanocomposites with the solvent method

Epoxy resin was diluted by adding acetone and stirred for one hour the ratio of the epoxy/ acetone (10gm epoxy /1 ml acetone). After that, the composition was left at room temperature for 24 hours after mixing with hardener for 5 minutes.To prepare epoxy/ZrO_2 nanocomposites with solvent method, ZrO_2Nano powder of percent 1,3,5,7,9% were added to the epoxy solution was put in a glass tube on magnetic stirrer at 50°C for one hour. After that, the composition was left at room temperature for 24 hours after mixing with hardener for 5 minutes.

Mechanical testing

Flexural test

The flexural strength of the composite was evaluated performing three –point bending tests on the composite. the test was performed at room temperature, at a crosshead speed of 5 mm/min. on according with ASTM d790 standard procedure. [12]Make was Shimadzu-japan. A range of machine was 1-100KN.The flexural strength of composites was found out using the following equation and maximum shear stress are calculated according to the equation. [13] Figure (2) shows the samples epoxy and Nano composites

F. S= 3PL/2bd^2 ……. 2-2
t=3P/4bd ………. …….2-3

where :- F. S=flexural strength(MPa) , P=force at fracture(N), L=length of the sample between predicate (mm) , b=thickness(mm) ,d=width(mm) , t=maximum shear stress (Mpa)

Hardness test

Hardness test maybe defined as a material resistance to permanent indentation. Durometer (shore D), like much other hardness tests ASTM D2240 , measure the depth of an indentation in the material created by a given force on a standardized press foot. This depth is dependent on the hardness of the material.

Compressive test

One of the most interesting mechanical tests for materials is the diametrical compression of a solid disk. This test was performed on disk using a compression test device Intron, the sample was fixed between the upper and lower platens of the device to start compressing at a rate (cross-head speed =0.5 mm/min) until fracture occurs. Figure (3) shows epoxy and Nano composites

Evolution of antibacterial and antifungal activity

The antibacterial activity of the samples was evaluated using disc diffusion method with Muller–Hinton agar and sample membranes were cut into disc shapes of 6 mm diameter the discs were placed on the bacterial culture, and a determination of inhibition zone in millimeters(mm).The films were scrutinized against Gram-negative bacteria *Escherichia coli* (E.coli) and Gram-positive *Staphylococcus aureus* (*S.aureus*) in 37°C for 6 hours for pure epoxy and epoxy with ZrO_2 nanocomposites and the films was scrutinized against Anti-fungal *Penicillin* and *Aspergillus* in 37°C for 5-7 days.

RESULTS AND DISCUSSION

Flexural Strength

Flexural strength indicates the ability of the material to withstand bending forces applied perpendicularly to its longitudinal axis. From load-deflection or stress-strain curves in flexural test we can get the flexural strength, a flexural modulus and energy fracture for epoxy pure and EP/ZrO_2 nano composite. Show the values of flexural strength for the epoxy resin rein forced with ZrO_2 . It can be noticed that the values of flexural strength increased with increasing of the weight ratio of ZrO_2. This is due to the ability of these particles to hinder the crack propagation inside matrix according to the strengthening mechanism additionally to the strong bonding between the epoxy matrix and these particles. Furthermore, this increase may be due to the factthe flexural strength of ZrO_2 particles are much higher than epoxy matrix, The flexural strength of the composites increases as the filler addition increases up to 5 wt% for both methods and starts degrading beyond 5wt% this maybe due to the excess filler addition and which leads topoorbondingin the fillers shown in figure (4). More addition of ZrO_2 nanoparticles lead to reduce in space distance (decrease free space distance) between epoxy chains when the addition of ZrO_2 nanoparticles which are polarparticles [14]. Figure (5) shows the flexural modulus with increasing of ZrO_2 nanoparticles concentration of EP/ZrO_2 nanocomposites. Flexural modulus has increase beyond 1% wt. in situ method and 3% wt. solvent method, modulus reach maximum increase, in general all the value obtained after the addition of ZrO2 nanoparticles to epoxy were higher than that of epoxy especially at low concentration of ZrO2 nanoparticles, This behavior of EP/ZrO2 nanocomposite singood agreement with the behaviour obtained by K.S.Harishan et al. [15]. The increase of the concentration of ZrO_2 nanoparticles lead to rising constraint of epoxy chains when chains deflections and mobility will decrease, so all the results of flexural modulus were higher than that of epoxy.

Hardness test

The hardness gives us a good idea about the strength of the material. The results of the hardness test in figure (6) show the influence of ZrO_2 weight ratio the epoxy matrix. the hardness values increase with the increasing weight ratio of ZrO_2 up 5% in situ method and 3% in solvent method, the samples with higher concentration of nanoparticles showed higher resistance to the indentation force, therefore, exhibiting higher shore D values and this has helped to increase the area of contact between the components of the composites materials ,and zirconium dioxides high strength, high hardness and high toughness [16] .this could be attributed to the inherent hardness of the ZrO_2 particles compared with neat epoxy, as well as the interface effect between the matrix and the filler, also the high adhesion between them . Which agree with [17]. Increase the values of hardness by adding but as soon as the loading of nanofiller increased beyond 5% in situ method, and 3% solvent method hardness value decreased. The hardness values increase by adding acetone because The addition of solvents to thermoset resins is a possible route to decrease resin viscosity, allowing a better distribution of fillers [18], including the acetone gave decrease the density of the cross-link in the polymer leading thus helps spread the nanoparticles between the epoxy bonds and to the increase of the values of the hardness.

Compressive strength

Compression strength increase in the epoxy matrix with increasing the ratio of ZrO_2 in 5%wt. both two methods(in situ and solvent).The Compressive strength of the epoxy pure sample was 7Mpa in situ method and 13 Mpa in the solvent method , which increased to a maximum value of 14 and 36 Mpa respectively .Increase in wt% beyond 5% caused a decrease in compressive strength trend is shown in figure (7)Increase in compressive strength with increase up to 5 wt % is a result of high strength of ZrO_2 which is transmitted uniformly to the host matrix due to very high interfacial area between resin matrix and nanoparticles assists in transfer of physical stress. Nanoparticles are uniformly dispersed in the matrix and occupy spaces between polymer chains decreasing mobility of the chains and increasing resistance of matrix to deformation and crack growth. The Possibility of air bubbles reduces by addition of ZrO_2 thus preventing crack initiation due to void spaces in the matrix. The decrease in compressive strength on increasing wt% beyond 5% was observed. This decrease can be due to agglomeration of nanoparticles and lack of resin material to accommodate the high content of ZrO_2. Cracks can initiate in such regions with stress concentrations present due to poorly dispersed reinforcement or lack of resin material to bond high content of reinforcement. Which agree with [17]. The formation of such H – bonds at the interface does not only affect the polymer, mechanical properties, but also the filler dispersion , limiting the aggregation that typically occurs with ZrO_2 .[18]

Antibactrial and Antifungal activity

Resin coat epoxy antibacterial and antifungal coating has been independently tested (iso 22196) and given according to biomaster. Our antibacterial and antifungal epoxy coating, reduction against the initial loading of bacteria for E-coil and S. aureus [19]. Epoxy and nano composites with ZrO_2 nanoparticles are tested for its antibacterial activity and antifungal against the bacterial pathogens, *S.aureus* (gram positive) and *E.coli* (gram negative) by Agar diffusion method, antifungal *Penicillium* and *Aspergillus*. Zone of inhibition values determined for epoxy and nanocomposites is shown in figure (8 a) .ZrO_2 nanoparticles pronounced significant growth inhibitory effect against both bacteria due to their large surface area by their nanosize .However ZrO_2 nanoparticles superior antibacterial activity against *E.coli* bacteria than with *S. aureus* bacteria which are clearly visualized in the anti bacterial photographs. This difference in antibacterial performance may be due to the following assumptions: active oxygen species generated from the ZrO_2- nanoparticles actively inhibits the growth of S.aureuscells by accumulation or deposition on the surface of S.aureuscells [20] . Antifungal images of Epoxy and epoxy with ZrO_2 nanoparticles in Fig. (8 b) clearly predict its antifungal activity by actively inhibiting the growth of both Penicillium and Aspergillusstrains. Due to its high surface area, ZrO_2 nanoparticles almost show similar and significant in hibition effect against both fungal strains.

CONCLUSIONS

ZrO_2 nano enhance mechanical strength (bending, hardness, compressive) ,Antibacterial and anti fungal of epoxy resin with different weight ratio of ZrO_2 for two method (in situ and solvent), the best value of addition of Zro_2 which is used to improvement of mechanical strength , anti bacterial , and anti fungal at 5% weight ratio. When addition acetone with solvent method improving mechanical strength compared with in situ method

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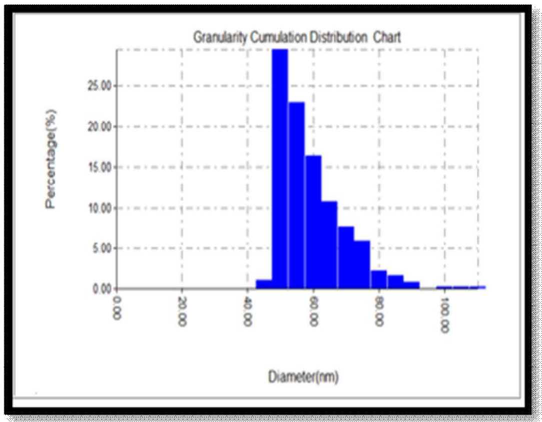

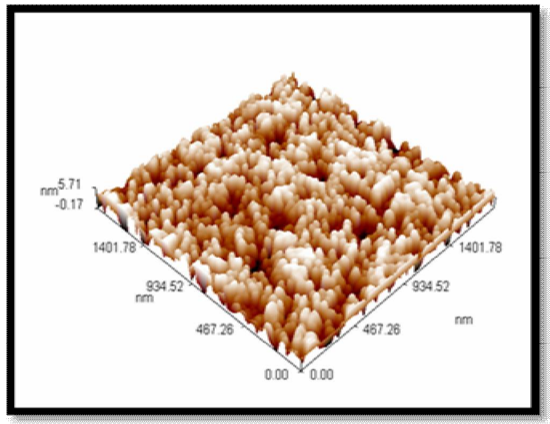

Figure1. AFM analysis images of ZrO_2 nanoparticles used in the work

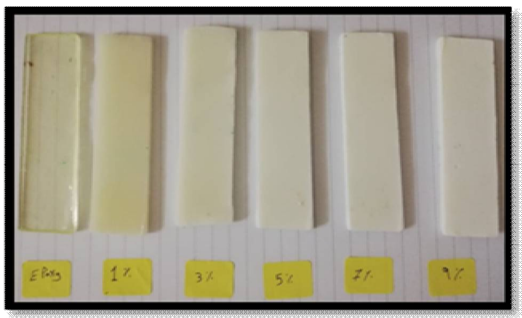

Figure 2. Samples of epoxy and Nano composites

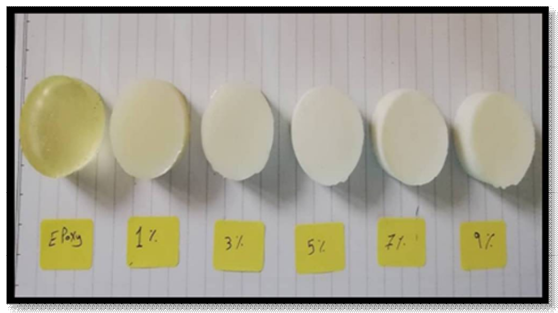

Figure 3. Shows epoxy and Nano composites

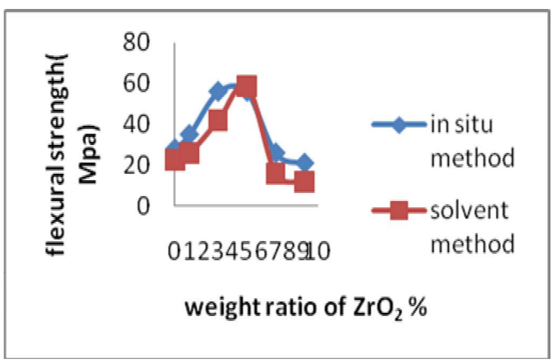

Figure 4. Flexural strength as a function

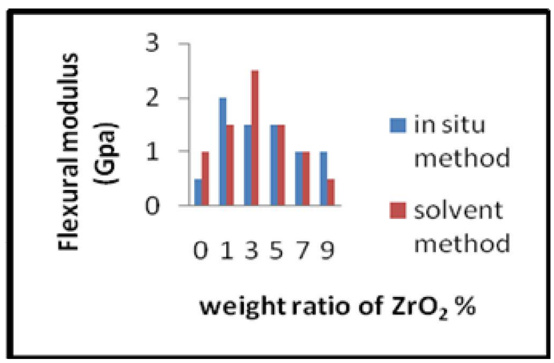

Figure 5. Flexural modulus as a function of weight ratio

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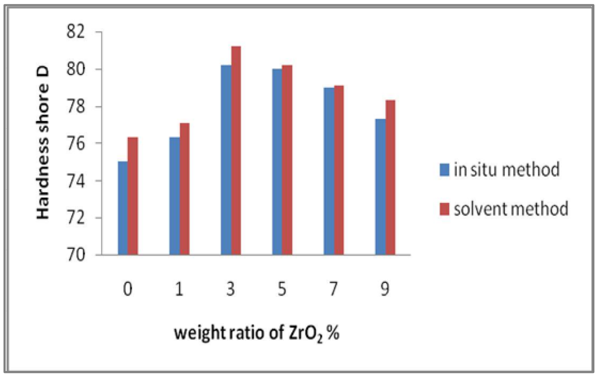

Figure 6. Hardness values as a function of ZrO_2 nano particles

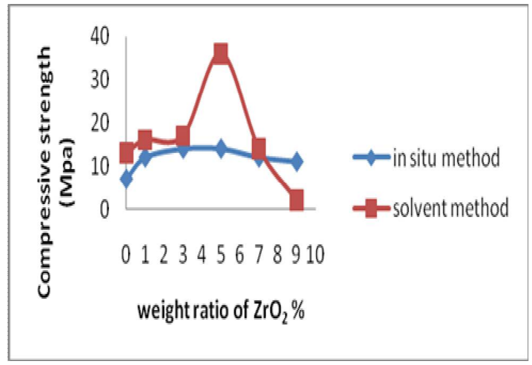

Figure 7. compressive strength as a function of ZrO_2

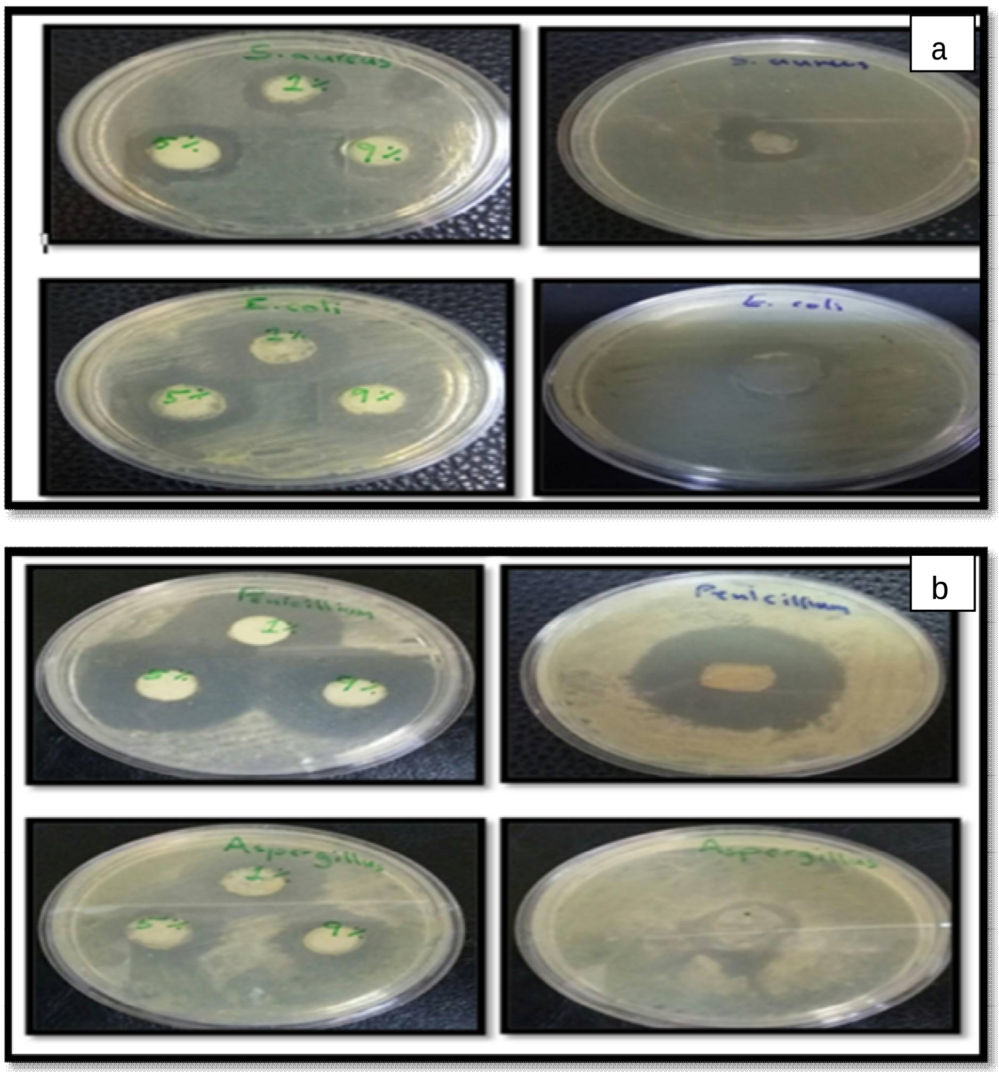

Figure 8. a-Anti bacterial and b-Anti fungal activity of epoxy with ZrO_2 nano composites