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Research Article

# Synthesis of cobalt oxide and cobalt ferrite nanoparticles by hydrothermal method and investigation of tensile properties of polymer matrix composites made with these nanoparticles

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**ABSTRACT**

The hydrothermal method synthesized the first cobalt ferrite and cobalt oxide nanoparticles in this article. The synthesized nanoparticles were then subjected to various analyzes such as X-ray diffraction patterns, scanning electron microscopy images, infrared spectroscopy, and vibration sample magnetometer to ensure their properties and prepare the nanoparticles for the next step. Then, 6% by weight of nanoparticles were added to the epoxy resin as a reinforce, and a polymer matrix composite was made. After making the composites according to the ASTM D638 standard, they were subjected to a tensile test. The results showed that the nanoparticles were prepared very fine, uniform, high purity, and had good magnetic properties. Also, hydrothermal was a suitable method for the synthesis of these nanoparticles. Furthermore, samples made using cobalt ferrite nanoparticles offer better tensile properties than samples made with cobalt oxide. However, in general, the tensile properties of composites have improved compared to pure polymers.

***Keywords:*** Nanoparticle synthesis, hydrothermal method, cobalt ferrite, cobalt oxide, polymer matrix composite

## 1. Introduction

Nanostructured materials exhibit novel and surprising properties quite different from their larger-scale counterparts. The properties of nanostructures always depend on their size, shape, and morphology of the nanostructures. Therefore, nanostructured materials are attracting a lot of attention due to their potential to advance and improve current devices as well as the development of future devices [1]. There are various methods for making nanostructures, which is one of the most important of them hydrothermal. In this method, the raw materials are first dissolved in an aqueous or organic solution, and in the next step, they enter the autoclave. In the autoclave machine, by increasing the temperature and pressure, the desired solution enters the critical zone, the raw materials in the solution react with each other, and nanoparticles are formed [2]. This method is one of the most powerful and widely used bottom-up methods for producing nanostructures. It has received much attention today due to its simplicity, acceptable size and shape control [3], no need for sintering and calcination, and cheapness. Usually, the nanoparticles produced by this method have acceptable quality and can be used as reinforcements to make nanocomposites. The use of nanocomposites is to compensate for the matrix's inherent defects or improve their properties with the help of different nanostructures. In polymer matrix composites, nanomaterials are used to eliminate the inherent defects of polymers, such as low mechanical strength, low thermal resistance, low electrical and thermal conductivity, and destruction against ultraviolet waves. Many researchers have made composites using synthesized nanoparticles. Zhu et al. [4] synthesized cobalt and iron ferrite nanoparticles in the presence of polyvinyl alcohol by hydrothermal method, subjected the nanoparticles to various analyses, and investigated the effect of experimental conditions on particle size and size distribution, particle morphology, and crystallinity. Their results showed that using the hydrothermal method can provide conditions for suitable ways to control the shape and size of nanoparticles. Zhang et al. [5] synthesized and produced ZnS and $CoFe_2O_4$ nanoparticles using the hydrothermal method. They obtained a fine and homogeneous structure with an average particle size between 10 and 20 nanometers. They also observed that the synthesized nanoparticles have the property of absorbing waves. Gomez et al. [6] synthesized magnetic nanoparticles using the hydrothermal method and investigated the effect of different temperatures on the quality of nanoparticles. They synthesized nanoparticles at temperatures of 120, 140, and 160 degrees Celsius. Their TEM and SEM results showed that the obtained nanoparticles have a high level of crystallinity with a uniform morphology at any temperature. Arun et al. [7] synthesized copper oxide nanoparticles using hydrothermal method and observed that their average particle size is 27 nm and CuO nanoparticles have high crystal quality with the monoclinic crystal structure. Rami Moghadam et al. [8] synthesized zinc oxide nanoparticles by hydrothermal method and used rice flour as a precursor. The results show that rice as a biological model can be used to modify the shape and size of zinc oxide particles. Different morphologies, i.e., flaky, rose, star, and rod-like structures with particle sizes in the range of micro and nanometers, were obtained. Zare et al. [9] synthesized zinc oxide nanoparticles using thyme leaf extract and the hydrothermal method. The use of thyme leaf extract as a size reduction agent and zinc nitrate as a precursor was considered the novelty of this work. The obtained ZnO nanoparticles with a size of 50-60 nm with an irregular shape were observed. The results of this study show that thyme leaf extract contains phytochemicals and has reducing properties for making zinc oxide nanoparticles, and the obtained zinc oxide nanoparticles can be effectively used for biological and food science applications. Hosseini et al. [10] synthesized nickel ferrite nanoparticles using the hydrothermal method and used them as a reinforcement for making composites. Their results showed that nanoparticles with fine and uniform structures were synthesized, and they had no impurity. Also, nanoparticles have magnetic properties that can be used for radar wave absorption applications. Sagadvan et al. [11] synthesized zirconium oxide nanowires by hydrothermal method and subjected the nanoparticles to different analyses. Their results showed that the nanoparticles were synthesized with high quality and purity, and their size is below 30 nm. Arikan et al. [12] made a polymer composite using glass fibers and epoxy resin and investigated their impact resistance properties. Their results showed that the deformation caused by delamination caused by the impact increases the absorbed energy. Layered composite designs in structures can increase the impact resistance of composites. Goji et al. [13] added carbon nanotubes to epoxy resin and investigated the mechanical properties of the composites. In the produced nanocomposites, strength and stiffness increased and more importantly, a significant increase in fracture toughness was observed. Makan et al. [14] added SiO2 nanoparticles to epoxy resin and investigated the tensile properties of the produced composites. They added 0.5 to 5% by weight of nanoparticles to epoxy resin. They reported that all composites offer better mechanical properties compared to pure epoxy. In this research, cobalt ferrite and cobalt oxide nanoparticles were synthesized by hydrothermal method. Then these nanoparticles were added to the epoxy resin and the polymer matrix composite was made and the mechanical properties of the composites were investigated.

## 2. Experimental

For synthesizing cobalt ferrite nanoparticles by hydrothermal method, 150 ml of distilled water is poured into a beaker, then 0.3 grams of cobalt acetate and 1.4 grams of iron nitrate are added to the beaker. In the next step, these materials are mixed with a magnetic stirrer. They are mixed for 30 minutes until a clear and uniform solution is obtained. In the next step, the 1 M sodium hydroxide solution that has been prepared before is slowly added to the original solution until the pH reaches eleven and the environment becomes alkaline. Then the solution is placed in a special hydrothermal container, and the particular hydrothermal container is placed in the oven at a temperature of 200 degrees for 4 hours. Afterwards, the solution is centrifuged, and nanoparticles, which are still wet, are placed in the oven to dry and prepare for the next steps. For the preparation of cobalt oxide nanoparticles, the steps are the same as for cobalt ferrite, with the difference that in the preparation of cobalt oxide, iron nitrate is no longer added to the original solution. After the nanoparticles are dried, they are subjected to various analyses. To produce nanocomposites, 4% to 8% by weight of nanoparticles were added to the base, and after the initial examination of the tensile test of the samples, the optimal amount for adding nanoparticles to the base was selected as 6% by weight. In the first step, 6% by weight of synthesized nanoparticles are added to the epoxy resin base and mixed with each other for 30 minutes using a stirrer to produce a polymer-based composite. In the next step, in order to debubble, the solution is placed in the laboratory environment for 30 minutes and in the vacuum chamber for 15 minutes so that the bubbles disappear and there are no voids. In the next step, the composite, which is still fluid, is poured into the tensile test mold according to the ASTM D638 standard, and the mold is placed on the epoxy resin box for 24 hours at ambient temperature and 24 hours in the oven at a temperature of 90 degrees. Until the composite hardens and cures. After this time, the composites are taken out of the mold and prepared for the tensile test. To perform the tensile test after the composites were made and prepared, they were subjected to the tensile test. To ensure the accuracy of the results, three numbers were made from each sample, and the test was repeated three times, and their average is reported here. The composites were tested by a tensile test machine and stretched at a speed of 1 mm/min. An image of the composite and pure polymer samples before and after the test is shown in Fig 1.

**Fig. 1**. Pictures of the samples before and after the tensile test

## 3. Results and discussion

The x-ray diffraction pattern of cobalt ferrite and cobalt oxide nanoparticles is shown in Figs 2 and 3. This pattern is completely consistent with the indices of pure standard materials. Miller indices for cobalt ferrite nanoparticles include (111), (220), (311), (222), (400), (422), (511) and (440). Also, the Miller indices for cobalt oxide nanoparticles include (220), (311), (222), (400), (422), (511), and (440).

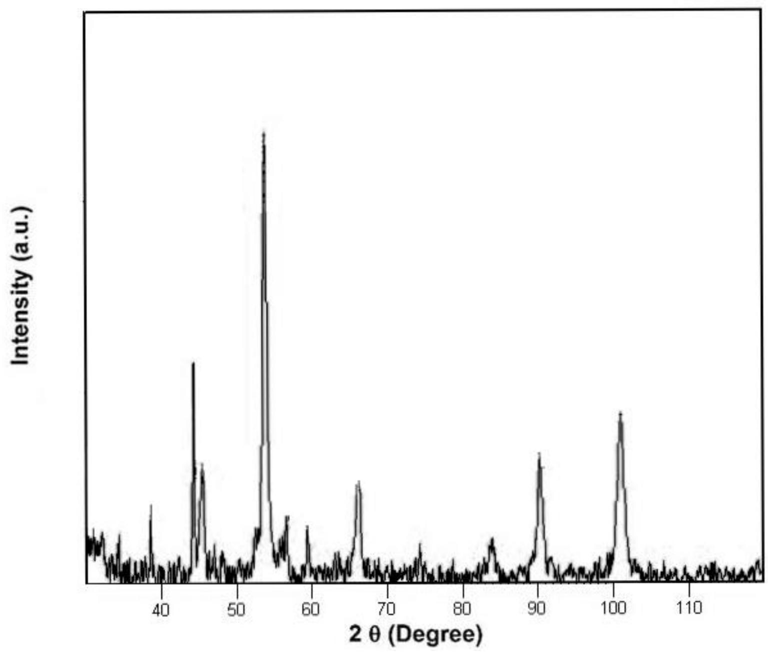



**Fig. 2.** X-ray diffraction pattern of cobalt ferrite nanoparticles

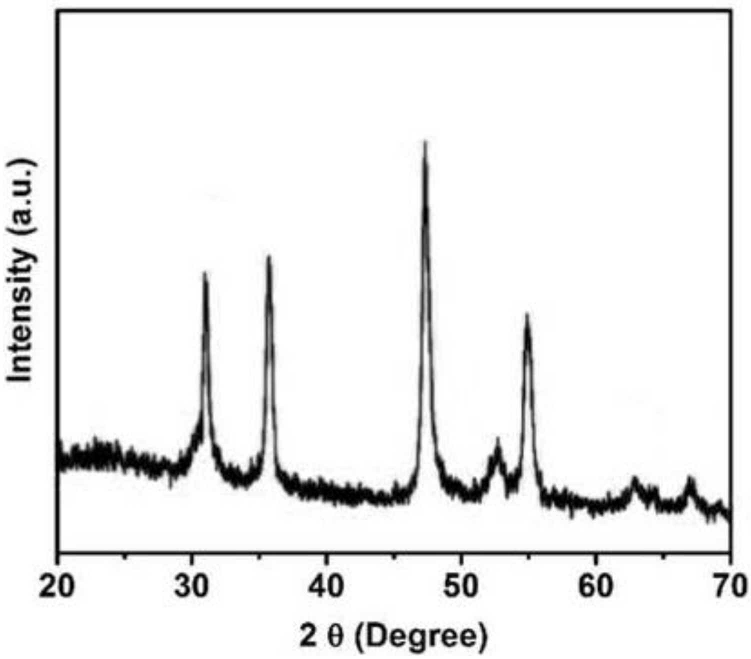
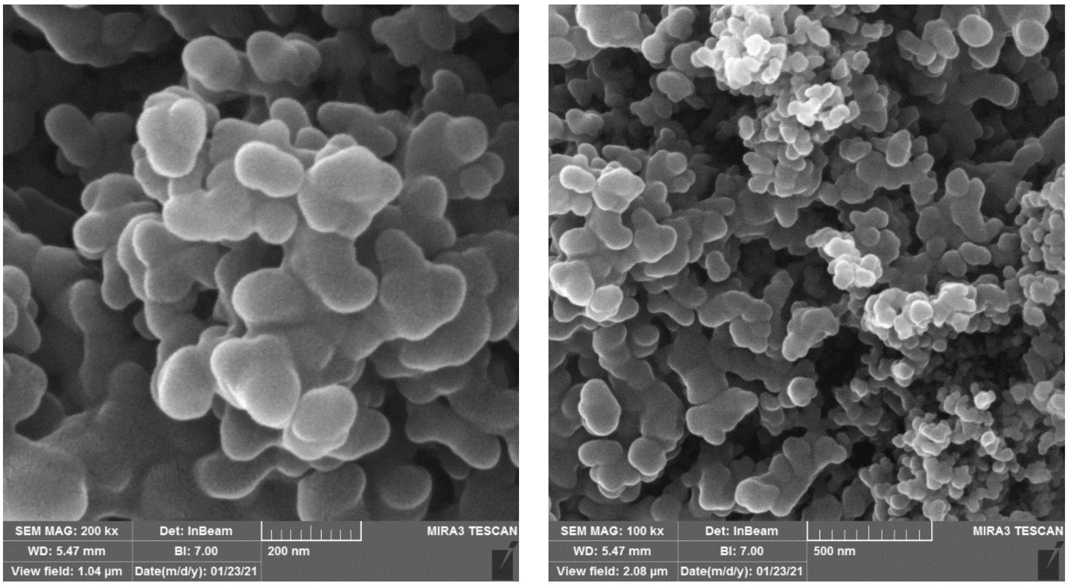


**Fig. 3.** X-ray diffraction pattern of cobalt oxide nanoparticles

Fig 4 shows the scanning electron microscope images of cobalt ferrite nanoparticles. These images were prepared with 100, 200, and 330 kx magnifications, 5.47, 5.5, and 5 mm working distances, and 100, 200, and 500 nm scales. As seen in the pictures, nanoparticles are prepared with an excellent and uniform structure without lumps and accumulation, and the average size of the particles is about 50 nm. Figure 5 shows the scanning electron microscope images of cobalt oxide nanoparticles. These images were prepared with magnifications of 50, 100, and 200 kx, a working distance of 5.47 mm, scales of 100 and 200 nm, and 1 µm. As seen from the pictures, the nanoparticles are prepared with a completely fine and uniform structure without lumps and accumulation, and the average size of the particles is about 50 nm.



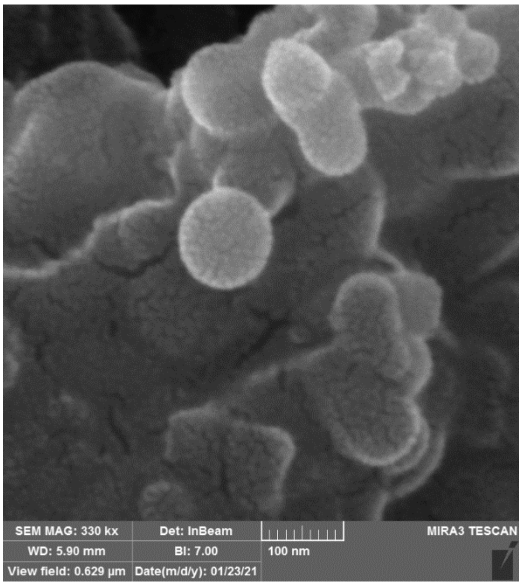
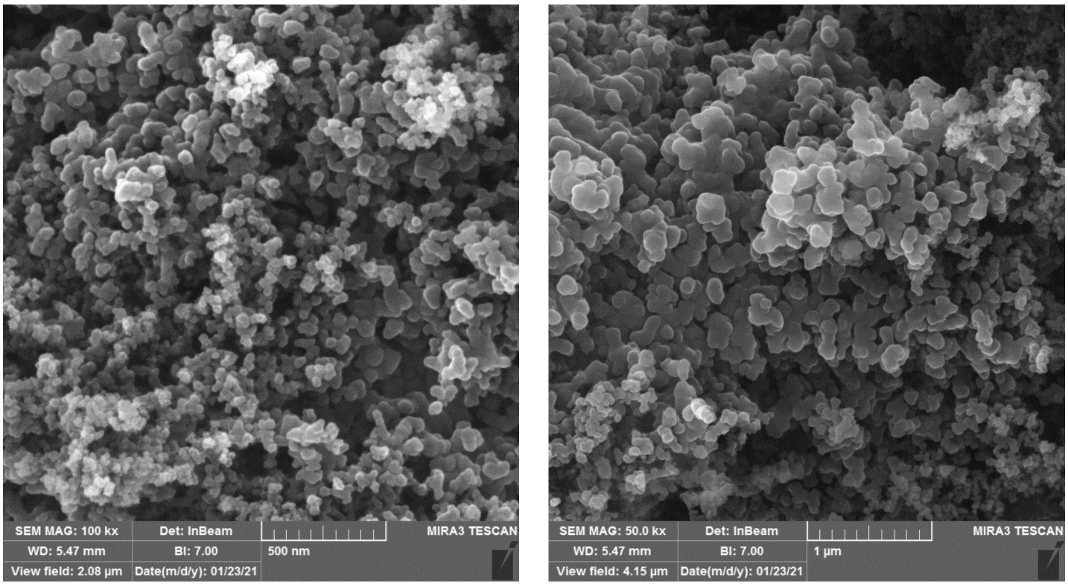



**Fig. 4.** Scanning electron microscope images of cobalt ferrite nanoparticles



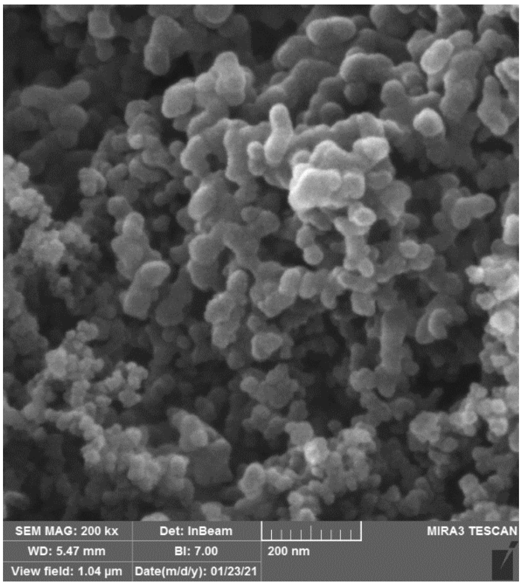



**Fig. 5.** Scanning electron microscope images of cobalt oxide nanoparticles

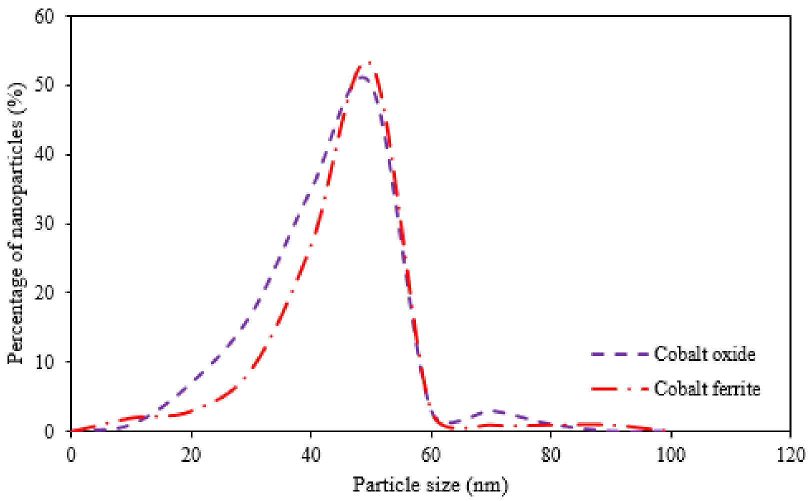



**Fig. 6.** Average particle size diagram of cobalt ferrite and cobalt oxide nanoparticles

The vibrating sample magnetometric graphs of the cobalt ferrite and cobalt oxide nanoparticles are shown in Figures 4-6 and Figure 4-7. The amount of saturated magnetism for cobalt ferrite is equal to 16 emu/g and for cobalt oxide is equal to 11 emu/g. The amount of residual magnetism for cobalt ferrite is equal to 7 emu/g and for cobalt oxide is equal to 3 emu/g. Also, the value of magnetic coercivity for cobalt ferrite is 500 oersted and for cobalt oxide is 350 oersted.

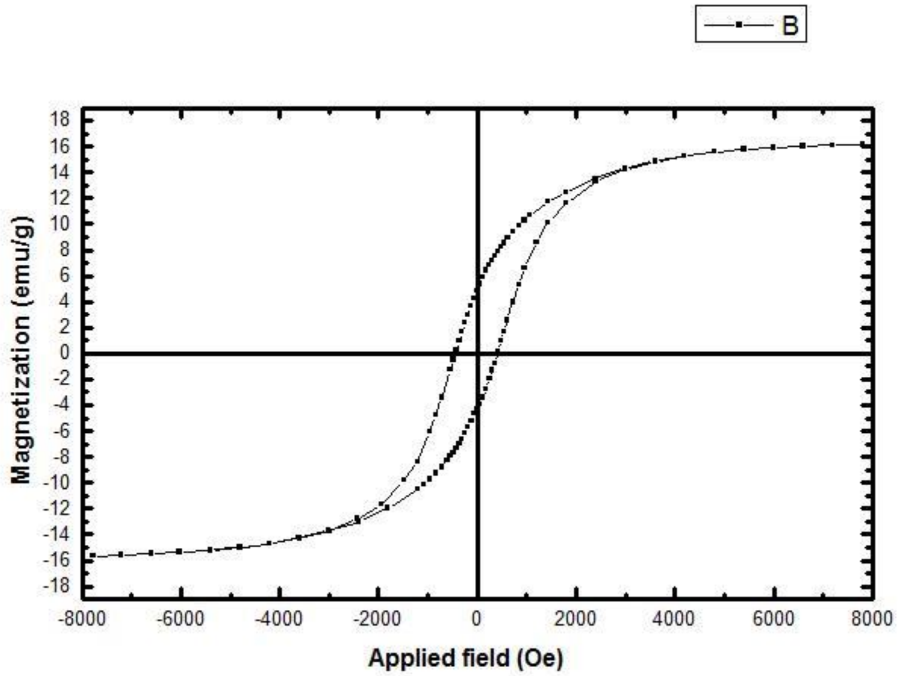



**Fig. 7.** Vibrating sample magnetometry of cobalt ferrite nanoparticles

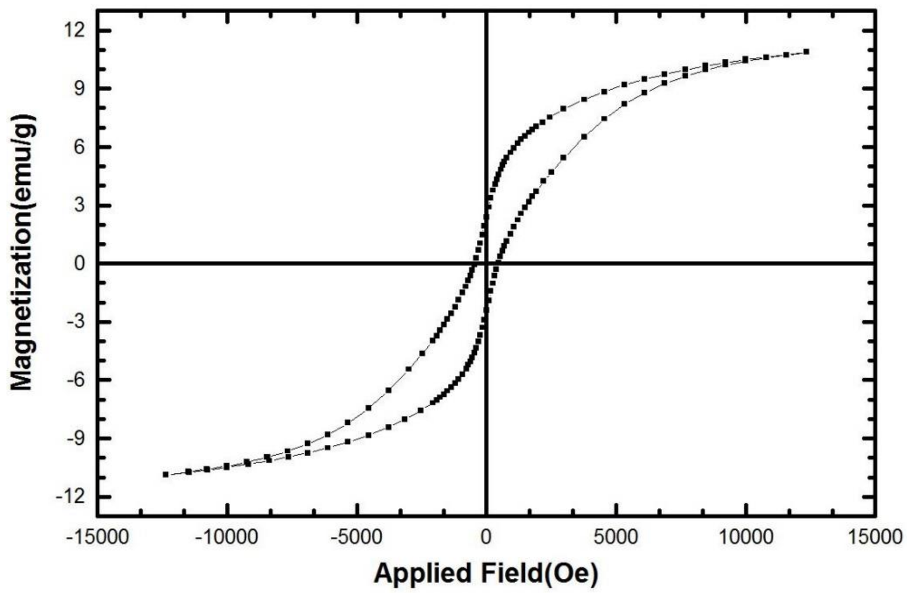



**Fig.8.** Vibrating sample magnetometry of cobalt oxide nanoparticles

Infrared absorption spectroscopy of cobalt ferrite and cobalt oxide nanoparticles is shown in Figures 9 and 10. For cobalt ferrite nanoparticles, the peaks in the 400 to 600 range are related to metal-oxygen bonding, the peaks in the 1119-1631 range are related to acetate, and the broad peaks in the 3425 range are related to oxygen-hydrogen bonding. For cobalt oxide nanoparticles, the peaks in the 400 to 600 range are related to metal-oxygen bonding, the peaks in the 1117 to 1625 range are related to acetate bonds, and the broad peaks in the 3430 range are related to hydrogen-oxygen bonding. This test showed that the nanoparticles were synthesized with an acceptable purity, and no other peaks related to impurity were observed in them.

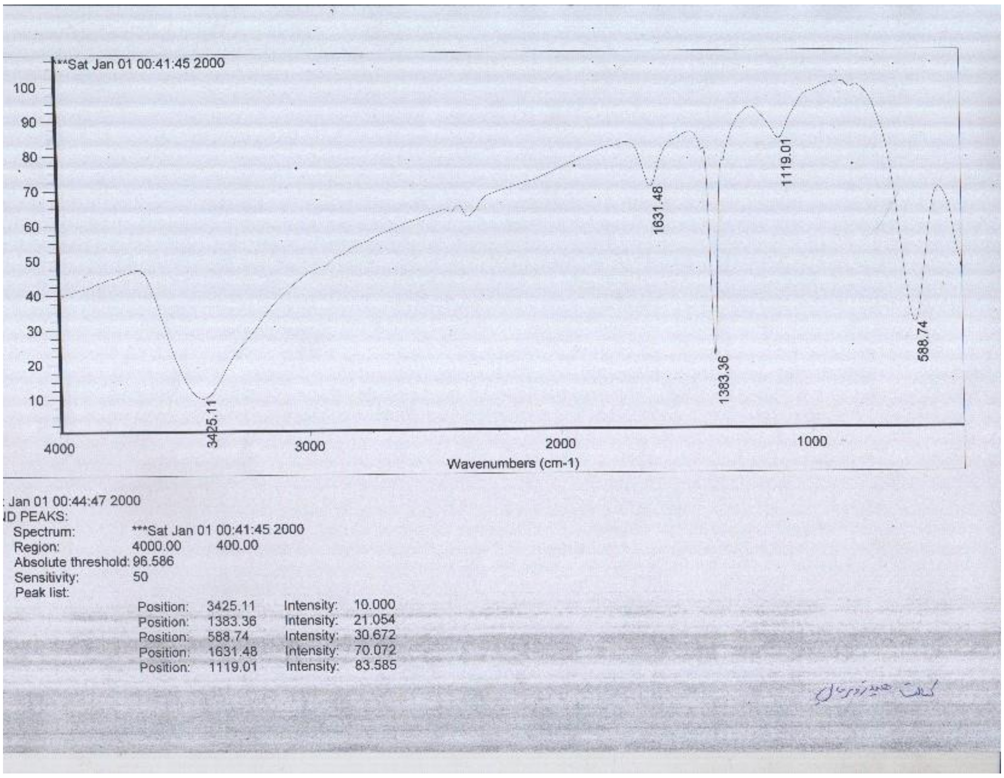



**Fig. 9**. Infrared absorption spectroscopy for cobalt ferrite nanoparticles

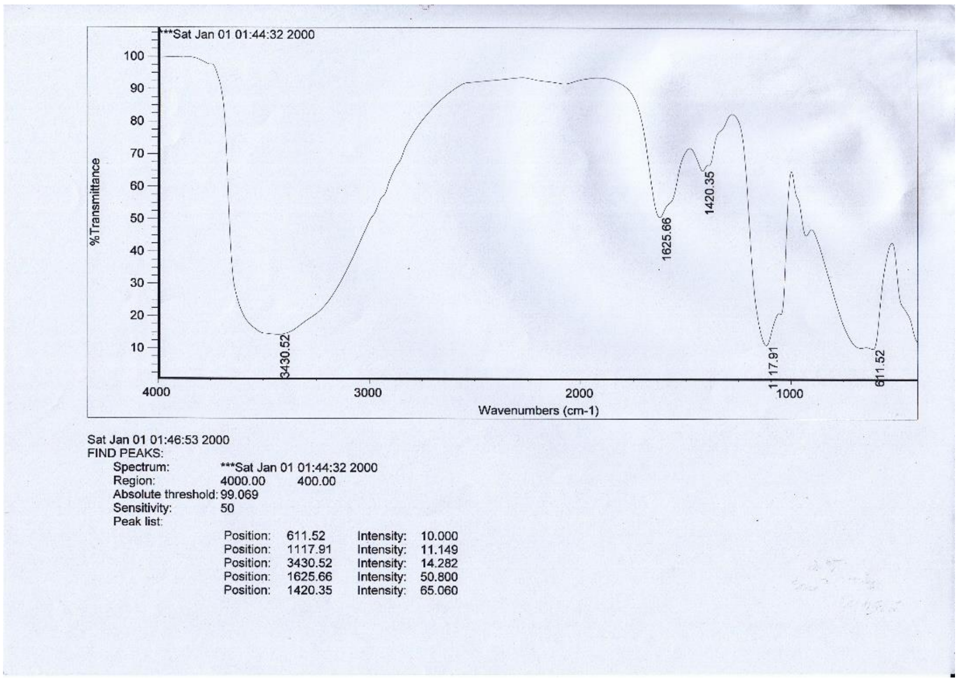



**Fig. 10. Infrared absorption spectroscopy for cobalt oxide nanoparticles**

In order to be able to predict the material's behavior against the applied load correctly, the material's stress-strain curve is needed. The force applied to a structure will change its shape. The length of this deformation depends on the hardness of the structure. The strain stress diagram of composites and the base polymer is shown in Fig 11. After the uniform distribution of nanoparticles in the epoxy matrix, the final tensile strength of the composites has improved compared to the pure polymer, which can be due to the uniform distribution of the nanoparticles in the epoxy matrix and the bond established between the nanoparticles and the matrix[15]. Also, the ultimate tensile strength of the composite reinforced with cobalt ferrite is better than the composite reinforced with cobalt oxide, which can also be due to the bond between nanoparticles and the matrix. In the manufactured samples, the composite reinforced using cobalt ferrite showed better toughness than the composites reinforced with cobalt oxide nanoparticles. However, the toughness of the pure polymer is better compared to the composites. This means composites have better strength, but their plasticity is reduced compared to pure polymers. The comparison chart of the ultimate tensile strength and toughness of composites and the base polymer is shown in Fig 12.

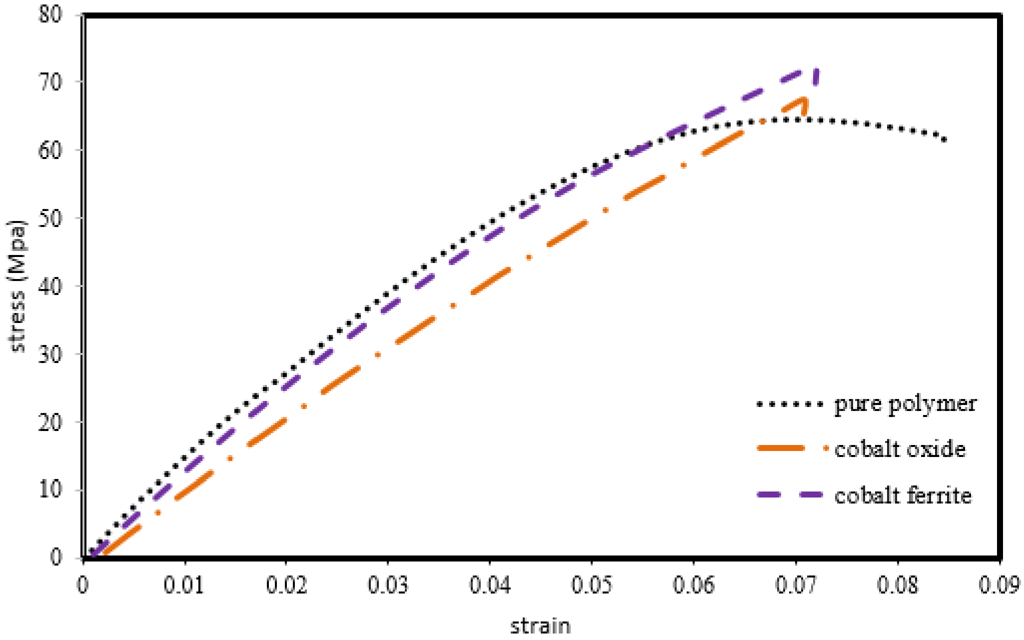



**Fig. 11.** Stress strain diagram of composites and pure polymer

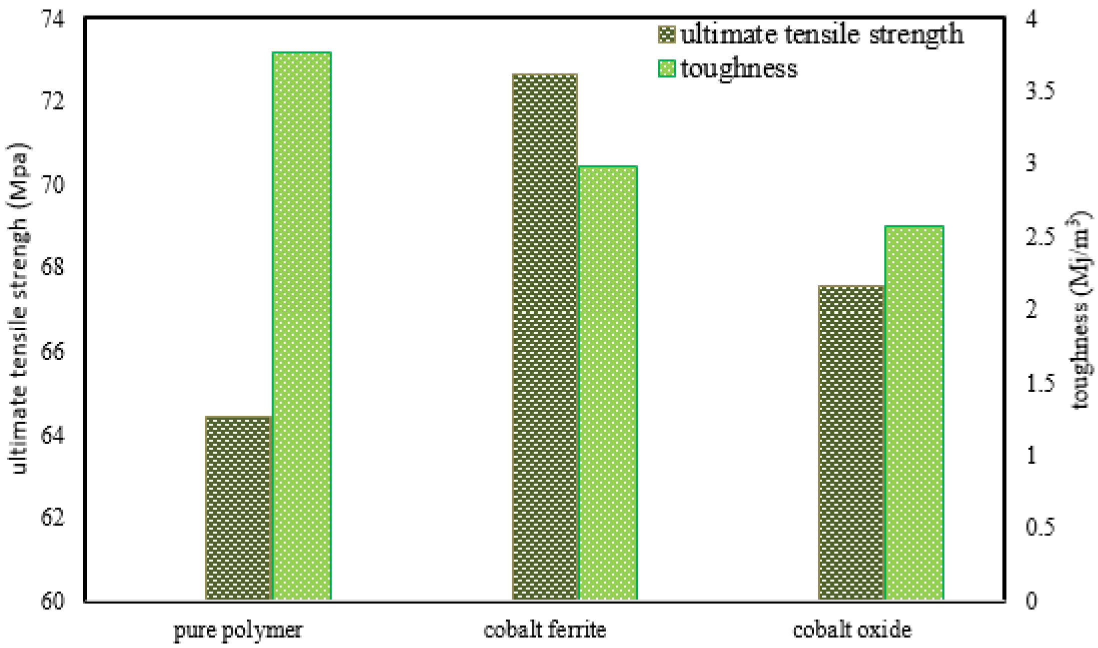



**Fig .12.** Diagrams of ultimate tensile strength and toughness of pure polymer and composites

## 4. Conclusion

In this research, cobalt ferrite and cobalt oxide nanoparticles were first synthesized by hydrothermal method, and their properties were investigated. After examining the different properties of nanoparticles, they were used as reinforcements for composite production, and the tensile properties of the composites were examined. The results obtained in this research are as follows:

• Nanoparticles were synthesized in a fine and uniform form with a homogeneous structure, and the peaks correspond entirely to the standard indicators.

• Nanoparticles have magnetic properties that can be used in the aerospace industry to produce wave-absorbing surfaces.

• The final tensile strength of the composites has improved compared to the pure polymer

• The ultimate tensile strength of the composite produced with cobalt ferrite is better than that of the composite produced with cobalt oxide.

• The toughness of the base polymer is better than the toughness of composites

• The toughness of the composite produced with cobalt ferrite is better than that of the composite made with cobalt oxide.

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