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Research Article

# Synthesis of NiO and $NiFe_2O_4$ nanoparticles by ultrasonic method and investigation of microhardness of polymer composites made with these nanoparticles and epoxy resin

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**ABSTRACT**

In this article, nickel oxide and nickel ferrite nanoparticles were first synthesized using an ultrasonic method as a simple, fast, eco-friendly, and cost-effective method. To ensure the properties of the nanoparticles and to avoid problems in the following steps, the nanoparticles are synthesized under various analyzes such as scanning electron microscopy (SEM) images, infrared spectroscopy (IR), an X-ray diffraction pattern (XRD), and Vibrating sample magnetometry (VSM). In the next step, using these nanoparticles and epoxy resin, a polymer matrix composite was made. Then, the composites were tested for corrosion against acid and hardness tests based on the ASTM D2583-13 standard. The results showed that the structure of the manufactured nanoparticles is very uniform and homogeneous. In addition, the hardness of composites made from nickel ferrite and nickel oxide nanoparticles was improved compared to pure polymer, and composites made from nickel ferrite had better hardness than composites made from nickel oxide. Also, the acid corrosion test results showed that creating a composite layer around aluminum can protect it against acid corrosion.

***Keywords:*** Ultrasonic method, nickel oxide, nickel ferrite, polymer matrix composite
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## 1. Introduction

The ultrasonic method is based on a process called cavitation. The waves emitted in the solution cause an increase in the local pressure and temperature in the reaction medium. By doing this, small transitory bubbles are formed and grow, and after these bubbles explode, a shock wave is created, and a more uniform and better structure is formed. This shock wave breaks covalent bonds, homogenizes, and carries out chemical reactions, especially synthesizing nanoparticles, organic materials, etc. [1]. Ultrasonication is a safe, fast, and cost-effective technology [2] that is used to produce many good quality nanostructures in various fields such as chemistry [3], physics [4], industrial applications [5,6], and medicine [7] is appropriate. Among the basic elements, nanoparticles are considered the most important and the first element and have many applications in various fields. It can be said that nanoparticle is the basis and the beginning of any type of nanomaterial construction. A nanoparticle is a particle whose size is between 1-100 nanometers in all three dimensions. One of the applications of nanoparticles is their use in producing nanocomposites. Nanocomposites are a group of composites with a nanoscale phase, such as nanoparticles, nanotubes, or a layered nanostructure. Nanocomposites are one of the best candidates to overcome the limitations of various engineering materials [8]. Nanoparticles, due to their high surface-to-volume ratio, when they are used as a reinforcing phase, in addition to increasing the various properties of the composite, do not change the weight of the structure too much. Polymers that are often used as composites are thermoplastic polymers, thermoset polymers or elastomers. They are a source of a wide range of low-cost raw materials that offer many advantages such as light weight, high corrosion resistance, good electrical and thermal insulation, ease of forming, and cheap and convenient mass production. Reinforcements are added to polymer materials to compensate for these deficiencies and improve their properties [9]. Epoxy resins have excellent electrical properties, high chemical resistance, strength, and low moisture absorption. They are versatile resins with a high strength-to-weight ratio, good corrosion resistance, dimensional stability, and good adhesion properties. Adding different materials and making composites can improve the properties of epoxy resin. In recent years, many researchers have synthesized different nanoparticles for various applications. Alizadeh et al. [10] used the ultrasonic method to synthesize core-shell CdS/TiO2 nanostructures, control their particle size, and optimize the effective parameters. In addition, the response surface method was used to optimize the shell thickness. They optimized four parameters: temperature (67-79°C), synthesis time (105-45 minutes), $TiO_2$:CdS ratio (1.5-7.5), and power of ultrasonic waves (37-53 Watt),. Their results showed that the power of ultrasonic waves and synthesis time have the greatest effect on particle size. Xia et al. [11] synthesized polyaniline nanoparticles using ultrasonic waves. They found that using ultrasonic waves increases the rate of polymerization of aniline, which is very slow under normal conditions. Ultrasonic radiation also emits HCL molecules and improves the degree of doping. Kartigayan et al. [12] produced nickel, cobalt, and copper ferrite nanoparticles green and eco-friendly way. They used these materials as anodes for batteries and reported that cobalt and nickel ferrites have a cubic spinel structure, while copper ferrite has a tetragonal structure. Gopi et al. [13] synthesized hydroxyapatite nanoparticles by ultrasonic method. They investigated the ultrasonic irradiation time on the size of nanoparticles in the presence of glycine acrylic acid hollow spheres. The results showed that the particle size decreases with the increase of ultrasonic irradiation time. Therefore, using ultrasound waves is an easy way to obtain nanoparticles with high quality and suitable morphology. Sheini et al. [14] synthesized tin (II) sulfide nanoparticles doped with indium (In) by ultrasonic method and investigated their optical and photocatalytic properties. The XRD patterns of the nanoparticles indicate the formation of orthorhombic polycrystalline SnS. Scanning electron microscopy confirmed the formation of flower-like nanoparticles with particle size below 100 nm for both SnS and doped SnS samples, and photocatalytic experiments showed that high power could be achieved using doped SnS nanoparticles. Nouri et al. [15] synthesized silver nanoparticles using the ultrasonic method as green and eco-friendly. The results showed that by using ultrasonic, small and uniform nanoparticles with an average particle size below 10 nm can be obtained. In addition, ultrasonic synthesized silver nanoparticles showed significant catalytic activity for the reduction of various types of dyes as environmental pollutants. Abdi et al. [16] added $CaCO_3$ nanoparticles to the epoxy resin matrix and investigated the mechanical properties of the composites. The results of three-point tensile and bending tests showed that with the dispersion of 3% by weight of $CaCO_3$, bending strength, bending modulus, tensile strength, and tensile modulus increase by 28%, 35%, 20%, and 30%, respectively. Hosseini et al [17] synthesized nanoparticles of cobalt, nickel and copper ferrite by ultrasonic method and added them to epoxy resin. They investigated the mechanical properties of the fabricated composites and showed that the composites have better tensile properties and surface hardness compared to the pure polymer. Wang et al. [18] investigated the effect of metal organophosphorus and graphene on the flame resistance and mechanical properties of composites made with epoxy resin. They showed that by adding these materials, flame resistance is significantly improved. In addition, the mechanical properties such as the ultimate tensile strength of the composites increase.

In this research, nickel ferrite and nickel oxide nanoparticles were synthesized by ultrasonic method and then added to epoxy resin as reinforcement, and their mechanical and acid corrosion properties were investigated.

## 2. Experimental

### *2.1. Materials and method*

In order to produce cobalt ferrite nanoparticles, using the ultrasonic method, first inside the beaker, in which 150 ml of distilled water was poured, the amount of 0.3 grams of nickel acetate and 0.9 grams of iron nitrate was added, and a magnetic stirrer mixes these materials together for 30 minutes to obtain a uniform and transparent solution. Then the solution is placed in the ultrasonic system for 20 minutes. (For every 3 minutes of the light pulse, the device is turned off for 2 minutes) and at the same time, 1 M sodium hydroxide solution is slowly added to the original solution until the pH reaches 11 and the medium becomes alkaline. Finally, the solution is centrifuged and placed in the oven so that the nanoparticles dry and can be used for the next steps. The method to produce nickel oxide nanoparticles is the same as the nickel ferrite production steps, with the difference that iron nitrate is not added to the solution. 6 percent by weight of the nanoparticles synthesized in the previous step is added to the epoxy resin as a reinforcement to make these composites and mixed for 30 minutes using a stirrer. In the next step, the composites are placed in the environment for 30 minutes and in the vacuum pump for 15 minutes to DE bubble and have no voids in them. In the next step, the composites were poured into the mold according to the ASTM D2583-13 standard to prepare for the hardness test. Before performing the test, the samples were kept for 24 hours in the standard conditions of the laboratory environment (temperature 23 degrees and humidity 50%). The hardness was measured on a sample of about 1.5 mm thickness. Then the made composite was coated on the aluminum used in the aircraft body, and their corrosion properties against acid were investigated.

## 3. Results and discussion

The X-ray diffraction pattern of nickel ferrite nanoparticles is shown in Fig 1 and 2. This pattern conforms to the standard indices of JCPDS: 2267-086-01, and the Miller indices include (220), (311), (222), (400), (422), (440), (622), and (444) and small sharps indicate the small size of nanoparticles and their correct synthesis. Also, the Miller indices of nickel oxide nanoparticles include (111), (200), (220), (311), and (222), and this pattern also corresponds to the standard indices.

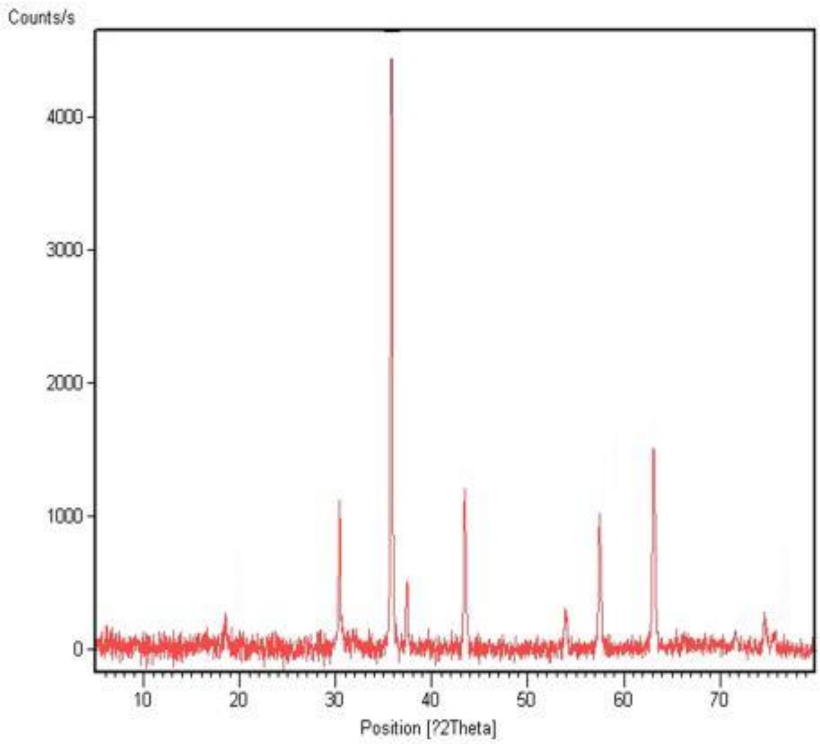



**Fig.1.** X-ray diffraction pattern of nickel ferrite nanoparticles

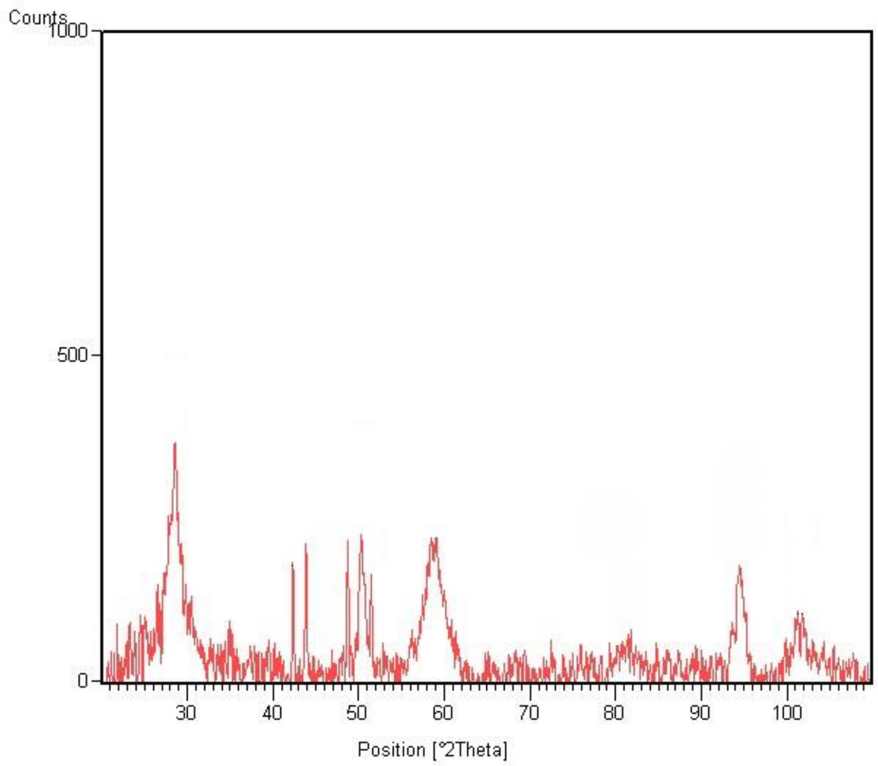
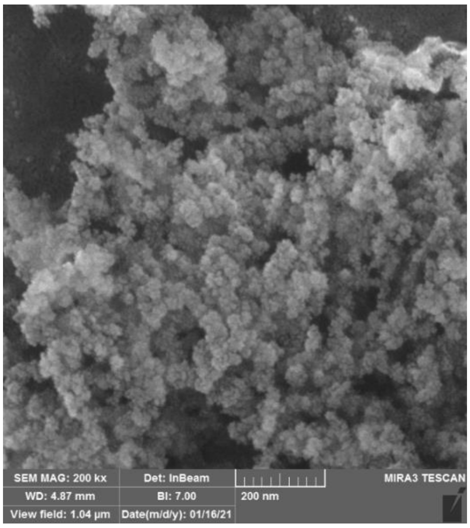
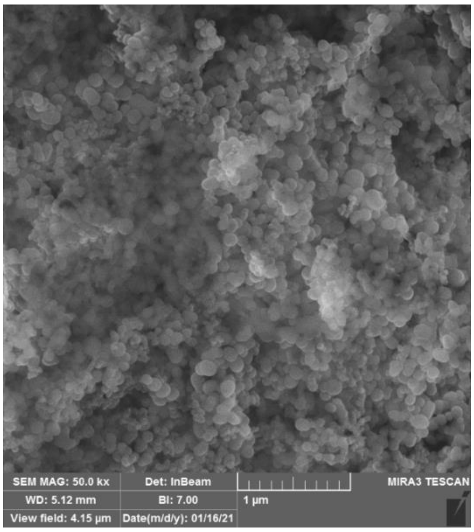



**Fig.2.** X-ray diffraction pattern of nickel oxide nanoparticles

Scanning electron microscope images of nickel ferrite nanoparticles are shown in Fig 3. These images were prepared with 25, 50, and 200 kx magnifications and working distances of 4.87, 5.11, and 5.12 mm and 1 and 2 μm and 200 nm scales. The images of nickel oxide nanoparticles are also shown in Fig 4. These images were prepared with 50, 100, and 200 kx magnifications, working distances of 4.77 and 4.80 mm, and scales of 1 μm and 200 and 500 nm. Both nanoparticles' images confirmed the fine and uniform structure without Agglomeration. Also, particle size diagrams and scanning electron microscope images confirmed the formation of particles below 50 nm. The graph of average particle size is shown in Fig 5.



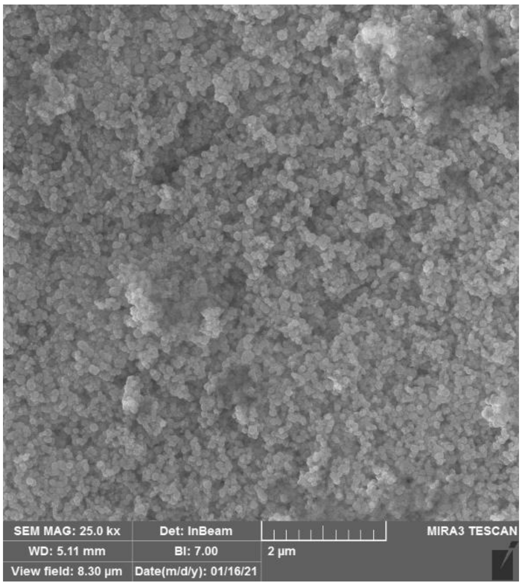
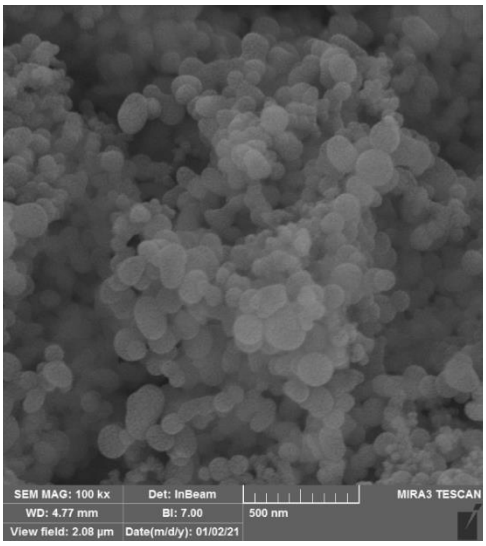
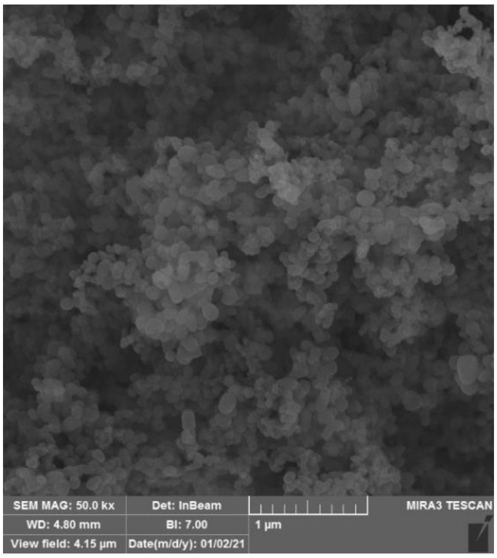



**Fig.3.** Scanning electron microscope images of nickel ferrite nanoparticles



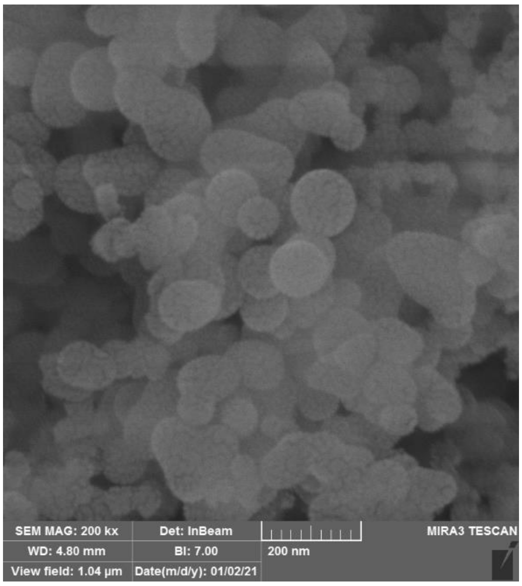



**Fig.4.** Scanning electron microscope images of nickel oxide nanoparticles

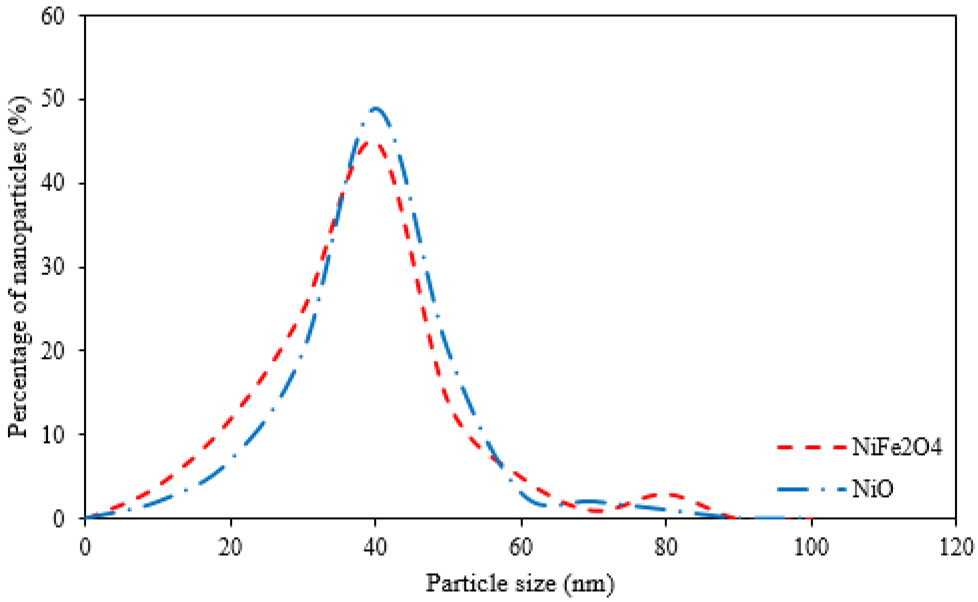



**Fig.5.** Graph of average particle size of ferrite and nickel oxide particles

The value of saturation magnetism for nickel ferrite and nickel oxide is 27 and 15 emu/g, respectively, the residual magnetism value is 12 and 7 emu/g, and the value of magnetic coercivity is about 250 orsted. The graphs show that nanoparticles have good magnetic properties and ferrite nanoparticles have better magnetic properties than oxide nanoparticles.

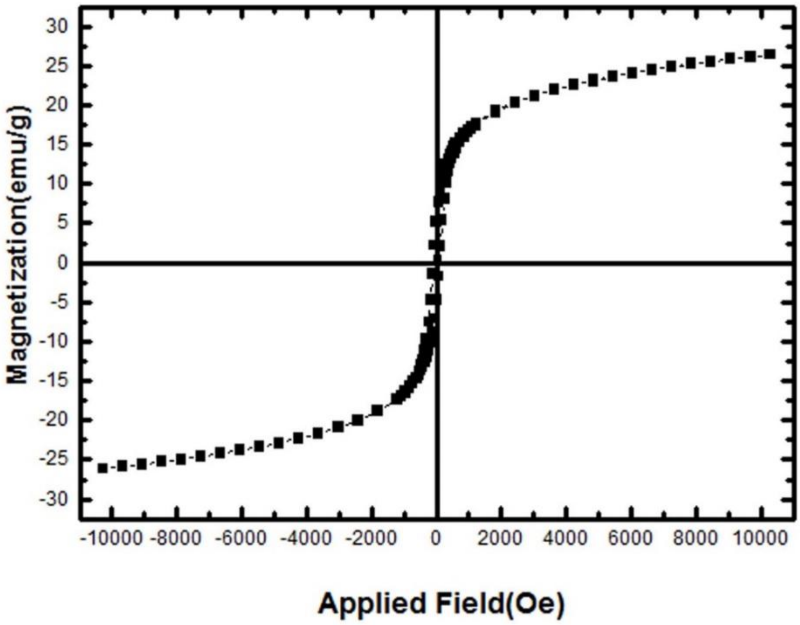



**Fig.6.** Vibrating sample magnetometry of nickel ferrite nanoparticles

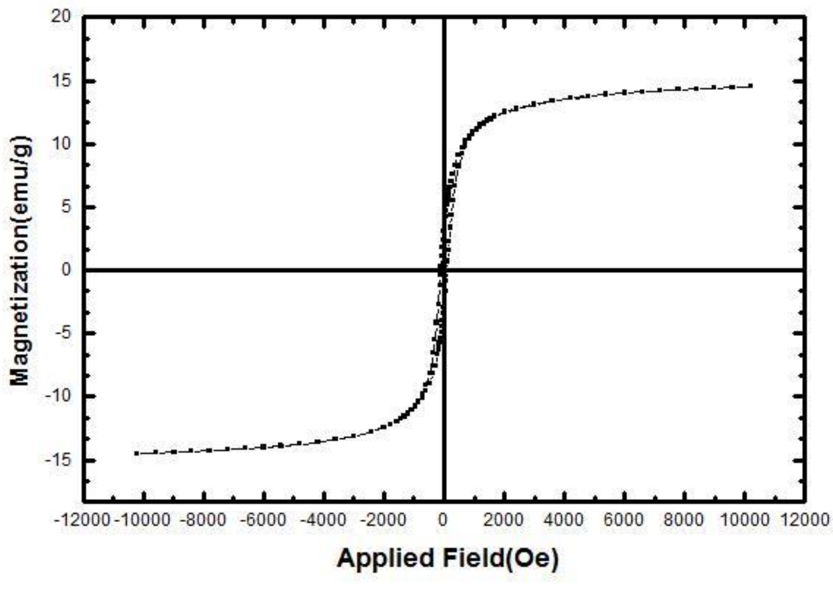



**Fig.7.**Vibrating sample magnetometry of nickel oxide nanoparticles

For ferrite, the peaks in the 616 regions are related to the metal-oxygen bond, the peaks in the 1117-1630 regions are related to acetate, and the broad peaks in the 3446 regions are associated with the oxygen-hydrogen bond. For nickel oxide, the peaks in the 400 to 600 range are related to the metal-oxygen bond, the peaks in the 1012 to 1374 range are related to acetate, and the peaks in the 3400 to 3650 range are related to the hydrogen-oxygen bond.

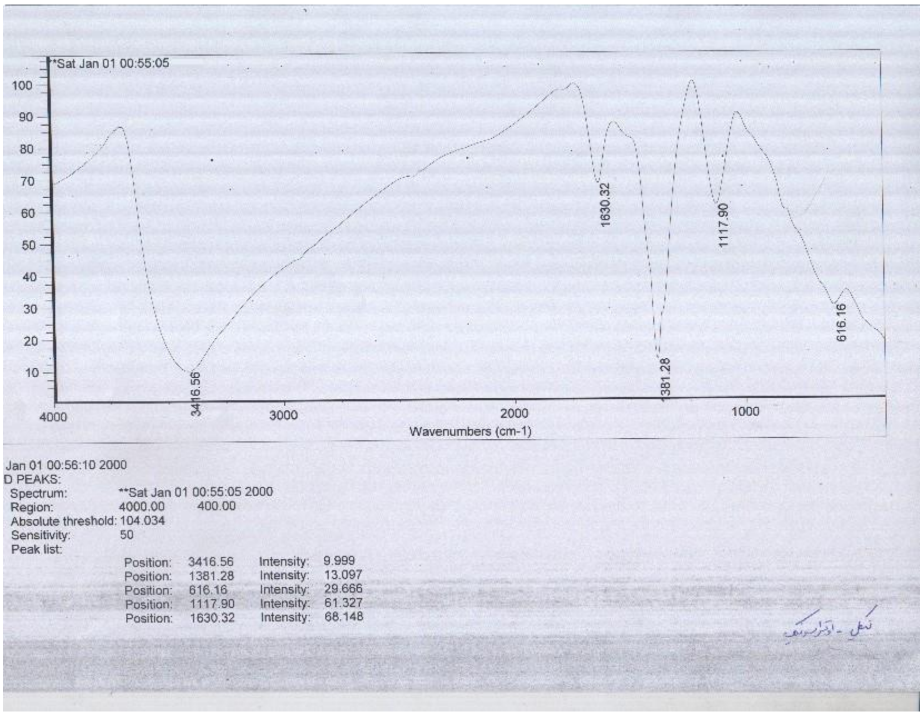



**Fig.8.** Infrared absorption spectroscopy of nickel ferrite nanoparticles

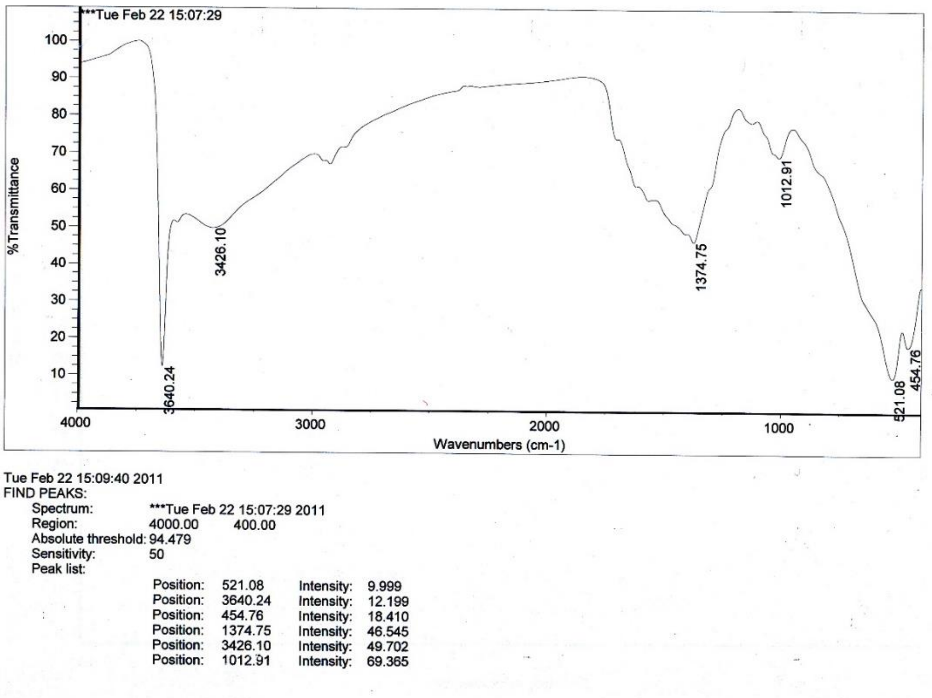



**Fig.9.** Infrared absorption spectroscopy of nickel oxide nanoparticles

Barcol hardness test was taken from pure polymer and composites, and the results are shown in Table 1. The test was repeated 10 times for each sample, and their average was reported. The results show that their surface hardness increases by adding nanoparticles to epoxy resin. Also, the hardness of ferrite-reinforced composite is better than oxide-reinforced composite, which can be due to the bonding between nanoparticles and the matrix.

**Table 1.** Hardness test results

| Average | | | Barcol microhardness value | | | | | | | | Name |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 | 17 | 15 | 17 | 16 | 17 | 15 | 16 | 16 | 18 | 16 | Epoxy |
| 19 | 19 | 20 | 18 | 18 | 20 | 21 | 20 | 18 | 19 | 19 | Epoxy/$NeFe_2O_4$ |
| 18 | 20 | 17 | 18 | 16 | 16 | 20 | 17 | 19 | 16 | 18 | Epoxy/NiO |

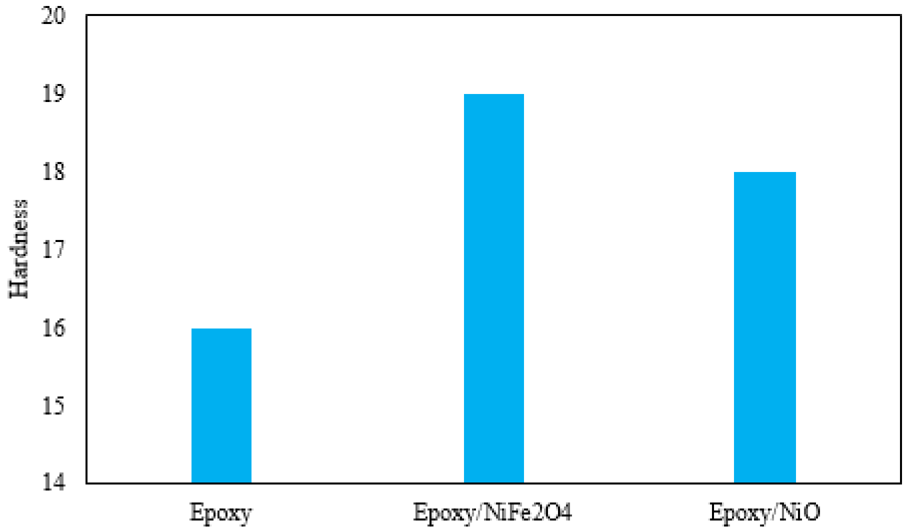



**Fig.10.** Average hardness diagram for pure polymer and composites

The results of this test show that uncoated aluminum is severely corroded by acid and destroyed. In contrast, when the manufactured composite is placed on the aluminum surface as a coating, it is entirely resistant to corrosion. Does an aluminum sample weigh 5 grams cut, and prepared for the test? Then it was exposed to hydrochloric acid corrosion for one hour. The results show that both composites improve corrosion resistance. Under the same conditions, the aluminum sample loses 57.2% of its weight, but the coated samples completely resist acid without losing weight and have become resistant.


**Fig.11.** Image of corrosion test against acid

**Table 2.** Acid corrosion test results

| Percentage of weight loss | Secondary weight | initial weight | name |
|---|---|---|---|
| 57.2 | 2.14 | 5 | Aluminum |
| 0 | 7.4 | 7.4 | Aluminum coated with Epoxy/$NiFe_2O_4$ |
| 0 | 7.4 | 7.4 | Aluminum coated with Epoxy/NiO |

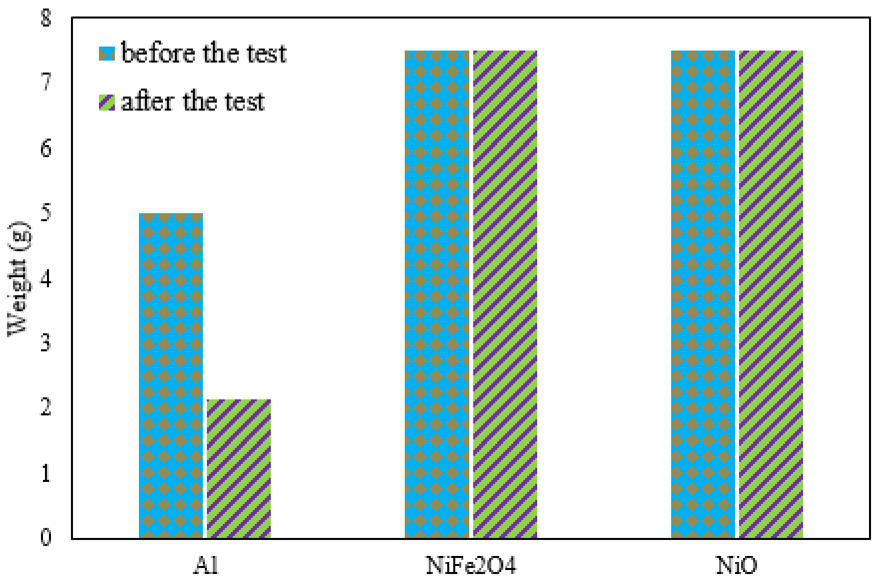



**Fig.11.** Acid corrosion test results

## 4. Conclusions

In this research, nickel oxide and nickel ferrite nanoparticles were first synthesized by the ultrasonic method, which is a green and eco-friendly method. They were subjected to XRD, VSM, SEM, and IR tests. In the next step, these nanoparticles were added to the epoxy resin as reinforcement, and their surface hardness and acid resistance were checked. The results obtained from this research are summarized below:

- Very fine and uniform nanoparticles were synthesized, and their peaks followed the standard indicators
- Nanoparticles had magnetic properties that can be used for wave absorption applications
- The high purity of nanoparticles was one of the points of ultrasonic synthesis
- The hardness of composites has improved compared to the base polymer
- The hardness of the composite prepared with ferrite nanoparticles was higher than the composite made with oxide
- Composites can be used as an acid-resistant coating

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