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Enhanced thermal expansion ,mechanical properties, and adhesion analysis of epoxy / ZrO₂ nano composites

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Abstract. The aim of the research is to enhance the specifications of adhesives used in the treatment of cracks in the walls of buildings and concrete ceilings in addition to the oxide zirconium nanoparticles . Use epoxy resins and added ZrO₂ by weight ratio (0,1,3,5,7, and 9)%and using the in situ method for Preparation nano composites . To make the mechanical tests (tensile and impact) , adhesion test (shear bonding and pull off tests) , thermal expansion .

The results of the mechanical tests and adhesion test 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 .

Key words :- thermal expansion, tensile , impact strength ,adhesive ,shear bonding , pull off ,

1-Introduction

In polymer nano composites with nano fillers content, graphene , carbon nano tube, TiO₂ ,and ZrO₂ in terms of enhancing mechanical properties , and this is partially attributed to improved mechanical interlocking / adhesion at the nano filler- matrix interface [1]. In most of the composite systems, fillers are selected as the reinforced hard phase. Among these composite systems, polymers have occupied an integral place in structural design of various products owing to its high resistance to environmental degradation and high strength to weight ratio [2]. 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[3] Thermosetting 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 [4]. use of Nano fillers is preferred. An addition of small amount of Nano fillers in epoxy matrix leads to a considerable enhancement of thermo mechanical properties of the base epoxy. Dispersion affects properties like toughness, stiffness, storage modulus and glass transition temperature. 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 [5]. Nanocomposite consists of two or 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 [6]. Generally,



nanofillers have a wide range of applications owing to their excellent mechanical and thermal properties which are largely due to the large surface area to volume ratio [6].

2.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 [7].

3. Interface and Bonding Force: -

The interface between the matrix and reinforcing phases can have a significant effect on the mechanical properties of the resulting composite material. The interface can be studied by a number of surface analysis techniques and the interaction modelled. Such studies, and such modelling, can help understanding of the mechanisms which composites undergo during their lifetime. [8]

Adhesion is the process of joining two bodies or surfaces through direct chemical bonding or through the formation of an interfacial layer. The “adhesive” is not a chemical substance in the usual sense, but arises from intermolecular forces acting between the bodies. These forces form the basis of physical chemistry. [9].

3.1 Mechanical Bonding: -

An entanglement in space between two or more molecular entities (component parts) such that they cannot be separated without breaking or distorting chemical bonds between atoms. [10]

3.2 Chemical Bonding: -

Chemical bonding, in general, is defined in several ways, for instance as: ‘forces that hold atoms together in stable geometrical configuration [11]. forces that hold atoms of elements together in a Compound [12]. a strong attractive force that holds together atoms in molecules and crystalline salts [13]. ‘the attractive force between atoms strong enough to permit the combined aggregate to function as a unit’ [14]. These forces between particles (e.g. atoms) arise from electrostatic attractions between opposite The reasons for bonding to occur in general terms are that bonding lower the potential energy between positive and negative particles, where the particles could be oppositely charged ions or atomic nuclei and the electrons between them.

4. Experimental work :-

1.Materials :- 1.Epoxy :- Epoxy as a matrix (Nitofill, EPLV with Nitofill EPLV hardener from Fosroc Company). Made in Jordan . The mixing ratio for resin and hardener is 3:1 .

2.Zirconium oxide (ZrO₂) :- zirconia nanoparticles were purchased from Sigma Aldrich Germany , density 0.5 gm/ cm³ .

3.Acetone :- BHD Chemical Ltd Poole, England , the purity 98 %

2. Atomic force microscopy analysis:-

The surface morphology of ZrO₂ powder nanoparticles was observed with AFM micrographs as shown in Figures(1).It is emerged that average diameter for ZrO₂ particles is 56.9 nm

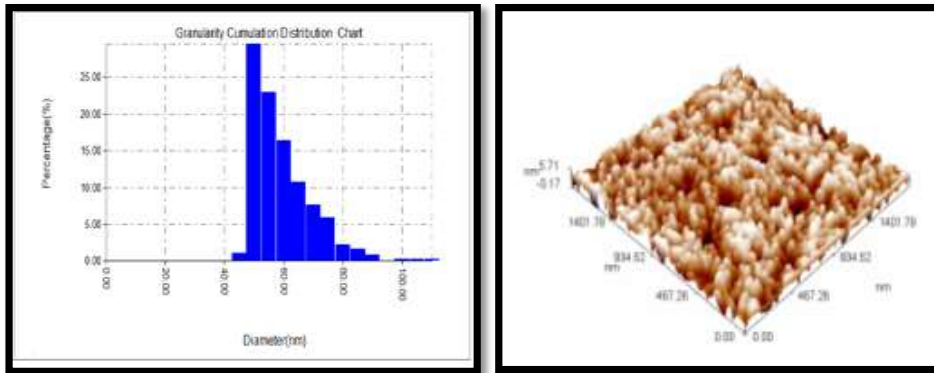


Figure1: AFM analysis images of ZrO₂ nanoparticles used in the work

3. preparation samples of epoxy and epoxy/ZrO₂nanocomposites by situ method :-

The solution of epoxy and hardener was formed with ratio of 3:1. the hardener liquid was added slowly to 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/ ZrO₂ nanocomposites using situ polymerization method, ZrO₂ powder of percent 1,3,5,7,9% were added to epoxy resin, then the resulting solution was putted in glass tube on 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.

4. Fourier transform infrared spectroscopy (FTIR) :-

FTIR is a technique which is used to obtain an infrared spectrum mostly of absorption and emission of a solid. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. FTIR is widely used to investigate the chemical bonds especially in those epoxy and nano composites both two methods (insitu and solvent). The FTIR used in research FTIR -8400S shimadzu on KBr pellets of the samples.

5. Mechanical testing: -

5.1 Thermomechanical test (TMA): - Coefficient of thermal expansion is the measure of the dimensional change of the samples after subjected to the temperature. The test is carried out in the thermo- mechanical analyzer TMA PT 1000 equipment. The samples are prepared according to the testing standards of the equipment TMA PT 1000. The dimension of the sample is height 20mm and diameter 5 mm. The sample is placed on the platform in the furnace and then the zero measure i.e. initial measurement of the sample is measured then set the final temperature value and range. The test is going on until the final temperature is reached. After reaching the final temperature the equipment stops and the values are noted by the software.

5.2 Tensile test and impact test :-

The tensile test was performed on flat specimens. Tensile tests were performed on instron Laryee at affixed crosshead speed of 5mm/min Samples were prepared according to ASTM D632 . Stander on computerized universal testing machine make was shimadzu –japan, randeof machine was 1-100 KN. Impact strength of a material is defined as the property of a material by virtue of which the material opposes it fracture under stress applied at high speed. The test with ASTM ISO 179. The instrument used for impact test in present study in charpy impact tester. Figure (2) shows the samples in the tests tensile and impact .



Figure (2) samples of nano composites for tensile and impact

6. adhesive tests :-

Shear bonding test :-Single-lap joints were mechanically tested under quasi-static conditions by using an Intron 4502 electromechanical tensile testing machine. According to ASTM D 1002 standard, a cross-head speed of 1.3 mm/min was adopted. All tests were conducted at ambient temperature (23°C), and at least six specimens were tested for each sample.

pull-off adhesion teste: - The portable, hand operated Posi Test pull-off adhesion tester measures the force required to pull a specified test diameter of coating away from its substrate rising hydraulic pressure. The pressure is displayed on a digital LCD and represents the coating's strength of adhesion to substrate . Figure (3) shows the samples in the tests shear bonding and pull off .



Figure (3) samples of nano composites for shear bonding and pull off

7. results and discussion :-

1. FTIR analysis :-

Fourier transform infrared (FTIR) Spectroscopy was used to analyze the epoxy and epoxy with ZrO₂ nano composites with two methods in situ and solvent .FTIR analysis of epoxy resins ,All the characteristic IR bands for epoxy resin are found in resin. The absorption bands at 1550 cm⁻¹ and 1643 cm⁻¹ are assigned to the aromatic ring in epoxy resin. The absorption band corresponding to stretching of C-H of the epoxide ring is at 3417 cm⁻¹ . The absorption band at 983 cm⁻¹ and 831 cm⁻¹ is assigned to the C-O and C-O-C stretching of epoxide group . In epoxy resin, the band around 3500 cm⁻¹ is assigned to O-H stretching of hydroxyl groups in epoxy resin shows in figure (4) which agree with [15] FTIR absorption peak at about 484 cm⁻¹ region is due to the Zr-O vibration, which confirm the formation of ZrO₂ structure , prominent peak of 1377 cm⁻¹ region corresponds to O-H bonding, peak in the region of 1510 cm⁻¹ may be due to the adsorbed moisture and in the 3434–3460 cm⁻¹ region is attributed to stretching of O-H groups, characteristic of a highly hydrated compound [16]

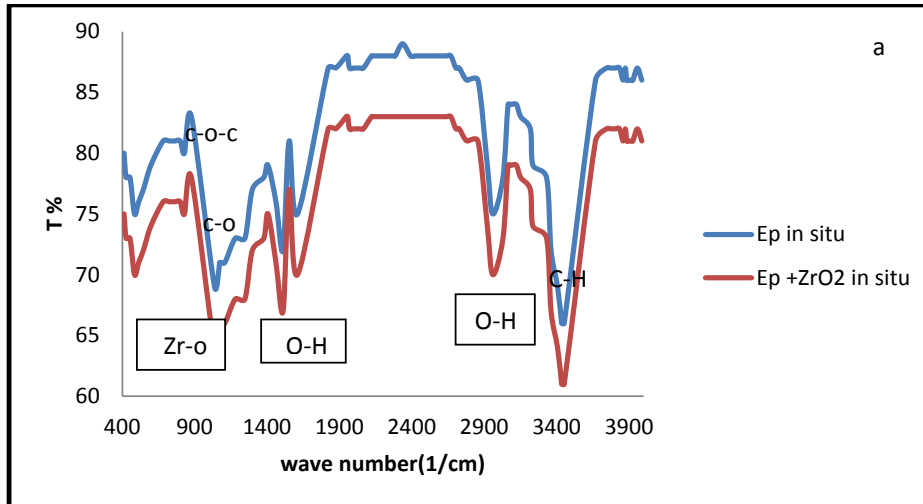


Figure (4) FTIR of epoxy and nano composites in situ method

2. Thermo mechanical test :-

The linear thermal expansion and volume thermal expansion for each epoxy / ZrO₂ nano composites for two methods. the average values are shown in Figure (5) From the test, it was found that the specimens have The coefficient of linear thermal expansion of plain epoxy matrix is found to be $29.2 \times 10^{-6} / \text{k}$ at 14 oC to $137.4 \times 10^{-6} / \text{k}$ at 200 oC for in situ method, when added ZrO₂ with epoxy the decreased coefficient of linear thermal expansion with increasing ZrO₂ and increasing with increase temperature. From the study, it has been observed that increase in the filler quantity decreases the coefficient of linear thermal expansion. A low CTE is desired to achieve dimensional stability [17]. coefficient of linear thermal expansion and volume thermal expansion change curves for the epoxy composites with various amounts of the ZrO₂ fillers are shown in Figure (6) in situ method. Dimensional changes for the composites were increase with increasing filler at 200oC for in situ. this may be due to the addition of concentration of the filler in nanocomposite material which provides the better filler-matrix interactions in the nanocomposites, the filler material toughens the matrix and hence preventing the nanocomposites from the expansion. The CTE of neat epoxy is about $115 \times 10^{-6} / \text{K}$ at 54 °C in situ method, and it gradually reduces to $59.3 \times 10^{-6} / \text{K}$ with increase in filler content at 5% ZrO₂. The constraint of mobility of the epoxy chain due to the interaction of ZrO₂ and epoxy are responsible for the reduction of CTE. Hence, the thermal stability of epoxy improves with addition of ZrO₂ which agree with [18].

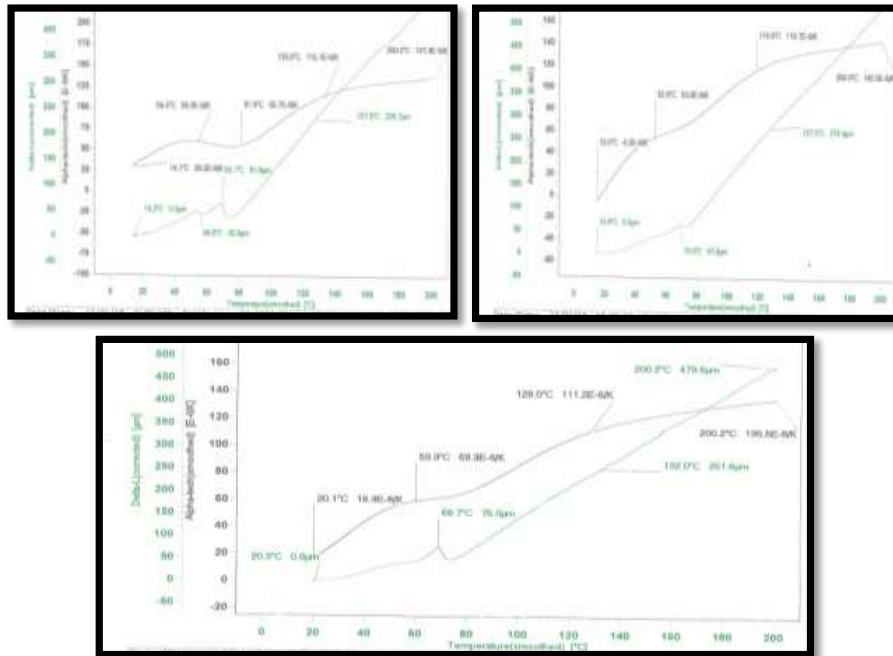


Figure (5) linear thermal expansion in and The coefficient of linear thermal expansion of a- epoxy b- 1% ZrO2 c- 5% ZrO2 in situ method

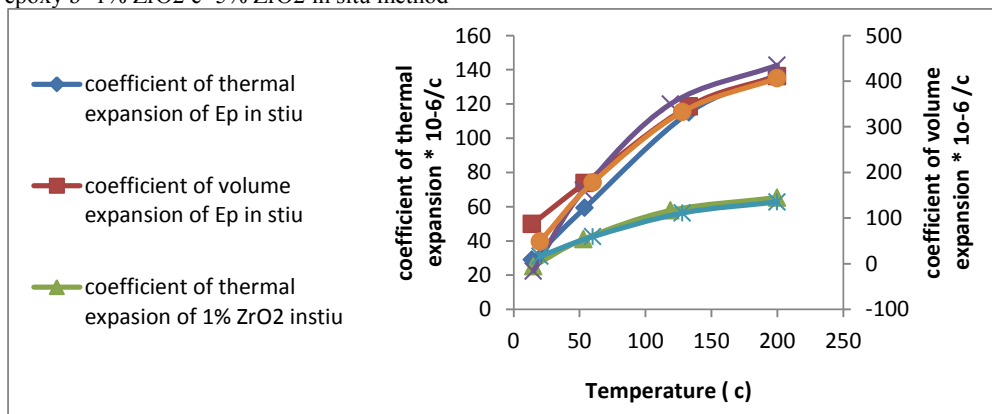


Figure (6) coefficient of linear thermal expansion and volume thermal expansion in situ method

3. Tensile strength :-

The tensile strength of polymer –nano particles composites depend mainly on the properties of its polymer, the reinforcement and the interface as well. From load-deflection or stress-strain curves in the tensile test we can get the yield strength ,and tensile strength for epoxy pure and EP/ZrO2 nano composite The figure (7) shows stress-strain curves for the epoxy pure and for EP/ZrO2 nano composites with different weight ratio of addition from (1-9%) in situ method.

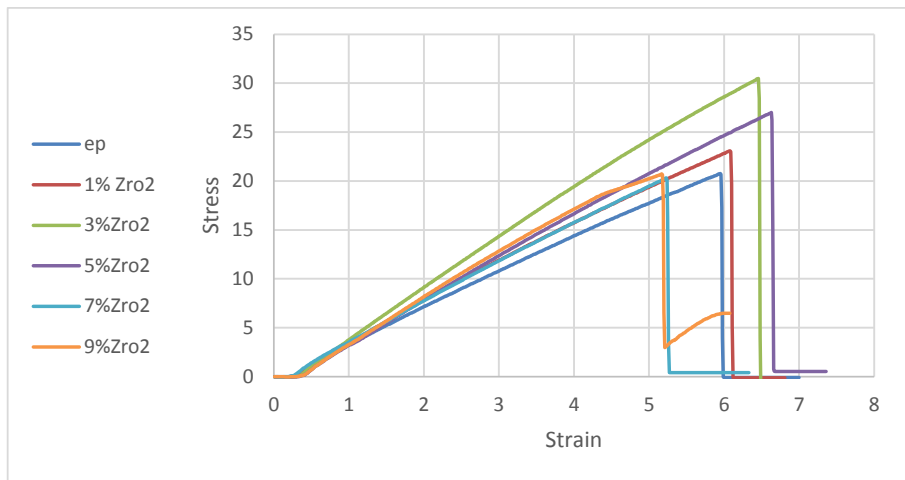


Figure (7). Stress-strain curves of epoxy and EP/ZrO₂ nanocomposites (in situ method)

The results values of the tensile strength of EP/ ZrO₂ nanocomposites in figure (8) show the difference of the tensile strengths of EP/ ZrO₂ nanocomposites. The results values of tensile strength have most possibly high values at 3% wt. At higher addition of ZrO₂ nanoparticles, tensile strength of EP/ZrO₂ nanocomposites starts degrading beyond 5%wt and 3%wt, but the results values of tensile strengths still higher than that of epoxy pure. This may be due to the excess filler addition and which leads to poor bonding in the filler, which agrees with [19].

The influence of several factors explain this behaviour in EP/ ZrO₂ nanocomposites, where the presence of ZrO₂ nanoparticles into the epoxy matrix leads to some change in the epoxy chains and structures, where good dispersion and distribution of nanoparticles into epoxy matrix perform decrease the mobility to the epoxy chains because of creation high immobility nano-layer about each nanoparticles, while the matrix chains (epoxy chains de-bonded to nanoparticles) the network of nanoparticle decrease the total mobility of the nanocomposites system.

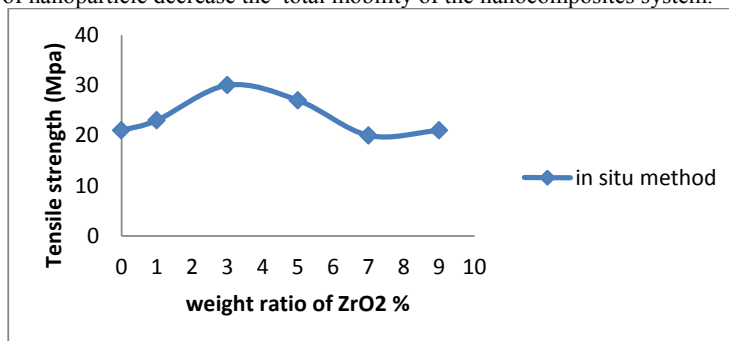


Figure (8) tensile strength as a function of weight ratio of ZrO₂

4. Impact Strength :-

The impact property of polymeric materials is directly related to the overall toughness of the material. The impact test is to measure the relative susceptibility of a standard test specimen to the pendulum type impact load. The results are expressed in terms of kinetic energy consumed by the pendulum in order to break the specimen. Figures (9) show the impact strength (Gc) for both methods. The results of impact strength test showed that the addition of ZrO₂ particles increased the value of the impact strength, 5wt% in situ method has the highest impact strength but increasing the percentage of ZrO₂ to 9wt% lowered the impact strength. Due to the interfacial shear strength between filler and matrix is high due to the formation of cross-links or supra molecular bonding which cover or shield the fillers that in turn prevents propagation of the crack. Also, the crack propagation can be changed by good bonding between filler and resin matrix. The aggregation of modified ZrO₂ at (7 and 9wt% in situ), that lead to the reduction in impact strength because of the higher surface area of the fillers, stress concentration around this aggregation which lead to crack proportion. Also, the increase in the

percentage of ZrO₂ particles affects the interface region lead to a lowering of energy dissipation per unit volume and consequently lowers the impact strength which agree with [20].

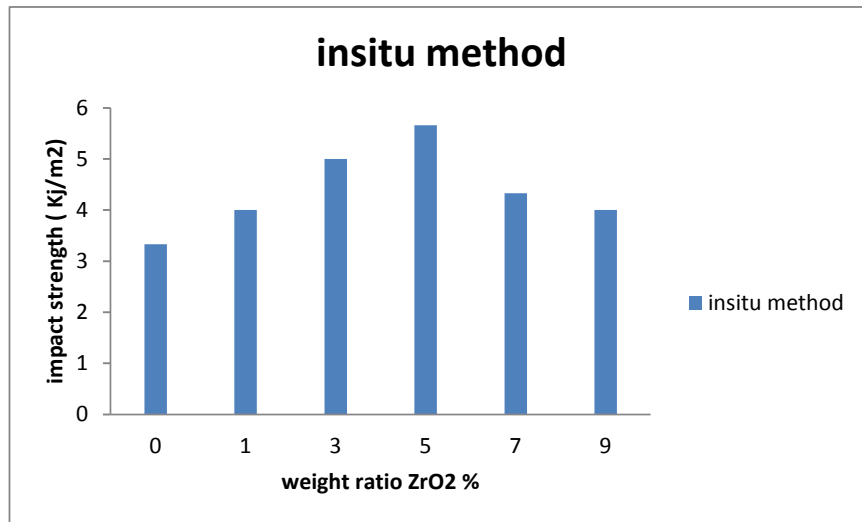


Figure (9) impact strength as a function of weight ratio

5. shear bonding strength

From load-deflection or stress-strain curves in bonding test we can get the bonding strength for epoxy pure and EP/ZrO₂ nano composite. The max stress in 5% wt. The bond strength of epoxy nanocomposites substrate concrete were significantly higher than epoxy adhesive pure . The bond strength of the neat epoxy was 3 Mpa (in situ) , when adding ZrO₂ weight ratio did make a significant improvement of bond strength of the epoxy nanocomposites up 5% wt. . Increase in particle loading due to increase in weight fraction leads to uniform and continuous interface that may create a strong polymer network improving the mechanical properties .The quality of interface and the strength of the adhesion at the interface determine load transfer between the matrix and the nano fillers [21,22]. bonding strength slightly increased until a filler concentration of 5 wt % , and then started to decrease for higher ZrO₂ concentration , probably because of agglomeration phenomena . shown in figure (10) The general improvements of these properties are due to good distribution of ZrO₂ Uniform dispersed ZrO₂ could improve the energy absorbing capacity of the material, restrict the epoxy chain mobility , and shorten the distance among cross linking points, this increasing the properties of the nano composites [23] which agree with [24]

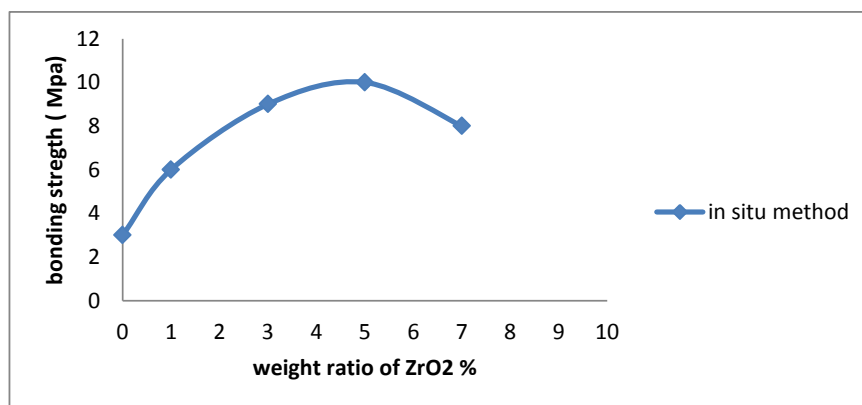


Figure (10) shear bonding strength as a function of weight ratio

6. pull off adhesion test :-

The bond strength of epoxy resin to substrate concrete was determined using a pull-off test. Figure (11) indicates the pull-off test results of concrete bonded with epoxy resin containing varying weight ratio of ZrO₂ filler . The bond strength of epoxy nanocomposites were significantly higher than the epoxy concrete with epoxy adhesive pure . The bond strength of the neat epoxy cement was 0.85

Mpa (in situ methods) , when adding ZrO₂ weight ratio did make a significant improvement of bond strength of the epoxy nanocomposites up 5% wt. for both methods . Increase in particle loading due to increase in weight fraction leads to uniform and continuous interface that may create a strong polymer network improving the mechanical properties .The quality of interface and the strength of the adhesion at the interface determine load transfer between the matrix and the nano fillers [21]. bonding strength slightly increased until a filler concentration of 5 wt % , and then started to decrease for higher ZrO₂ concentration , probably because of agglomeration phenomena . Uniform dispersed ZrO₂ could improve the energy absorbing capacity of the material, restrict the epoxy chain mobility , and shorten the distance among cross linking points, this increasing the properties of the nano composites [22].

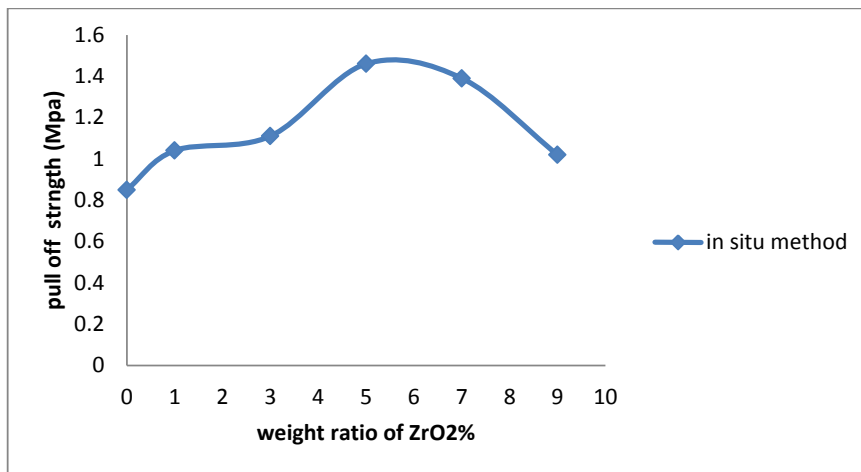


Figure (11) pull off strength as function of weight ratio

8- conclusion :-

ZrO₂ nano enhance thermal expansion , mechanical strength (tensile and impact strength) and adhesion test (shear bonding and pull off) of epoxy resin with different weight ratio of ZrO₂ , the best value of addition of ZrO₂ which is used to improvement of thermal expansion , mechanical , and adhesion tests at 5% weight ratio .

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