JCRS

Journal of Chemical Reactivity and Synthesis 2023: 13(2) 112-128

Research Article

Making epoxy/copper ferrite and copper hydroxide composite using nanoparticles synthesized by hydrothermal and ultrasonic method and checking the thermal properties of composites

Elaf ayad Kamel Aljahlavi, Mohammad Moarrefi Romeileh*, Azadeh Azami Gheymasi

Department of Chemistry, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran

ARTICLE INFO:

Received:
25 February 2023

Accepted:
12 May 2023

Available online:
1 July2023

✉: M. Moarrefi
mohamadmoarrefi@gmail.com

ABSTRACT

In this research, nanoparticles of copper ferrite was synthesized by hydrothermal method and nanoparticles of copper hydroxide was synthesized by ultrasonic method. Then, to check the properties of these nanoparticles, analyzes such as X-ray diffraction pattern (XRD), scanning electron microscope (SEM), vibrating sample magnetometry (VSM) and infrared spectroscopy (IR) were taken. The results of analyzes showed that the nanoparticles were prepared in a completely uniform, fine and homogeneous manner and no agglomeration was seen in them. In addition, these nanoparticles had good magnetic properties and the peaks of the X-ray diffraction pattern were consistent with the standard peaks. In the next step, 5% by weight of copper ferrite and copper hydroxide nanoparticles were added to the epoxy resin and then mixed together by a stirrer. In the next step, the epoxy resin was subjected to ultrasonic waves and after the complete distribution of nanoparticles in the field, it was placed in the vacuum chamber for bubble removal and finally poured into the mold. Finally, various tests were taken from the composites, such as: thermal properties test (TGA) and flame resistance test (UL-94).

Keywords: synthesis of nanoparticles; ultrasonic method; hydrothermal method; polymer composite

1. Introduction

Today, the use of nano materials is increasing all over the world. Nano materials are materials that have at least one dimension in the nanometer range. These materials have different optical, magnetic, electrical, etc. properties than larger and bulk materials. This issue has caused them to be used in various fields such as electrical biomedicine, food and

drug science, etc [1]. By reducing the size of these materials, their surface-to-volume ratio increases and reactivity increases [2]. One of the methods of making nanomaterials is hydrothermal. In this method, shape and size control is more possible than other methods and it is a cost-effective method [3,4]. One of the other methods of making nanoparticles is ultrasonic [5]. The use of ultrasonic waves makes the production of fine, uniform and high-quality nano materials [6]. One of the applications of nano materials is their use in making nano composites. Nano materials can be used as reinforcement in the composite and produce different composites with different applications [7]. Song et al [8] synthesized magnesium hydroxide nanoparticles using ultrasonic method. Their results showed that ultrasonic waves can limit the growth of magnesium hydroxide crystals in each lattice plane and improve the hydrophobicity of magnesium hydroxide nanoparticles. Xia et al [9] synthesized polyaniline nanoparticles using ultrasonic waves. They observed that the use of ultrasonic waves increased the polymerization rate of aniline, which is usually much lower under normal conditions. Also, ultrasonic radiation causes the release of HCL molecules and improves the degree of doping. Hosseini et al [10] synthesized nanoparticles of copper ferrite, nickel ferrite and cobalt ferrite using ultrasonic method and added these nanoparticles to epoxy resin base to make a polymer based composite. Their results showed that the use of ultrasonic waves is a very suitable method for making uniform and high-quality nanoparticles. Also, adding these nanoparticles to the epoxy resin base increases the tensile properties of the composite compared to the base polymer. The highest ultimate tensile strength was observed in the composite made with nickel ferrite nanoparticles and the highest toughness was observed in the composite made with copper ferrite nanoparticles. Sun et al [11] added furan phosphamide (POCFA) to modified polyamide 6 to investigate their thermal properties and flame resistance through multiple reactions between them. Their results showed that 5% by weight of POCFA makes the polyamide reach the V0 rating in the UL-94 test. Wang et al

[12] added metal phenylphosphonate (M = Co, Ce, Al, Zn)/reduced graphene oxide nanomaterials to the epoxy resin matrix and investigated the flame resistance. Their results showed that by adding 3 weight percent of additives, the limiting values of oxygen index of composites increase. Also, according to the UL-94 flame test, the flame resistance is improved. Also, they reported that PMPhP-PGO (M = Ce, Al) element can work in dense and gas phase, while MPhP-PGO (M = Co, Zn) only works in dense phase. Therefore, MPhP-PGO/EP (M = Ce, Al) shows a better strengthening effect on flame retardancy. Yang et al [13] synthesized the bio-flame retardant material through the polymerization of dopamine hydrochloride under alkaline conditions and produced polydopamine nanoparticles with diameters between 50 and 100 nm. They showed that the addition of a small amount (2 wt%) of PDA nanoparticles to an epoxy can significantly reduce the heat release rate by 53.6%, exceeding the performance of aluminum trihydroxide (ATH) particles at 10 wt%. According to their reports, this flame resistance can have several reasons, the most important of which is more coal efficiency and CO_2 production. In addition, the addition of PDA nanoparticles to epoxy resin increases the tensile strength by 6%. Han et al [14] produced a polymer composite using two-dimensional reinforcing materials and epoxy resin and investigated the mechanical and thermal properties of the composites. They added boron nitride and graphene sheets to the epoxy resin base and investigated their properties. They reported that both BN and GN improve the mechanical and thermal properties of composites. Hithum et al [15] synthesized copper ferrite nanoparticles (CuFe2O4) by sol-gel method with different annealing temperatures (200, 450, 650 and 850) degrees Celsius and evaluated their different properties using different tests. Their XRD patterns showed that the system structure in copper ferrite at 650 °C changed from a cubic system to a tetragonal system with an apparent secondary phase of CuO. By observing the FT-IR spectrum of the sample under investigation, it showed two significant absorption bands, which indicated the formation of a

single-phase cubic spinel. The nanoparticles showed mild ferromagnetic behavior for the composite sintered at 850°C. Saturation magnetization and residual magnetization were 32 emu.g-1 and 11.64 emu.g-1, respectively. Yao et al [16] stated that polymer nanocomposites with 3D nanofillers can form a 3D network and be uniformly distributed in the field. These polymer nanocomposites with high mechanical properties have high potential for thermal and electrical conductivity as well as electromagnetic interference (EMI) shielding. Jalal Jardi et al [17] synthesized CuFe2O4 nanoparticles by microwave method. They added the obtained nanoparticles and modified carbon nanotubes to the polystyrene matrix and subjected the composites to various tests. They studied the effect of $CuFe_2O_4$ nanostructures on the flame resistance of polystyrene (PS) using UL-94 analysis. Their results showed that the increase in thermal stability and flame resistance of nanocomposites is due to the creation of a $CuFe_2O_4$ magnetic barrier against the flame, and the reduction of oxygen transfer to the previous layers. Rahmawati et al [18] synthesized and prepared magnetic nanoparticles (Fe_3O_4) using ultrasonic waves. According to the results presented by them, the size of Fe_3O_4-crystal from 21 to 25 nm depends on the ultrasonic frequency and stirring speed. These sizes were obtained using Debbie-Scherr's equation. Mahdavi et al [19] synthesized ZnO nanoparticles using ultrasonic waves and studied the effect of these waves on the morphology and structure of ZnO nanoparticles. Their results showed that the irradiation time and the power of the waves have a direct effect on the morphology and structure of the nanoparticles, and it causes the purity of the samples to improve and their size to decrease. Also, these waves reduce the amount of clumping of nanoparticles. Utara et al [20] synthesized barium titanate nanoparticles using ultrasonic waves. They prepared nanoparticles at 25°C and atmospheric pressure without calcination. They reported that increasing the ultrasonic time can create a more regular and uniform structure, and increasing the wave irradiation time, the lumpiness

decreases. Also, other researchers synthesized various nanoparticles using ultrasonic waves and used them for various applications [21–23].

In this research, nanoparticles of copper ferrite was synthesized by hydrothermal method and nanoparticles of copper hydroxide was synthesized by ultrasonic method and subjected to various tests. In the next step, the prepared nanoparticles were poured into the epoxy resin as reinforcement to prepare the polymer composite. Different tests were taken from the composite made and their mechanical and thermal properties were checked.

2. Experimental

2.1. Synthesis of nanoparticles

Copper ferrite nanoparticles were synthesized by hydrothermal method. First, 200 ml of distilled water is poured into a beaker, then 0.01 mol of copper chloride ($CuCl_2$) and 0.02 mol of iron nitrate ($Fe(No_3)_3$) are added to the beaker. In the next step, these materials are mixed together by a magnetic stirrer for 45 minutes to obtain a clear and uniform solution. In the next step, 1 M ammonia that was prepared before is slowly added to the original solution until the PH reaches 10 and the medium becomes alkaline. Then the solution is placed in the autoclave, which is a special hydrothermal container, and the autoclave is placed in the oven at a temperature of 200 degrees for 12 hours. After this time, the solution is centrifuged and the nanoparticles, which are still wet, are placed in the oven to dry and prepare for the next steps. Copper hydroxide nanoparticles were made by ultrasonic waves. 1 gram of copper chloride is dissolved in 200 ml of water and subjected to 400 watt ultrasonic waves. Ammonia is added as a precipitant. Finally, the blue sediment is centrifuged and washed. Figure 1 shows the copper ferrite solution after being placed in a centrifuge And Figure 2 shows copper hydroxide nanoparticles under ultrasonic waves.

Figure 1. Copper ferrite solution after centrifugation

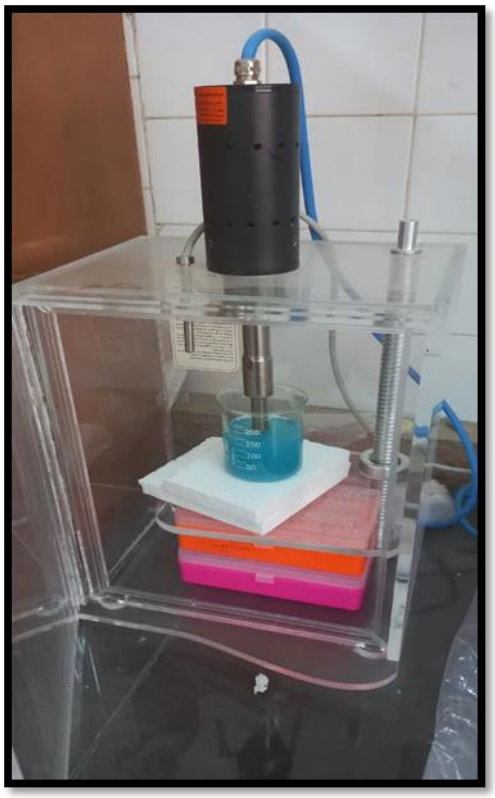

Figure 2. Copper hydroxide nanoparticles under ultrasonic waves

2.2. Fabrication of polymer nanocomposites

To make polymer nanocomposite, 1 gram of copper ferrite and 1 gram of copper hydroxide are added to a total of 20 grams of epoxy resin. In the next step, 5 percent by weight of the synthesized nanoparticles is added to the epoxy resin base and then they are mixed with each other for 45 minutes using a stirrer. The epoxy resin is subjected to 400 W ultrasonic waves for 1 hour. In the next step, in order to debubble, the solution is placed in a vacuum chamber for 20 minutes at a temperature of 25 degrees so that no bubbles remain and finally it is poured into the mold.

3. Result and discussion

The x-ray diffraction pattern of copper ferrite and copper hydroxide nanoparticles is shown in Figure 3 and Figure 4. These patterns correspond to the indices of pure standard materials. Miller indices for copper ferrite nanoparticles include (111), (220), (311), (222), (400), (511), (440), (533), (444), (731) and (751) and the Miller indices for copper hydroxide nanoparticles include (220), (311), (222), (400), (422), (511) and (440).

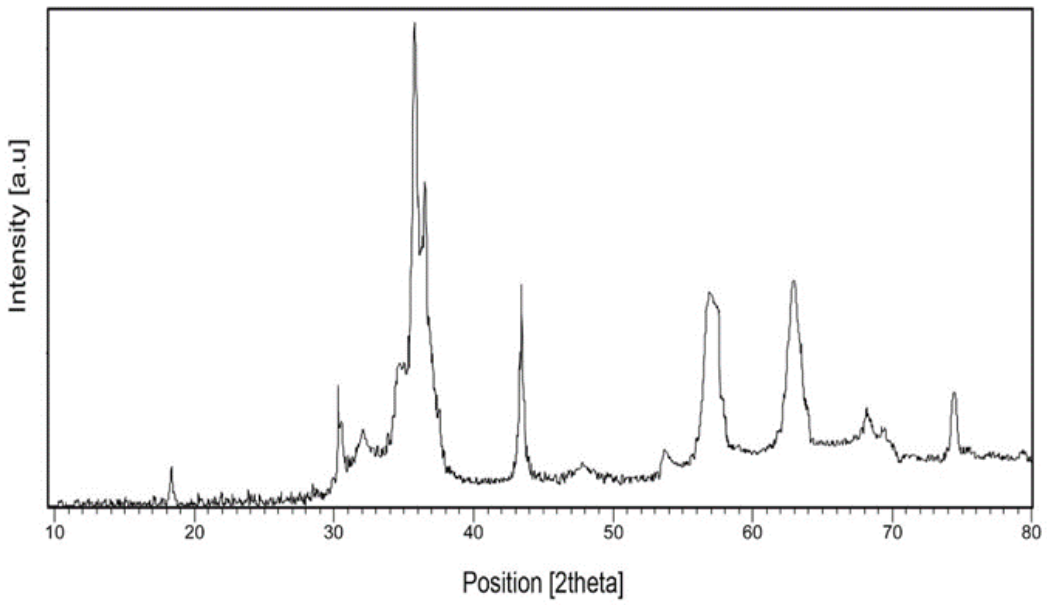

Figure 3. X-ray diffraction pattern of copper ferrite nanoparticles

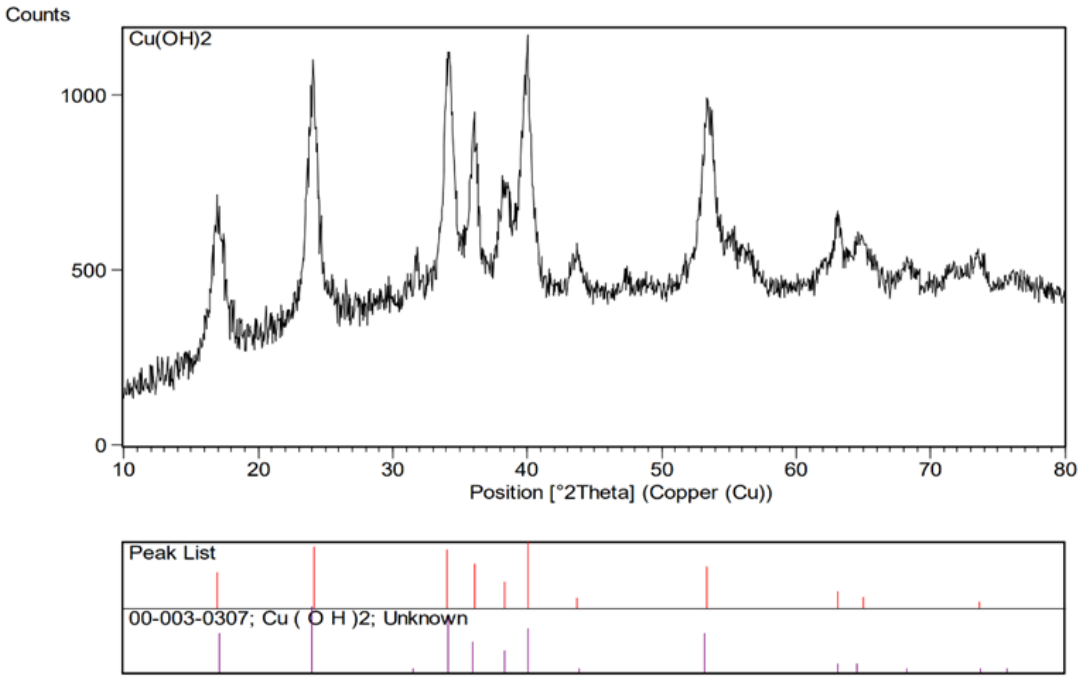

Figure 4. X-ray diffraction pattern of copper hydroxide nanoparticles

Figure 5 shows the scanning electron microscope image of copper ferrite nanoparticles. This image was prepared with a magnification of 500 kx and a working distance of 5.78 mm. As can be seen from the picture, the nanoparticles are prepared with a fine structure, without lumps, accumulation and completely uniform, and the average size of the particles is about 50 nm.

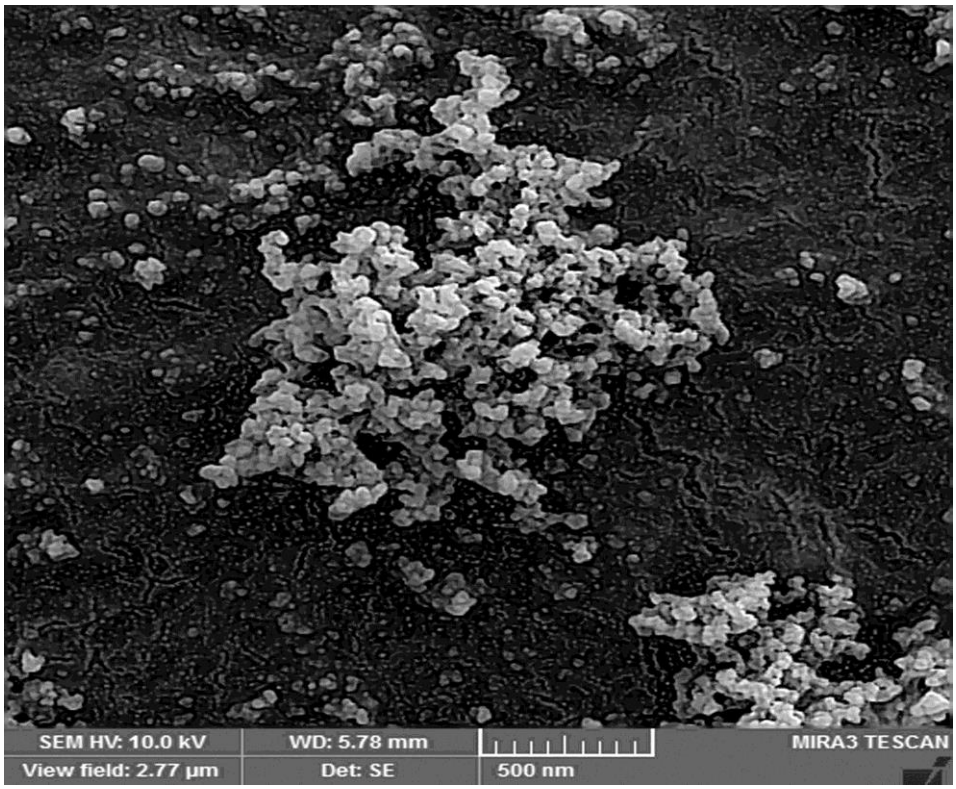

Figure 5. Scanning electron microscope images of copper ferrite nanoparticles

Figure 6 is also a scanning electron microscope image of copper hydroxide nanoparticles. This image was prepared with a magnification of 1 micrometer and a working distance of 5.93 mm. As it can be seen from the pictures, the nanoparticles have been prepared with a completely uniform structure, without lumps and accumulation, and the average size of the particles is about 80 nm.

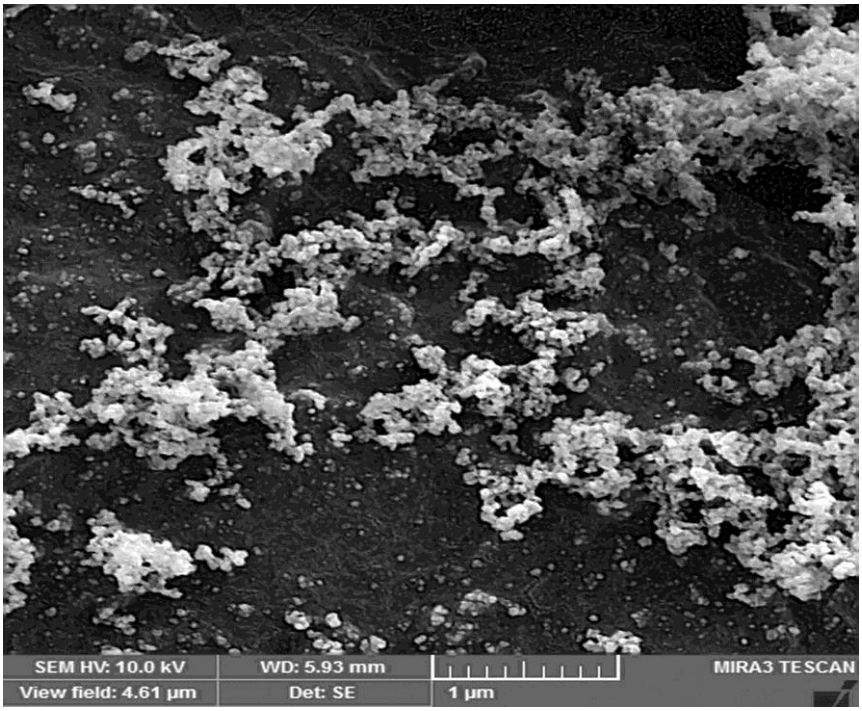

Figure 6. Scanning electron microscope images of copper hydroxide nanoparticles

The vibrating sample magnetometry diagrams of copper ferrite and copper hydroxide nanoparticles are shown in Figures 7 and 8. The amount of saturation magnetism for copper ferrite is equal to 26 emu/g and for copper hydroxide is equal to 2.2 emu/g. The amount of residual magnetic for copper ferrite is equal to 0 emu/g and for copper hydroxide it is equal to 0.5 emu/g. Also, the value of magnetic coercivity for copper ferrite is 500 oersted and for copper hydroxide is 350 oersted.

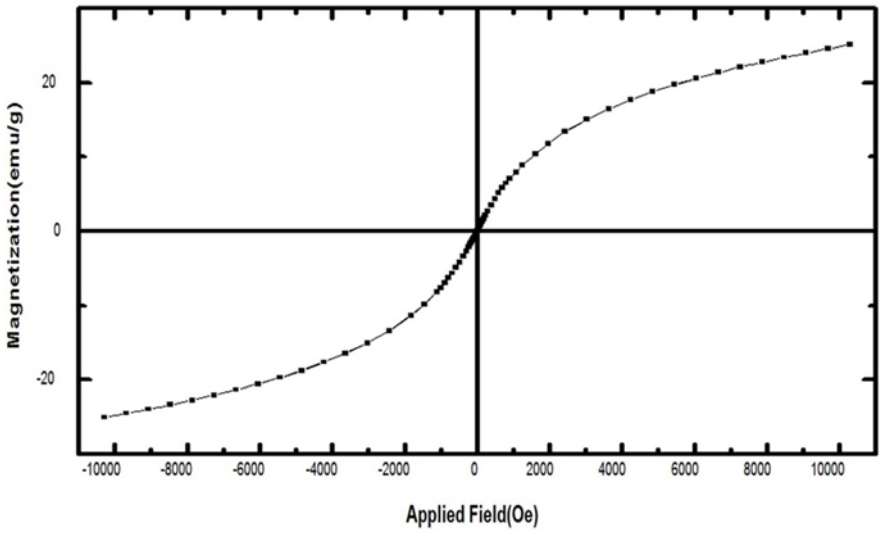

Figure 7.vibrating sample Magnetometry of copper ferrite nanoparticles

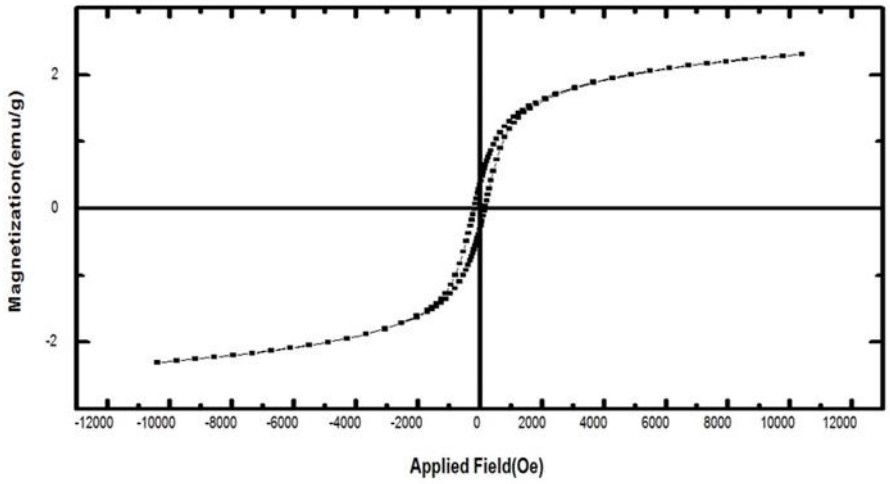

Figure 8. Vibrating sample magnetometry of copper hydroxide nanoparticles

Infrared absorption spectroscopy of nanocomposite of copper ferrite and copper hydroxide is shown in Figure 9. This nanocomposite is related to the metal-oxygen bond in the 400-600 range, the peaks in the 950-1100 range are related to the single carbon-oxygen bonds, and the peak in the 1400 range is related to the double carbon-carbon bond. Bonds in the range of 1600 are related to double carbon-oxygen, bonds of 2900 to 3000 are related to aliphatic carbon-hydrogen, bonds of 3000 to 3100 are related to aromatic carbon-hydrogen, and finally bonds of about 3300 are related to oxygen-hydrogen. The results of this test showed that

nanoparticles were synthesized with acceptable purity and no other peaks related to impurity were observed in them.

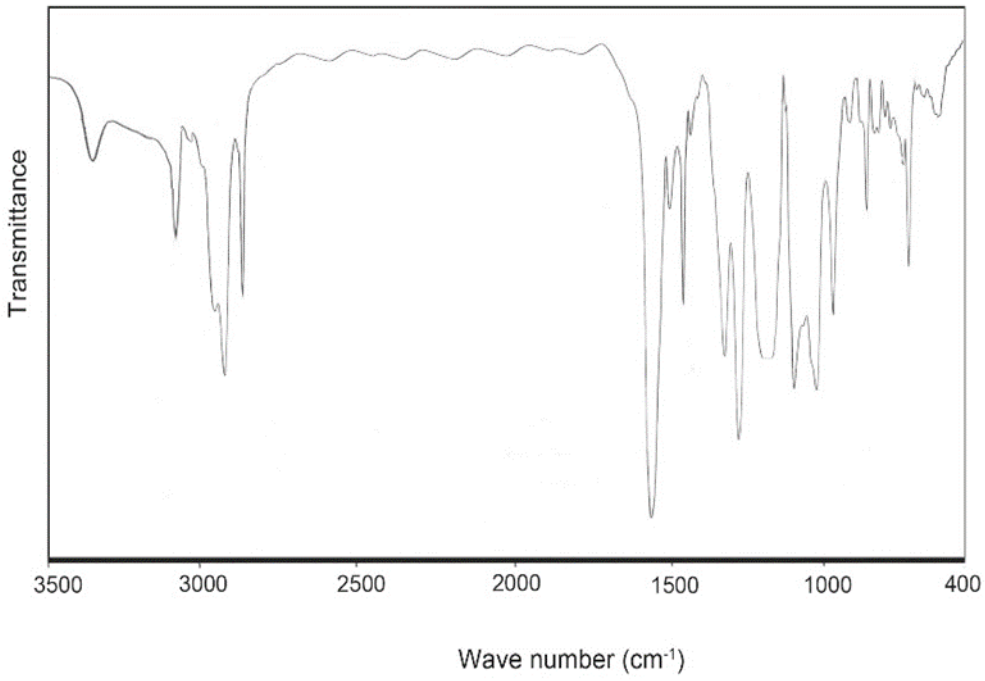

Figure 9. Infrared absorption spectroscopy for copper ferrite and copper hydroxide nanoparticles

Thermography analysis (TGA) is a method of thermal analysis in which changes in the physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and mass loss constant) is measured. The TGA curve in Figure 10 shows the weight loss (%) due to the increase in temperature, as the temperature increases, the weight percentage decreases because different reactions are carried out with the increase in temperature. It can be seen in the TGA curve that the weight percentage decreases with increasing temperature. Therefore, it shows that mass is continuously changing due to heat treatment. In the TGA curve, the decomposition starts at a lower temperature and continues up to a higher

temperature by changing the weight percentage. The uniformity of the curves in the last part is related to the crystallization of the material.

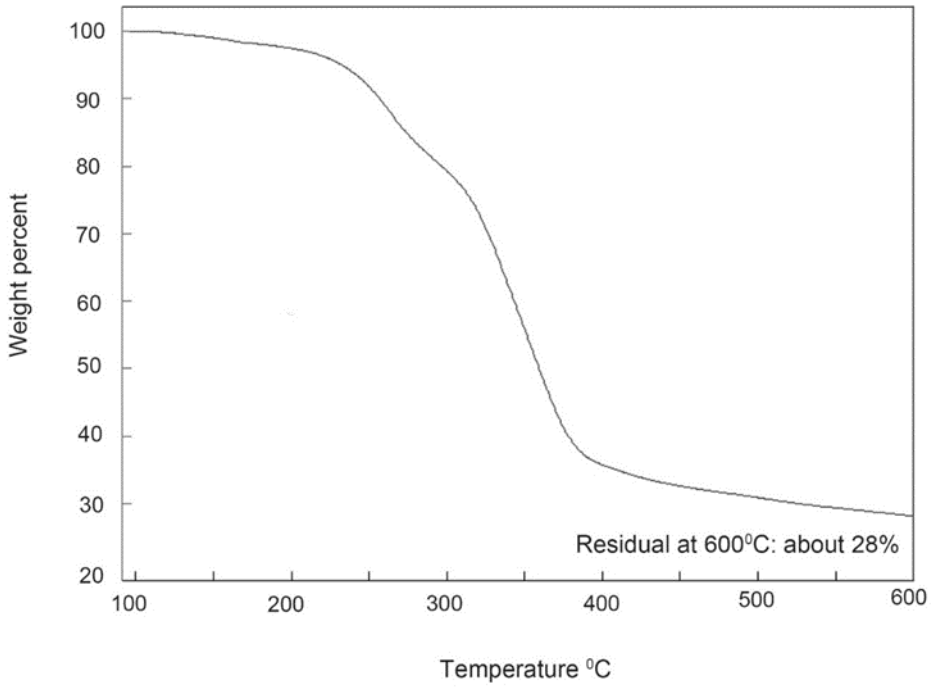

Figure 10. Thermography analysis (TGA) for epoxy/ferrite copper and hydroxide copper composite

Differential thermal analysis (DTA) measures the heat input required to raise the temperature of the sample. In this analysis, sample changes are measured with respect to a standard reference material. The peak observed in Figure 11 shows the heat exchange. Considering that the peak is upward, it can be concluded that the process was exothermic.

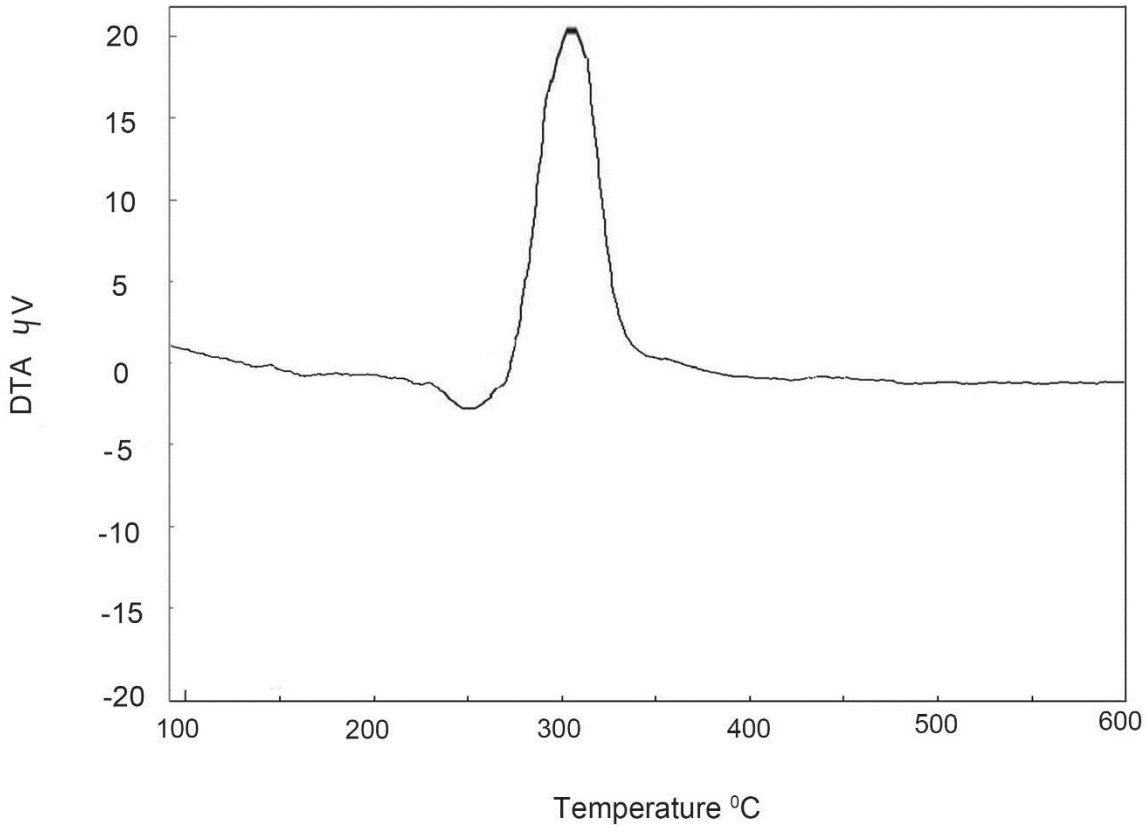

Figure 11. Analysis DTA for epoxy/ferrite copper and hydroxide copper composite

In general, the UL-94 standard is a standard that checks the flammability of polymers. In figure 12, pure resin is exposed to flame. As can be seen, the pure polymer is burned by the flame. In figure 13, epoxy/copper ferrite and copper hydroxide composite is exposed to flame. As it can be seen, the composite made is not completely burnt like the pure polymer and the composite turns charcoal in color. For this reason, it can be concluded that the nanoparticles added to the composite resist fire like a dam and add slow-burning properties to the resin.

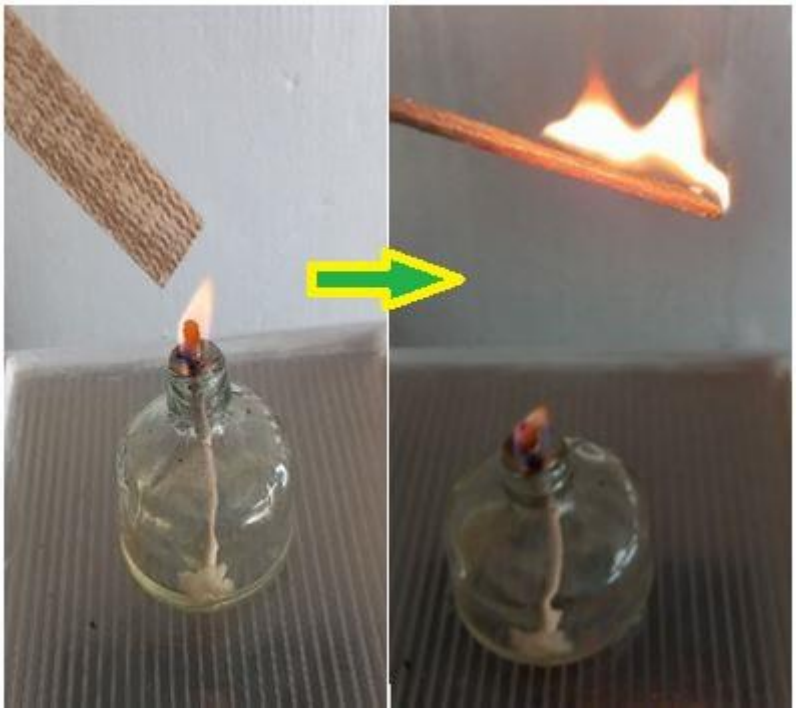

Figure 11. Pure polymer under the UL-94 test

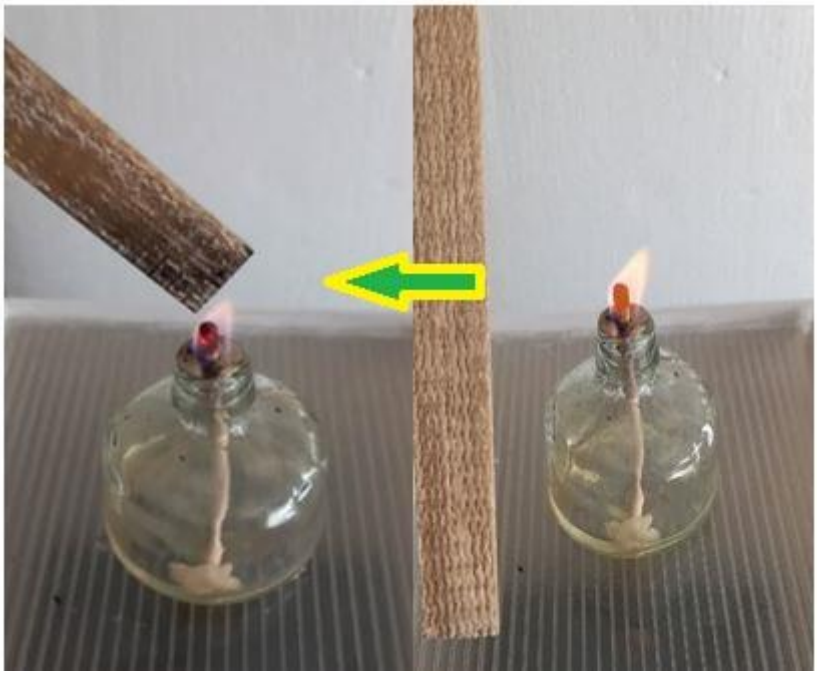

Figure 12. The composite made under the UL-94 test

4. Conclusion

In this research, copper ferrite and copper hydroxide nanoparticles were first synthesized. Then, to check the properties of these nanoparticles, different analyzes were taken from them.

These nanoparticles were added to the epoxy resin as a reinforcing phase and the polymer base composite was made. In the next step, the thermal properties based on the TGA test and the flame resistance based on the UL-94 test were taken from the composites. The results obtained in this thesis are as follows:

1. In the transmission electron microscope (SEM) analysis, the images of nanoparticles were completely uniform, fine and synthesized with a homogeneous structure, and no accumulation or lumpiness was observed in them.

2. In X-ray Diffraction (XRD) pattern test, the peaks showed that they completely correspond to the standard peaks, which indicated their correct synthesis.

3. According to the VSM analysis, it was observed that nanoparticles have magnetic properties that can be used in various industries.

4. According to differential thermal analysis (DTA), it was observed that the process was exothermic.

5. All the nanoparticles were synthesized with high purity and no impurity peak was observed in them.

6. The resulting nanocomposite has high flame resistance compared to pure epoxy resin.

Acknowledgments

This work was supported by the research facilities of Ahvaz Branch, Islamic Azad University, Ahvaz, Iran.

References

[1] M.S. Thomas, S. Thomas, L.A. Pothen, Science and Technology of Nanomaterials: Introduction, in: Nanotechnol. Environ. Remediat., John Wiley & Sons, Ltd, 2022: pp. 1–15.

[2] L. Qi, Z. Xu, X. Jiang, C. Hu, X. Zou, Carbohydr. Res. 339 (2004) 2693–2700.

[3] C. Yao, Y. Shin, L.-Q. Wang, Windisch Charles F., W.D. Samuels, B.W. Arey, C. Wang, Risen William M., G.J. Exarhos, J. Phys. Chem. C. 111 (2007) 15141–15145.

[4] N. Baccile, G. Laurent, F. Babonneau, F. Fayon, M.-M. Titirici, M. Antonietti, J. Phys. Chem. C. 113 (2009) 9644–9654.

[5] A. Gedanken, Using sonochemistry for the fabrication of nanomaterials, 11 (2004) 47–55.

[6] S. Barcikowski, A. Plech, K.S. Suslick, A. Vogel, MRS. Bull. 44 (2019) 382–391.

[7] G. Qiu, Q. Wang, M. Nie, Macromol. Mater. Eng. 291 (2006) 68–74.

[8] G. Song, S. Ma, G. Tang, X. Wang, Eng. Asp. 364 (2010) 99–104.

[9] H. Xia, Q. Wang, J. Nanoparticle Res. 3 (2001) 401–411.

[10] M. Hosseini, H. Rezaei Ashtiani, D. Ghanbari, Ultrasonic Preparation of Cobalt, Nickel, J. Nanostructures. 12 (2022) 588–597.

[11] J. Sun, L. Qian, J. Li, Polymer (Guildf). 210 (2020) 122994.

[12] X. Wang, T. Chen, J. Hong, W. Luo, B. Zeng, C. Yuan, Y. Xu, G. Chen, L. Dai, Compos. Part B Eng. 200 (2020) 108271.

[13] W. Zhang, X. Qi, X. Li, Y. Dong, W. Yao, L. Liang, Y. Zhang, Eng. Asp. 625 (2021) 126906.

[14] S. Han, Q. Meng, Z. Qiu, A. Osman, R. Cai, Y. Yu, T. Liu, S. Araby, Polymer (Guildf). 184 (2019) 121884.

[15] S.A. Jasim, I. Patra, M.J.C. Opulencia, K. Hachem, R.M.R. Parra, M.J. Ansari, A.T. Jalil, M.E. Al-Gazally, M. Naderifar, M. Khatami, R. Akhavan-Sigari, 11 (2022) 2483–2492.

[16] F. Yao, W. Xie, C. Ma, D. Wang, Z.M. El-Bahy, M.H. Helal, H. Liu, A. Du, Z. Guo, H. Gu, Compos. Part B Eng. 245 (2022) 110236.

[17] R. Jalajerdi, D. Ghanbari, J. Nanostructures. 6 (2016) 278–284.

[18] R. Rahmawati, M.G. Permana, B. Harison, Nugraha, B. Yuliarto, Suyatman, D. Kurniadi, Procedia Eng. 170 (2017) 55–59.

[19] R. Mahdavi, S.S. Ashraf Talesh, Sonochem. 39 (2017) 504–510.

[20] S. Utara, S. Hunpratub, Ultrason. Sonochem. 41 (2018) 441–448.

[21] J.K.Y. Lee, N. Chen, S. Peng, L. Li, L. Tian, N. Thakor, S. Ramakrishna, Prog. Polym. Sci. 86 (2018) 40–84.

[22] M. Etminan, G. Nabiyouni, D. Ghanbari, J. Mater. Sci. Mater. Electron. 29 (2018) 1766–1776.

[23] Compos. Part B Eng. 161 (2019) 564–577.