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Study the effect of ZnO nanoparticles reinforced sawdust /epoxy composites on mechanical properties

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In the last few decades, Composites reinforced with natural fibre have generated more interest by researches and engineers due to their law density, high strength, low cost, light weight, recyclability and biodegradability and has gained a special category of green composite. In this work, wood dust reinforced epoxy composites were prepared with 20:80 % filler vol. zinc oxide nanoparticles (ZnONPs) sawdust/epoxy composites were synthesized by a simple casting method with five different ratios [0.1, 0.3, 0.5, 0.7 and 1% Vol.] of ZnONPs. The samples of the nanocomposites were characterized by the scanning electron microscopy (SEM) technique. The flexural strength and hardness tests were carried out to study the mechanical properties of the composites. From the observation it was found that the mechanical property increases up to certain filler 0.5 vol. % and then properties gradually decrease.

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1. Introduction

Recently, interest in engineering, scientific and industrial researches has shifted to polymeric compounds. Polymers and their compounds have the across-the-board attraction in materials technology, due to their density and better strength compared to homogeneous metallic alloys[1, 2]. Polymer composites have considerably attracted many researchers to replace traditional materials, i.e, ceramics, metals, and plastics in many engineering applications. Nowadays, composite materials are selected as materials in engineering products due to their high strength, lightweight, high hardness, wear resistance, low thermal expansion, and long life[3, 4].

Composite materials are well-known as strong reinforcement material fused to the more fragile matrix. The role of the matrix in the reinforced composite is to transmit pressure and provide a barrier against the adverse environment and protect the surface from mechanical abrasion. The components of the compounds retain their individual, physical and chemical properties. Nevertheless, together they create a powerful set of specifications that separate components cannot produce individually[4-6]. In the same context, current scientific studies based on the recycling of metal waste and wood are important in enhancing the efficiency of the surroundings. Sawdust is waste from the carpentry process, i,e, routing, drilling, sanding, grinding, planning, and publications. It can play an important role in improving the properties of polymeric materials[7, 8].

Epoxy resins were marketed in the late 1940s and used in multiple engineering, industrial, and commercial applications. It has good resistance to chemicals and corrosion, low shrinkage, better toughness, great adhesion properties, suitable thermo-mechanical properties, good dielectric strength[9, 10]. Unlike other polymer resins, epoxy can maintain its physical and mechanical properties under the influence of aggressive solvents. Also, epoxy resin will adhere to almost all materials such as wood, stone, glass, fibers, ceramics, plastics, and metal[11-13].

Nanomaterials are of very importance in the fields of science, engineering, and commercial industries, due to their small size, unique surface area, and distinctive properties. Therefore, the incorporation of nanostructured into polymers provides successful solutions to

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many deficiencies in polymer applications[14-16]. Nowadays, ZnONPs have great attention due to their applications in UV absorption, antibacterial, photocatalytic, and its highly photosensitive properties, improving mechanical properties[17-19]. Also, ZnONPs contributes to improving the optical, electrical, thermal, and mechanical properties of many polymers due to heat conductivity, high heat capacity, low thermal expansion and high melting temperature, high hardness (approximate 4.5 on the Mohs scale)[20-22].

In this study, an attempt was made to develop sawdust/epoxy composites by adding ZnONPs to the polymer matrix. For this purpose, surface roughness, three-point bending, and hardness tests were carried out. Then the results of all samples were evaluated and interpreted. The compound could be a promising future material for many advanced applications.

2. Materials and methodology

2.1. Materials

The materials used to prepare nanocomposites were epoxy resin (Bisphenol A diglycidyl Badge Ether), hardener (4,4diamino diphenyl methane DDM) manufactured by the Swiss-Egyptian chemical industries company. The ratio of epoxy to hardening was 3 to 1. Sawdust (SD) was a by-product of woodworking operation obtained from local industry, The SD particles were sieved through a sieve with a particle diameter of 0.063 mm and a density of about 0.2 g/cm^3, as shown in Fig.1. The sawdust was dried at a temperature of 60^{o}C to remove moisture and any other impurities. ZnONPs were obtained from a sky-spring Materials company in the USA with a purity of 99%; particle size of about 10-30 nm, and modified by silane coupling agents.

Fig. 1. Sawdust after cleaning and sieving.

2.2. Composite preparation

In a typical preparation, ZnONPs with ratios [0.1,0.3,0.5,0.7 and 1vol.%] were added to the hardener in a glass flask and mixed for 30 min by an ultrasound instrument. Then a 80% moisture-free epoxy resin and 20% SD was mixed vigorously with first mixture by glass rod to obtain a homogeneous solution. The mixture is then poured into glass molds with dimensions (15 x 10 x 0.3) cm^3, and covered with a release agent. A homogeneous SD/epoxy composite was also prepared in a separate glass mold. The whole mixture in the molds is cured for 24 - 48 hours at room temperature. Table 1 shows the preparation concentrations for all samples.

Table 1. Volume percentages for the prepared samples.

ZnO Vol.%	SD% (Sawdust)	ER% (Epoxy resin)
0	20	80
0.1	20	80
0.3	20	80
0.5	20	80
0.7	20	80
1	20	80

2.3. Scanning electron microscopy (SEM)

SEM has an essential role in the characterization of the morphology of surfaces and their components in determining the causes of failure. Also used to analyze agglomeration, voids, homogeneity of components, and dispersion of fillers in materials. The morphology of the specimens' surface was examined by a Inspect™ - Scanning Electron Microscope from FEI Company in Baghdad/Iraq.

2.4. Flexural test

The three-point flexural tests of ZnO-SD/epoxy composites are carried out using (TIANQIAO TESTING EQUIPMENT) testing machine as per ASTM D 790- at 24 °C. The specimens were tested at crosshead speeds of 1 mm/min, The sample of rectangular cross section rests on two supports and is loaded by means of a loading nose midway between the anchors.

Flexural strength can be calculated from Eq.1[23]:

$$F = \frac{3PL}{2bd^2} \quad \text{(eq. 1)}$$

where F: Flexural strength of specimen (MPa), P: failure load (N), L: Effective span of the beam (400mm), d and b: the thickness and width of the specimen.

The flexural modulus E is a measure of the stiffness during the first initial part of the bending process.

$$E = \frac{L^3}{4bd^3} \cdot \frac{P}{D} \quad \text{(eq. 2)}$$

P/D refers to the slope of tangent of the steepest initial straight-line portion of load-deflection curve

2.5. Hardness test

Shore Hardness is a measure of the resistance of a material to penetration of a spring-loaded needle-like indenter. The hardness test is performed at room temperature with Digital Micro Shore D (Durometer Model: TH210 ISO 9001) according to (ASTM D2240), made in the USA.

2.6. Surface roughness test

The surface roughness influences the mechanical properties as a concept describing the surface (microstructure). It's important to know this effect for the contacting surfaces of the nanocomposites because it is an important characteristic to be taken into consideration. The roughness measurement by Portable Digital Sr220 Surface Roughness Tester (Resolution:0.02µm/±40µm: Accuracy: Less than or equal to ±10%; made in PRC).

3. Results and discussion

3.1. Surface morphology

Fig. 2(a-c) shows the morphological images of the SD/epoxy composites sample and the results at the Nano- and micro-level indicate the presence of cracks on the surface. Fig. 2(a-c) shows the morphological images of the SD/epoxy composites with 0.5% vol. of ZnONPs sample the results confirm the presence of nanoclusters on the surface like-clusters of NPs, and their presence can be attributed to the ZnONPs effect. In Fig. 4(a-c) after added 1% vol. of ZnONPs also the result show the presence of agglomeration of NPs on the surface. In comparison, the results indicate a significant effect of adding ZnONPs on the morphology of the epoxy polymer reinforced with SD.

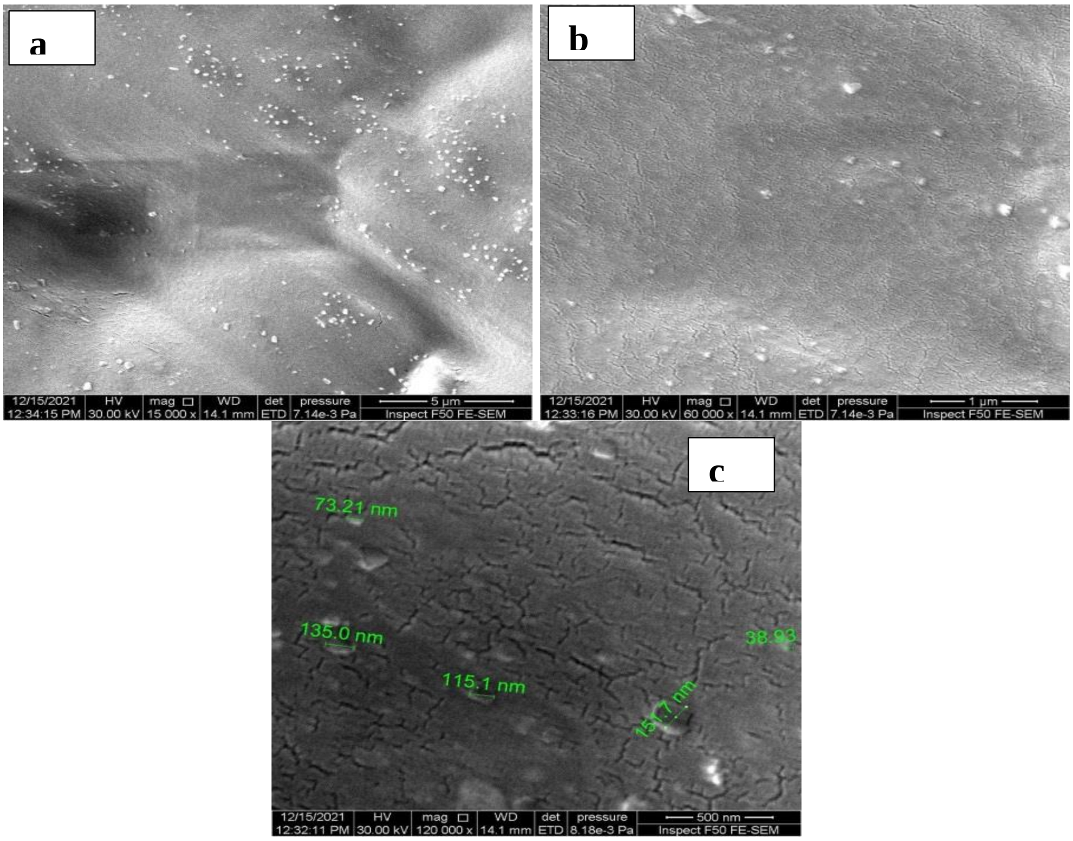

Fig. 2. SEM images of sawdust/epoxy composites.

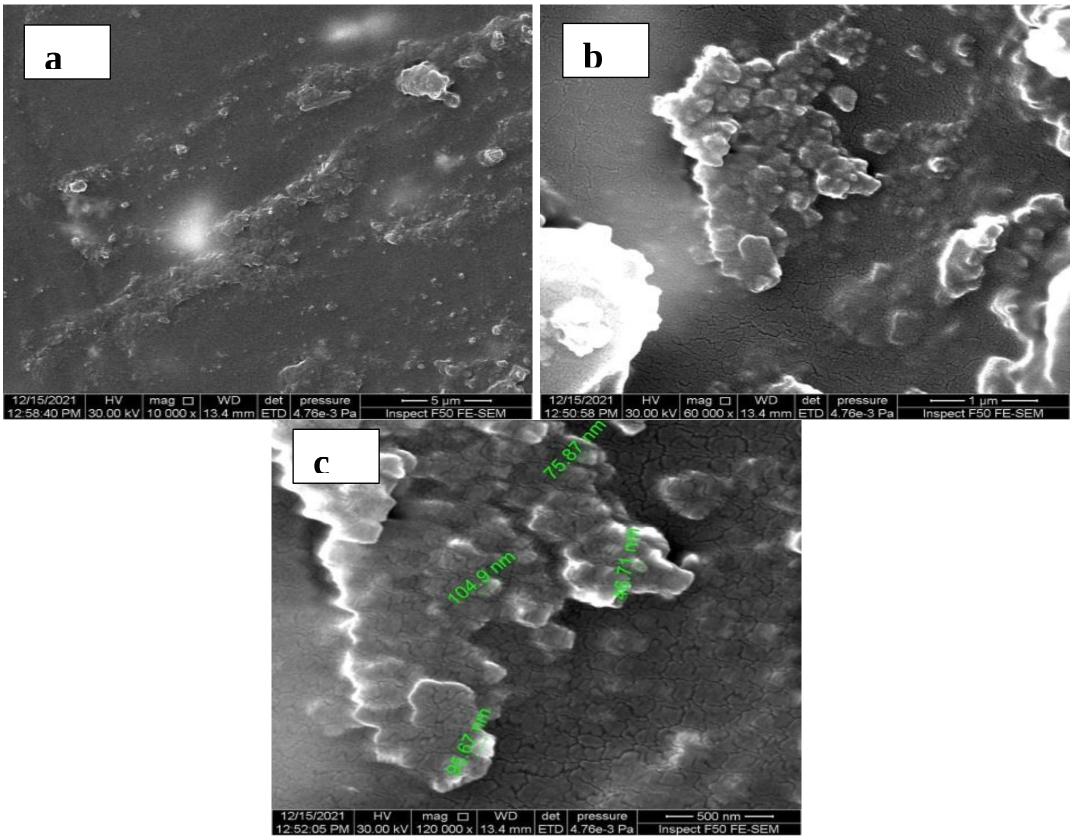

Fig.3. SEM images of sawdust/epoxy composites with 0.5% vol. of ZnONPs.

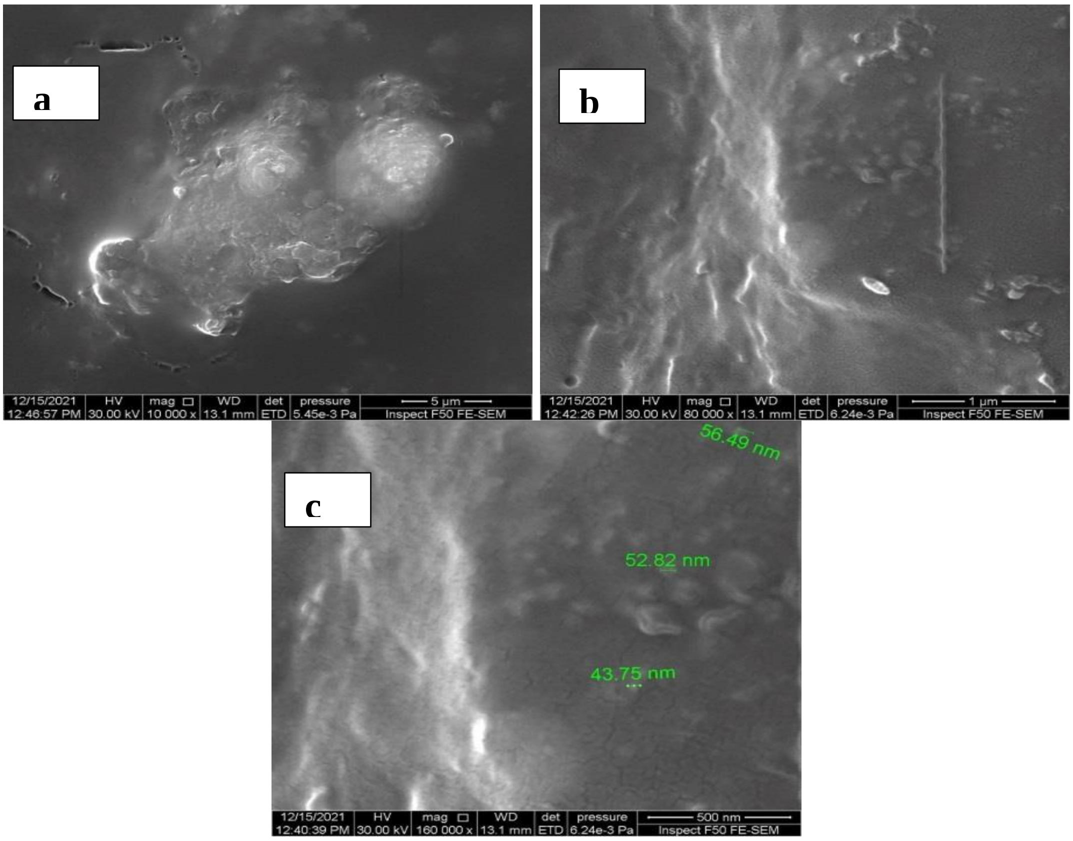

Fig. 4. SEM images of sawdust/epoxy composites with 1%vol. of ZnONPs.

3.2. Flexural test results

Flexural represents the ability of a material to resist deformation under load and it can be measured by applying the stress law, which states that it is the amount of the vertical force per unit cross-sectional area of the sample. Fig. 5 shows the change in flexural strength values as a function of increasing the ZnONPs content in the epoxy polymer matrix. The results indicate that the flexural strength increased with the increase of ZnONPs content compared to the pure sample. Also, the results confirm that the flexural strength values begin to gradually rise at the ZnONPs content (0.1 and 0.3 % Vol.) to reach the highest value at the ratio (0.5% Vol.) and then return to gradually decreasing at the values (0.7% and 1% Vol.). There are several reasons for this decrease in flexural strength. The weak boundary between ZnONPs and trapped bubbles or due to agglomeration of ZnO NPs at high content and loss of ability to take distinct sites in the polymer matrix, then loss homogeneity in the cross-linking of epoxy polymer and ZnONPs. The interlayer region of the particles is high and their interaction with the epoxy polymer chain will result in lower homogeneity in cross-linking density [24, 25]. Here the fracture is brittle and may be attributed to cavitation and crazing in the structure of the polymer. Cavitation occurs due to the formation of holes (a few nanometers to several micrometers) in the matrix of Epoxy during deformation due to extreme stress which is usually a precursor to crazing[26, 27]. Fig. 6 shows the samples before and after the Flexural test.

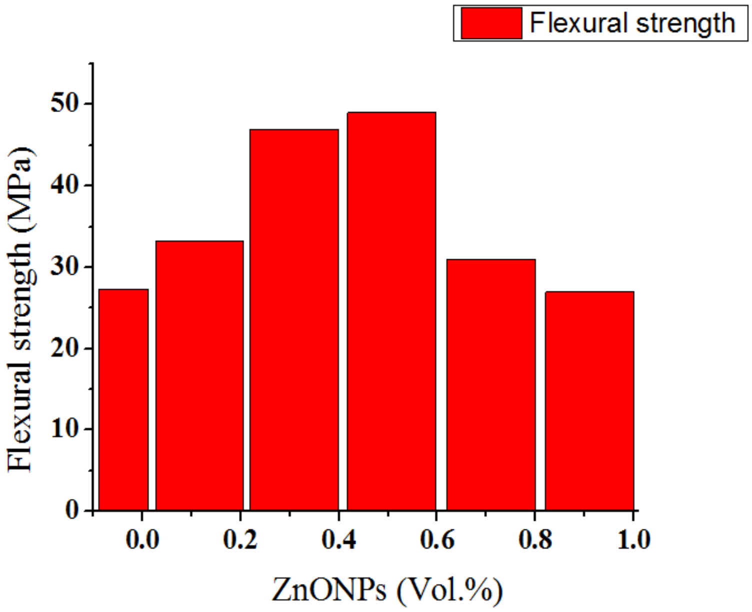

Fig. 5. Flexural strength of SD/epoxy composites vs. ZnONPs vol%. at maximum load.

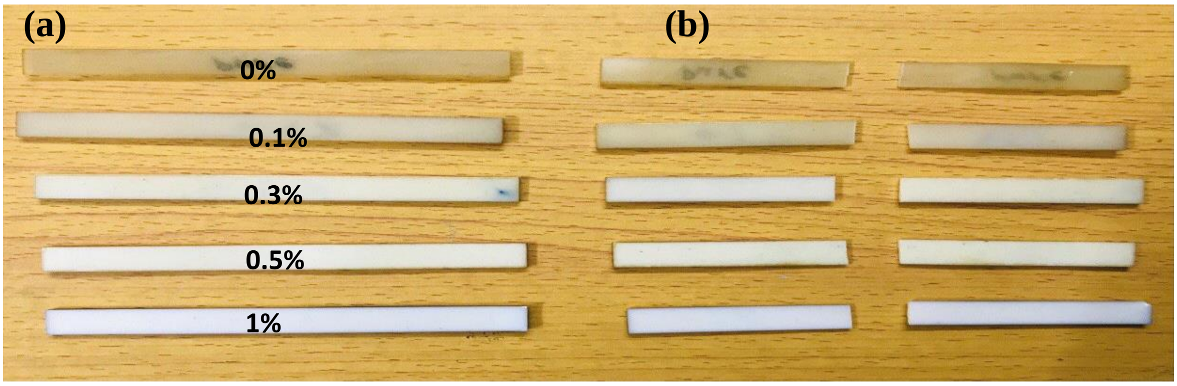

Fig. 6. The samples (a) before and (b) after the flexural test.

The young's modulus (E) is a property of matter that shows how much it is deformed and stretched. It is defined as the ratio of tensile stress to tensile strain[28]. The flexure stresses known as stresses caused by the bending moment[29]. Table 2 show the values of flexural strength (S_{max}) and Young's modulus (E) as a function of volume ratios of ZnO NPs. The results confirm that the flexural stress increases with the entry of ZnONPs into the epoxy polymer matrix. And the sample 0.5%Vol of ZnONPs has a better flexural stress value. The results of Young’s modulus show that the elasticity of the material decreases with the addition of ZnONPs in the epoxy polymer as a result of the effect of nanomaterials on the properties of the polymer, these results are in agreement with the results[30].

Table 2. Flexural strength (S_{max}), Young's modulus (E) for SD/epoxy composites at different concentration of ZnO NPs.

ZnO vol.%	S_{max} (MPa)	E (GPa)
0	23.99	0.93
0.1	27.88	1.53
0.3	46.53	2.10
0.5	71.75	3.00
0.7	61.42	1.17
1	24.09	0.77

3.3. Hardness test

A hardness test is a property that enables a material to maintain the shape of its cohesive surface under the influence of static and dynamic loads. Also, it refers to the resistance exhibited by components of a pure and treated compound being indented on the surface of the material[31, 32]. Fig. 7 shows hardness values with ZnONPs content, and results showed an increase in the hardness of the nanocomposite with increasing ZnONPs content up to 0.5% vol., and then the hardness values return to decrease with increasing ZnONPs content up to 1% Vol.

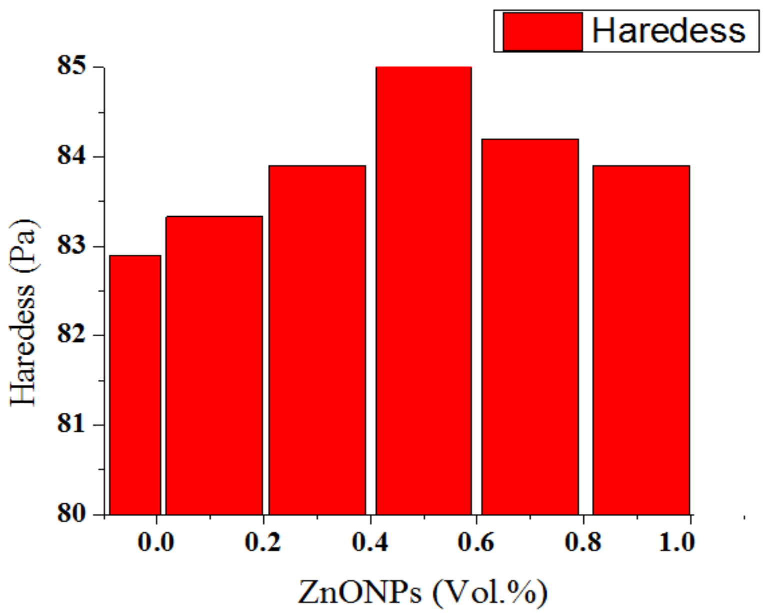

Fig. 7. Hardness of SD/epoxy composites vs. ZnONPs Vol%. at maximum load.

The increase of hardness may be attributed to the homogenous dispersion of ZnONPs in the epoxy polymer matrix. In contrast, the decrease in hardness is due to the inhomogeneous dispersion in the epoxy polymer matrix. Therefore the agglomeration of ZnONPs allows making defects in the structure and thus reduces the mechanical properties[33].

3.4. Surface roughness results

The surface roughness test was carried out for the SD /epoxy composite and SD /epoxy composite reinforced with ZnO the average values between the fine roughness and the maximum height of the sample were determined. The results show an improvement in the surface roughness for 0.5%vol. of ZnO reinforced SD /epoxy composite sample as compared with SD /epoxy composite sample. With surface roughness values of 0.109 and 0.146 µm, respectively. This improvement in surface roughness is due to the presence of ZnONPs in the epoxy composition and its surface. In the same context, the roughness plays an important role in improving the surface properties of the samples, especially improving the wettability property and increasing the water contact angles (WCAs) of surfaces[34, 35]. Therefore, the increase in the surface roughness of the epoxy samples leads to an increase WCAs of the sample.

4. Conclusions

Flexural strength results indicate an increase with increasing zinc content until concentration (0.5%Vol) then return to gradually decreasing at the values (0.7% and 1% Vol). Due to the difference in the dispersion of nanostructures in the polymer matrix and the agglomeration of NPs. Hardness increases sharply when the ZnONPs content is at (5% Vol) and then decreases slightly but remains higher than that of the pure composite polymer matrix. And this decrease attributed to the agglomeration of ZnONPs allows making defects in the structure then decreases Hardness. The surface roughness increases with increasing ZnONPs content in the polymer matrix, due to the unique properties and structures of nanoparticles. This conclusion is consistent with the SEM results that confirm the increased roughness on the surface. The results achieved in the current work can contribute to the fabrication of polymeric nanocomposites with unique properties that can be used to support a variety of industrial applications.

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