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RESEARCH PAPER

The Effect of Different Morphologies of Carbon Nanostructures and Calcium Ferrite Nanoparticles on the Flame Retardancy, Thermal Stability and Mechanical Property of the Epoxy Polymer

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ABSTRACT

In this work the synergism influence of magnetic calcium ferrite nanoparticles and three morphologies of carbon nanostructures, carbon dot (zero-dimensional), carbon nanotubes (one dimensional) and graphene oxide (two dimensional) on the flame retardancy and thermal stability of the epoxy polymer were investigated. Nanoparticles were synthesized by hydrothermal method in the water as a green solvent. Ultrasonic waves (100-1000W, 1-60 min) were used in all synthesis methods of nanocarbons and magnets as well as polymer nanocomposite as a dispersing tool. The morphology of the nanostructures was investigated by scanning electron microscopy (SEM), phase of the product was approved by X-ray diffraction pattern (XRD) and Fourrier transform infra-red (FT-IR) spectroscopy. Magnetic calcium ferrite has suitable effect as a barrier in front of heating, oxygen and fire. Cone calorimeter, UL-94 test and limiting oxygen index (LOI) tests were used for examination of flame retardancy. Thermal gravimetric (TGA) analysis confirms thermal stability of the products.

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INTRODUCTION

The use of synthetic polymers has increased exponentially in the last few decades, so that it is impossible to imagine life without synthetic polymers, for example, if butadiene polymers did not exist in the rubber industry, no cheap and suitable substitute for this polymer would come to mind [1-3]. The interesting thing about polymers is that by adding an organic or inorganic additive, the basic properties of the polymer change. Modifiers and organic binders easily cause cross-linking in polymers and change the properties of the base matrix. From the past years, cheap and available additives such as clay, calcium carbonate and glass fibers were added to polymer bases. [4,5] This additive has sometimes only played the role of filler and bulking to reduce the cost of the polymer base, but in most cases it has been used to improve a property. For example, for more than fifty years, automobile companies have been using clay to make polymer composites [6,7]. Various improvements in polymer base properties including mechanical improvement, heat resistance, flame retardancy, abrasion resistance, hydrophobicity, magnetization, etc. have been reported in thousands of published papers [8].

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One of the most famous and tangible polymers that are used from home decorations to industrial equipment are epoxy based polymers. Various metal, ceramic, organic additives have been added to the epoxy base polymers [9,11]. In this work the effect of synergism of calcium ferrite nanoparticles and three morphologies of carbon dot (zero-dimensional), carbon nanotubes (one dimensional) and graphene oxide (two dimensional) on the flame retardancy and thermal stability of the epoxy polymer were investigated. nanoparticles were synthesized by hydrothermal method in the water as a green solvent. Carbon nanostructures increase the thermal resistance of the polymer base. On the other hand, as a relatively new work, calcium ferrite was added in order to increase the properties of slow burning and thermal resistance, because it prevents the penetration of heat and flame into the polymer by creating a magnetic barrier [12, 13]. Also, due to the lack of combustible droplets, it prevents the spread of the flame. One of the most important points about different fires is preventing the spread of flame and the exponential growth of the flame. Especially for inflammable polymers such as epoxy, 100% fireproofing is not operational and the efforts of researchers are to slow burning and prevent flame propagation [14-16].

In this work the effect of calcium ferrite nanoparticles and carbon nanoparticles on the flame retardancy and thermal stability of the epoxy polymer were investigated. Calcium ferrite nanoparticles because of magnetic property have a appropriate role as a barrier against flame and oxygen and protect inner layer. Carbon nano structures are material for thermal stability of the polymer matrixes.

MATERIALS AND METHODS

XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered CuKα radiation. Size and morphology of nanoparticles were investigated via scanning electron microscopy (model KYKY-EM3200). The golden thin film was used as a conductive coating on the surface of the samples (Prevent the accumulation of electrical charge and make better contrast(. Magnetic attributes were studied using a vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping between ±10000 Oe.

One hundred moles of calcium nitrate ($6H_2O$) and two hundred moles of iron nitrate ($9H_2O$) are dissolved in 200 ml of deionized water and one molar sodium hydroxide is used to adjust the pH in the eleventh, and the solution is transferred to

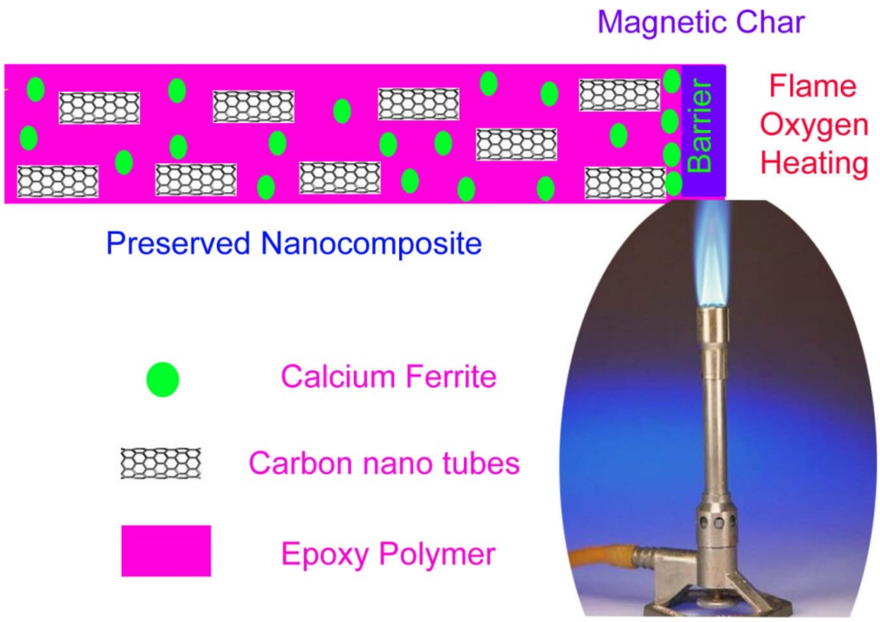

Fig 1. Schematic of synergistic effect against flame and heating

the autoclave reactor and it is placed in 180 ^{0}C for 12 hours. After washing, it is washed with alcohol and acetone solvents.

Carbon dots were synthesized by hydrothermal method, the reaction was carried out by dissolving citric acid and ethylene diamine in 200 ml of deionized water with the same stoichiometric ratio and transferring it to the autoclave reactor.

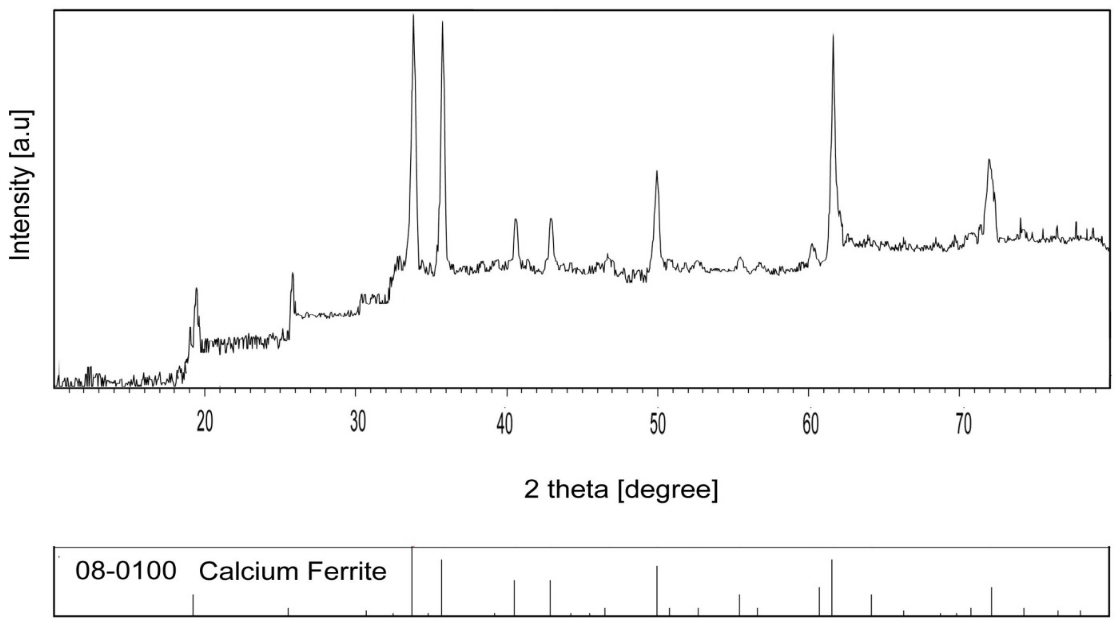

Fig 2. XRD pattern of calcium ferrite nanoparticles

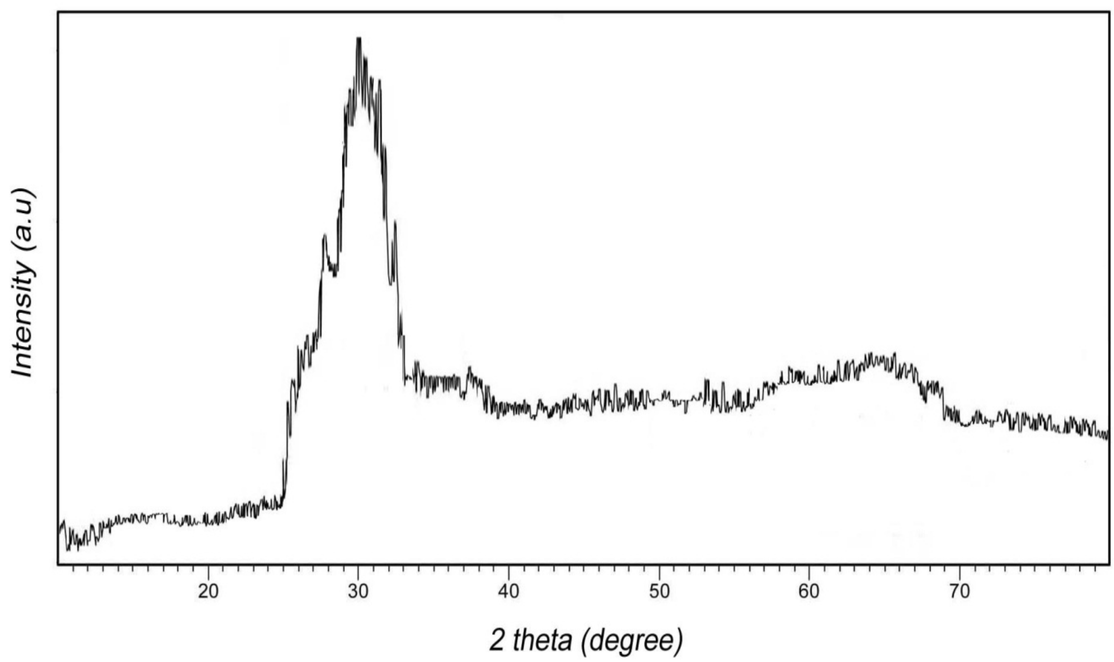

Fig 3. XRD pattern of carbon nanotubes

We heat the autoclave at 240 degrees Celsius for 48 hours. At the end, after cooling, with the help of a centrifuge at a speed of 10,000 rpm, nanoparticles are separated from the solution and ready to be identified and added to the polymer. Carbon nanotubes were obtained from Sigma-Aldrich. The length of the nanotubes is about a few micrometers, and the outer diameter of the nanotubes is about 15 nm.

Place the beaker in an ice bath with a temperature below 10 ^{0}C and pour 25 ml of sulfuric acid and 1 gram of graphite was added to it. Pour 4 gram of potassium permanganate slowly into the solution and try to keep the temperature below 10 ^{0}C, under stirring for three hours. Add 50 ml of distilled water slowly and was hold until the oxidation reaction begins. After 60 min, the solution turns from black to brown due to the formation of graphene oxide. Add 100 ml of distilled water once to the mixture to complete oxidation. Add 5 ml of hydrogen peroxide to the reaction mixture to remove excess potassium permanganate and stop the reaction.

To make epoxy polymer, the ratio of hardener to epoxy was considered to be one to three. In this way, 25 grams of hardener is added to 75 grams of epoxy resin, and after 20 minutes, it is poured on the mold. During the manufacture of nanocomposite, five percent of each additive is added to the epoxy resin by ultrasonic waves before adding the hardener. The rest of the steps of making nanocomposite are done exactly like pure polymer.

RESULTS AND DISCUSSION

Fig. 1 depicts schematic of synergism of this product against flame and heating result to increase thermal resistance and fire retardancy. On the other hand, calcium ferrite nanoparticles are placed next to each other with magnetic attraction and with the help of modified carbon plates, they create a strong barrier against heat and flame and protect the underlying polymer.

Fig. 2 show XRD pattern of calcium ferrite

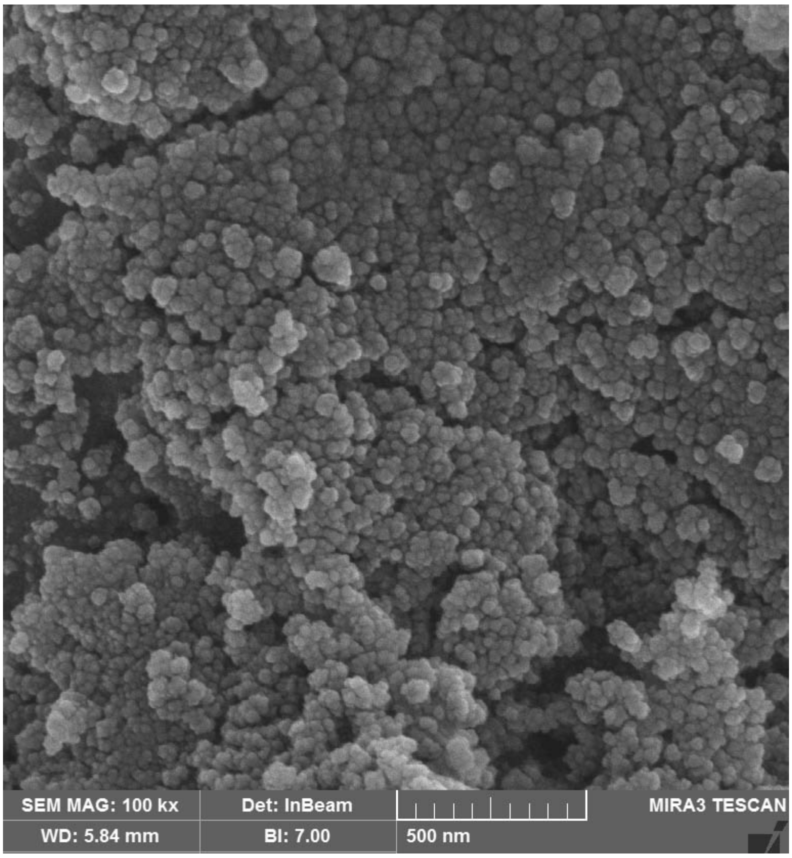

Fig 4. SEM image of calcium ferrite nanoparticles

nanoparticles, results confirm the prepared calcium ferrite nanoparticles show appropriate crystallinity and have a suitable agreement with standard peaks with JCPDS card: 08-0100, according to data it has Orthorhombic structure with space group:Pnam and space group number of 62. The cubic unit cell dimensions are equal to 9.18, 10.62 and 3.02 angstroms.

Fig. 3 show XRD pattern of carbon nanotubes, carbon nanotubes usually have a semi-crystalline and amorphous structure and do not show sharp and separated peaks in X-ray analysis. The results show that the spectrum is in good agreement with the reports presented in the articles.

Fig. 4 illustrates scanning electron microscopy (SEM) image of calcium ferrite nanoparticles, The images were prepared with a magnification of 10000 times and with a scale of 500 nm and a working distance of 5.84 mm. The results show that despite the magnetic attraction between calcium ferrite nanoparticles, nanoparticles with an average particle size of 50 nm

Fig. 5 illustrate scanning electron microscopy (SEM) image of carbon nanodots , The images fully confirm that monodisperse nanospheres with an average particle size of less than 20 nm were formed

Fig. 6 illustrates scanning electron microscopy (SEM) image of carbon nanotubes, the modified nanotubes have also been prepared in a completely monodisperse manner. After applying modifications on the surface of the nanotubes, uniform nanostructures with a diameter of less than 20 nm have been synthesized.

Fig. 7 illustrates scanning electron microscopy (SEM) image of carbon nanoplates, images approve nano graphene plate (two-dimensional nano structures) were prepared.

The magnetic properties of the calcium ferrite nanoparticles and polymer-based nanocomposite were investigated using the vibrating sample magnetometer technique. are shown in Fig. 8 and Fig. 9 respectively. Calcium ferrite nanoparticles show super-paramagnetic property with saturation magnetization of 16 emu/g and a coercivity of about 5 Orsted. On the other hand, with adding of

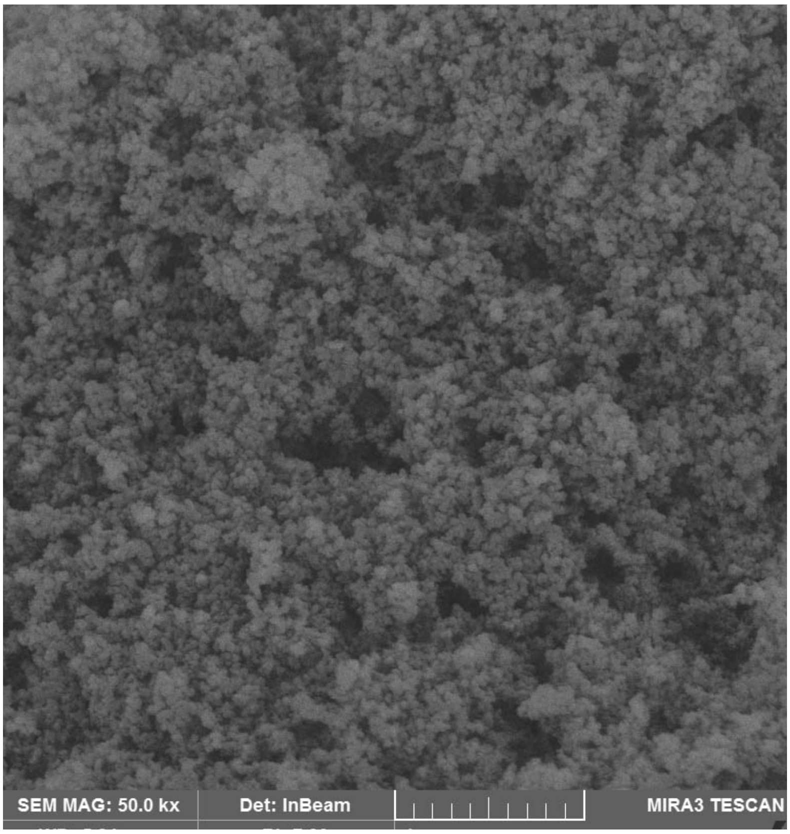

Fig 5. SEM image of carbon nanoparticles

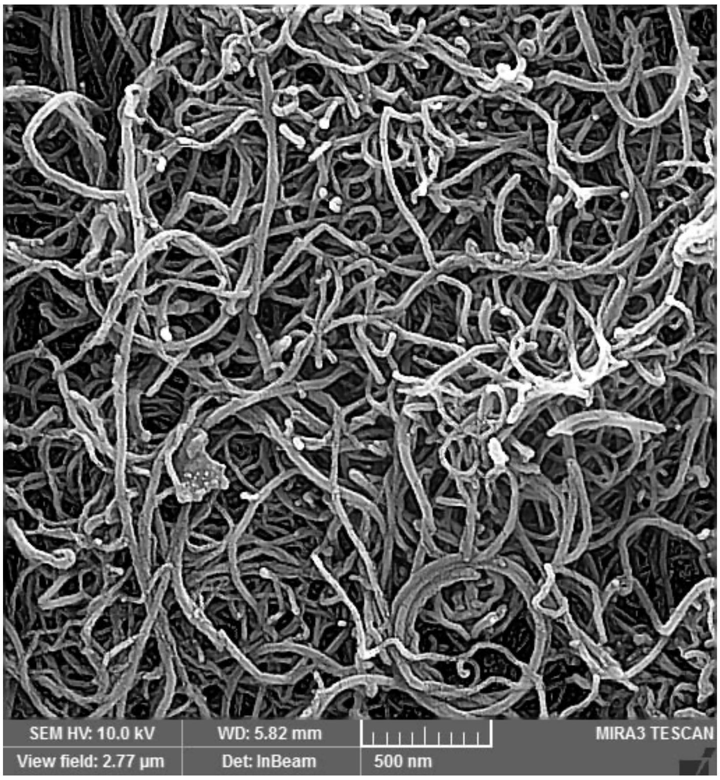

Fig 6. SEM image of carbon nanotubes

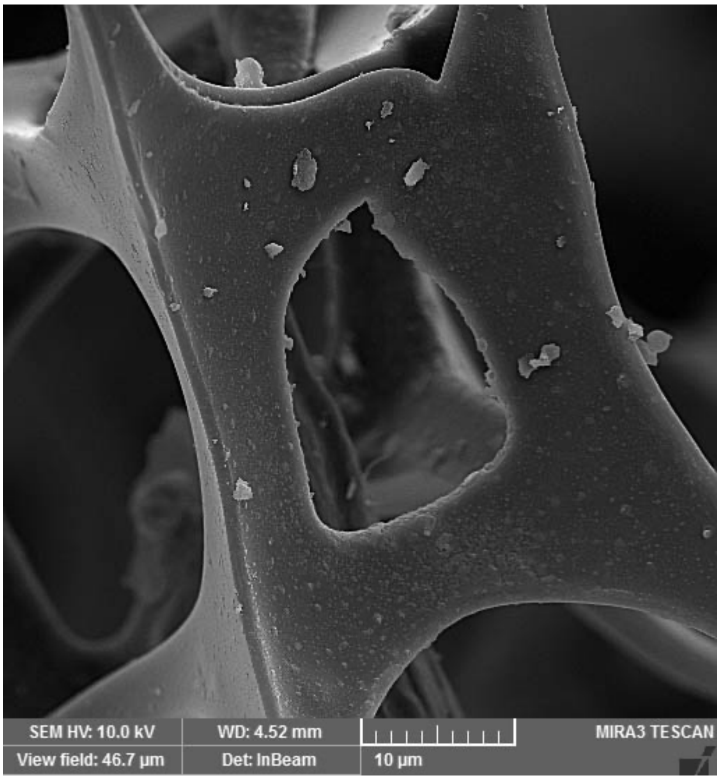

Fig 7. SEM image of graphene nano plates

nanoparticles to polymeric resin, nanocomposite has a saturation magnetization of about 2 emu/g and a coercivity of about 20 Orsted. Magnetization is a quantitative quantity in nanocomposite, there is a non-magnetic polymeric matrix, so the magnetization of nanocomposite is reduced compared to pure calcium ferrite. Also, the interaction between nanoparticles surrounded by polymer, this interaction leads to an increasing 5Oe to 15Oe of nanocomposite coercivity compared to pure ferrite nanoparticles.

Fourrier transform infra-red (FT-IR) spectroscopy of polymeric nanocomposite is shown in Fig. 10. Peaks around 900 to 1100 cm^{-1} are responsible

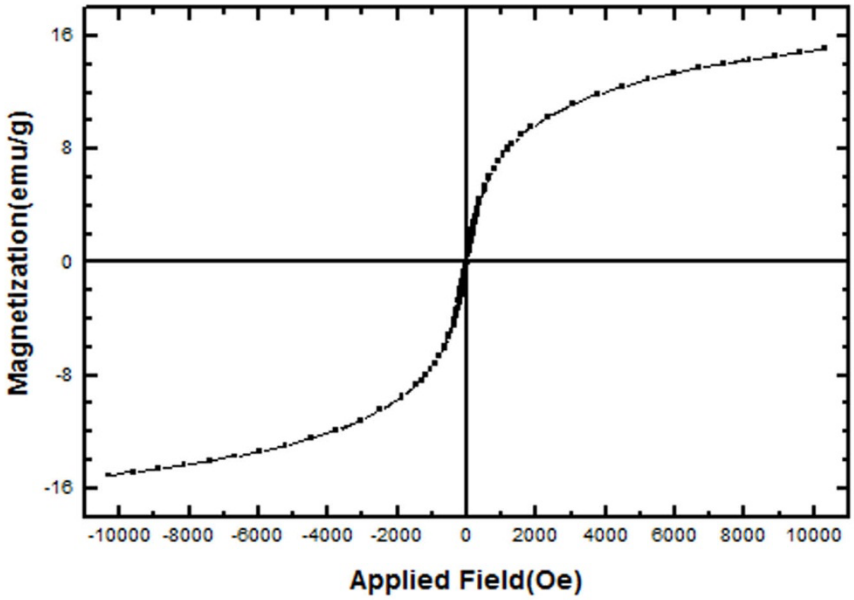

Fig 8. VSM curve of calcium ferrite nanoparticles

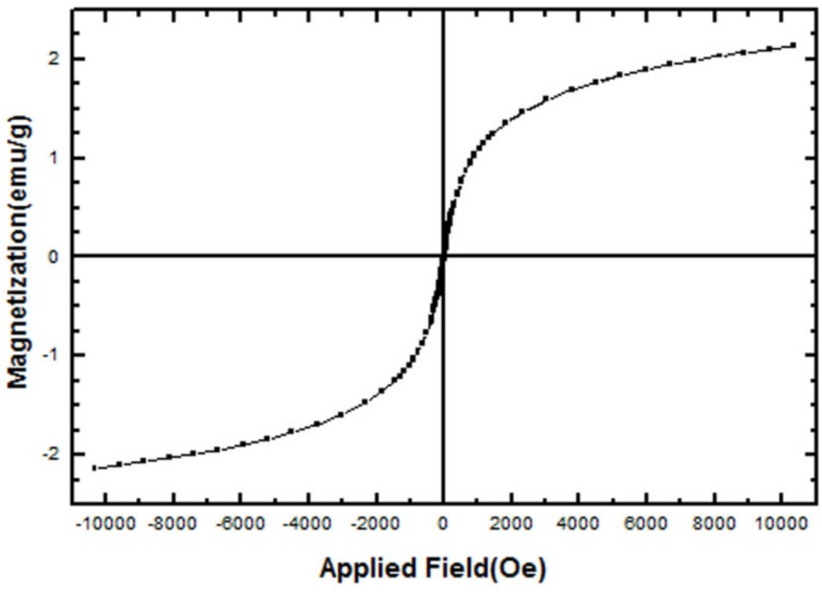

Fig 9. VSM curve of epoxy-calcium ferrite- CNTs nanocomposites

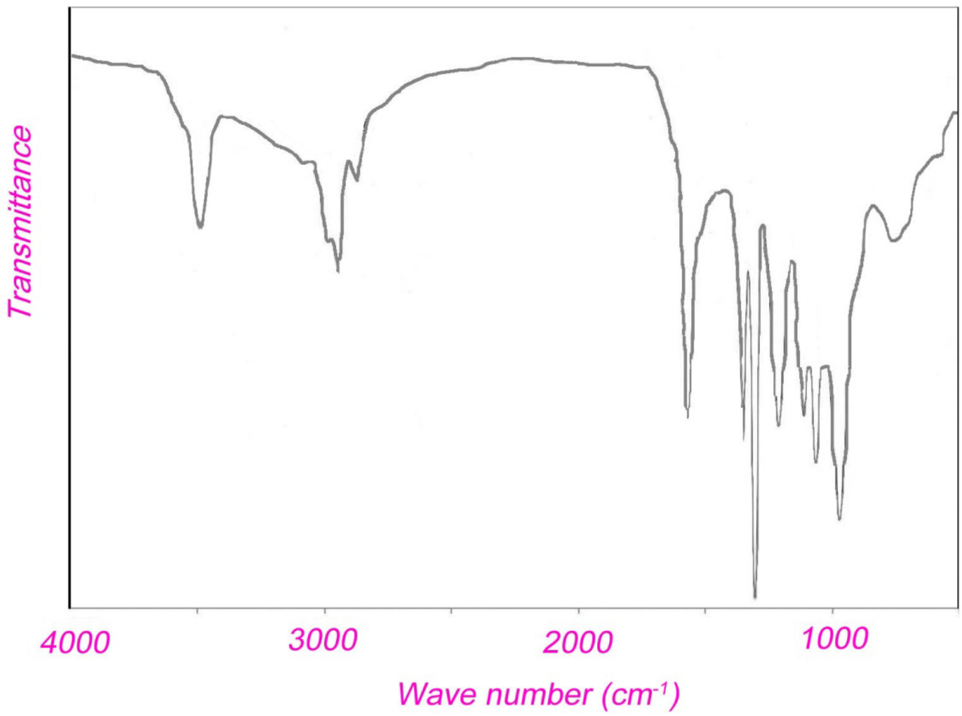

Fig 10. FT-IR spectrum of epoxy nanocomposites

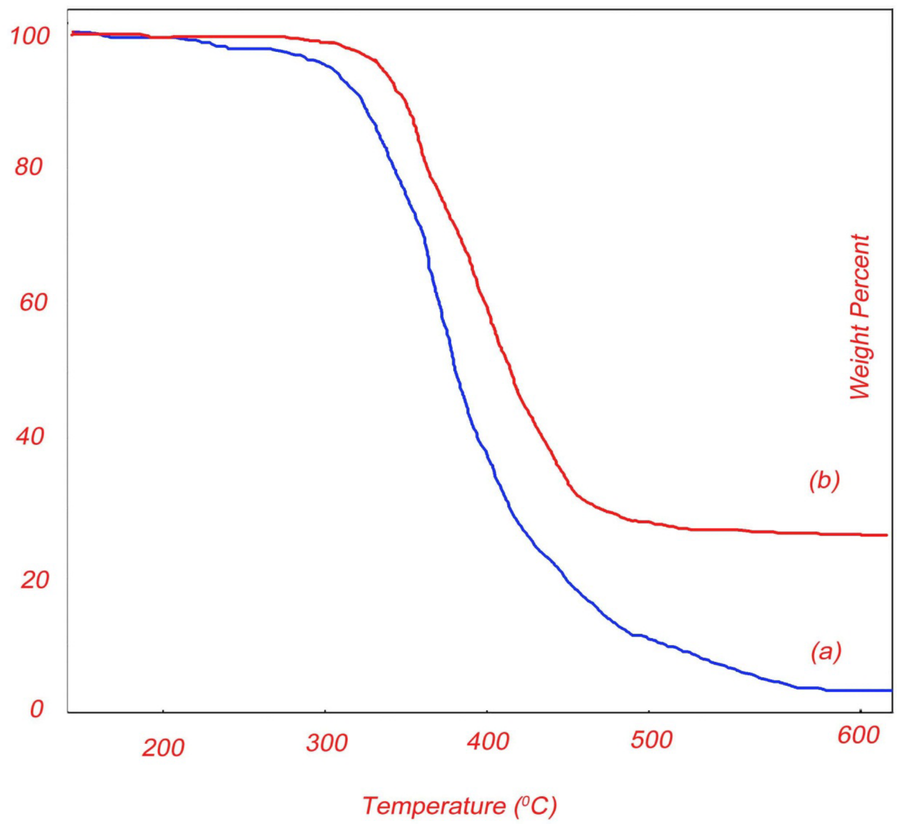

Fig 11. TGA curve of (a) epoxy polymer (b) epoxy nanocomposit

to the C-O bonds in epoxy polymer. Absorptions around 1400 to 1600 cm^{-1} are for C=O bonds. The absorption peak around 3400 cm^{-1} is related to hydroxyl groups.

Thermal gravimetric analysis curve of pure epoxy polymer and epoxy-CNT-calcium ferrite nanocomposite are illustrated in Fig. 11a and 11b respectively. The results confirm that with the addition of these nanoparticles, the starting temperature of the thermal degradation of the composite increases compared to the pure polymer, thus increasing from 300 degrees to 350 degrees Celsius. Also, at 500^0C, more than 30% of the nanocomposite remains, this remaining amount as a barrier protects the underlying polymer from fire, heat and oxygen.

Cone calorimeter is shown in Fig. 12, it measures the oxygen consumption of a 100 *100 * 5 mm sample, due to the presence of magnetic nanoparticles and carbon nanotubes, appropriate magnetic char was prepared that has barrier effect in front of flame and oxygen, which leads to flame retardancy.

In UL-94 test, a sample is prepared from plastic with a length of 120 mm and a width of 13 mm and thicknesses of 0.8, 1.6 and 3.2 mm depending on the intended application. A Bunsen flame (height: 19 mm) is used to burn the sample vertically, Materials that are extinguished in less than 10 seconds are classified in the V-0 category. If maximum burning time is less than 50 seconds is classified to V-1 class. V-2 class is similar to V-1, except that cotton fire drops are also included. UL-94 test for pure Epoxy polymer, Epoxy-CNTs

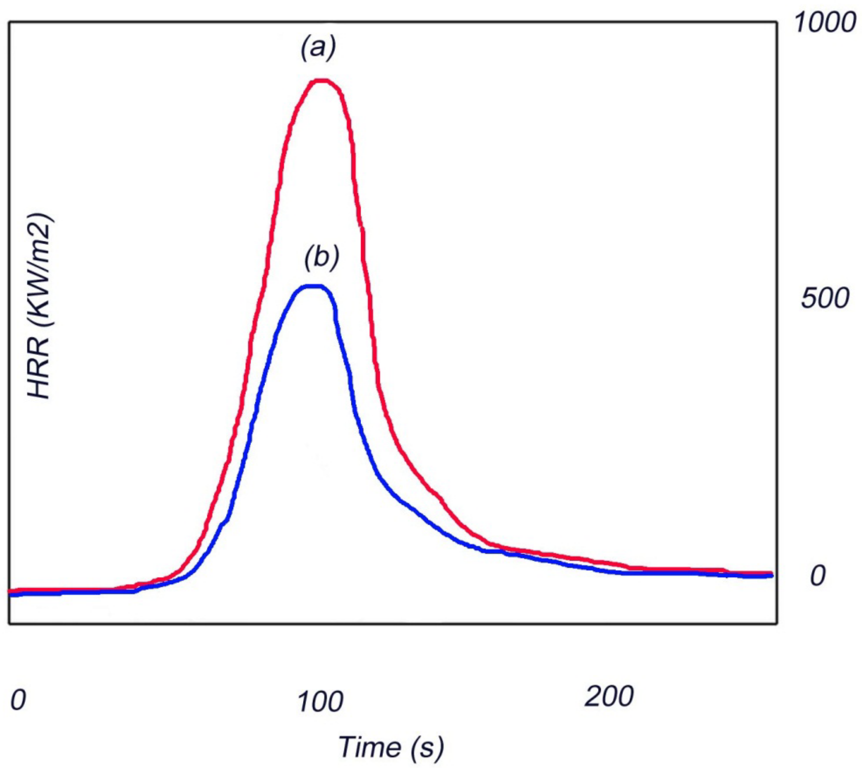

Fig 12. Cone calorimeter curve of (a) pure epoxy (b) epoxy nanocomposites

Table 1. UL-94 test of pure polymer and nanocomposites

Sample	UL-94 test
Epoxy polymer	NC
Epoxy-CNTs nanocomposite	V-2
Epoxy-CNTs-calcium ferrite nanocomposite	V-1

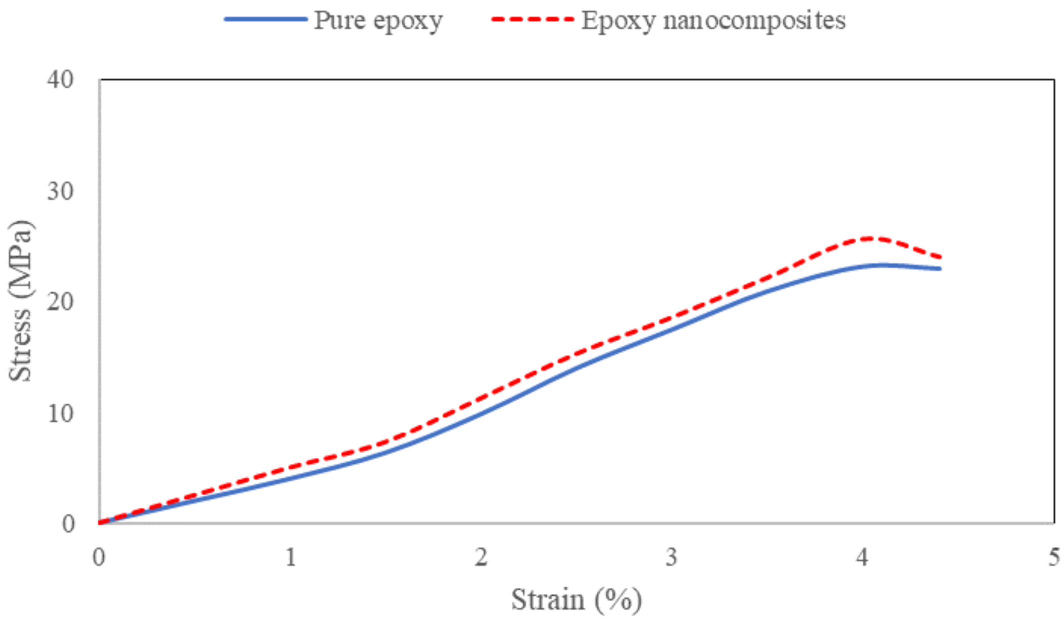

Fig 13. Stress-strain curve of (a) pure epoxy (b) epoxy-CNTs nanocomposites

Table 2. LOI test of pure polymer and nanocomposites

Sample	LOI test
Epoxy polymer	19
Epoxy-CNTs nanocomposite	19
Epoxy- CNTs-calcium ferrite nanocomposite	22

nanocomposite and Epoxy-CNTs-calcium ferrite nanocomposite are NC, V-2 and V-1 respectively.

On the other hand, limiting oxygen index (LOI) test measures oxygen precisely. The sample size is usually 100 * 65 * 3 strips. A flame from a Bunsen lamp is applied until the surface of the sample catches fire. The value of LOI, the minimum concentration of oxygen, is necessary for the sample to be extinguished in less than 3 minutes, while the length of the sample is less than 5 cm. LOI test for pure Epoxy polymer, Epoxy-CNTs nanocomposite and Epoxy-CNTs-calcium ferrite nanocomposite are 20, 20 and 22 respectively.

The stress-strain curve presented in Fig. 13, was used to determine the tensile properties of the epoxy composites. The peak stress and the initial slope of the curve correspond to the tensile strength (Ts) and elastic modulus (Em), respectively. Fig. 13 demonstrates that the incorporation of 1 wt% MWCNT into the composite resulted in a marginal increase in tensile strength compared to the reference sample. However, these improvements were accompanied by brittle failure immediately following the achievement of peak stress. The tensile strength increased from 23.2 MPa for the neat epoxy to 25.61 MPa for composite containing 1 wt% MWCNTs. This initial reinforcement effect is attributed to the role of MWCNTs as fillers within the epoxy matrix. Due to their high aspect ratio and needle-like morphology, MWCNTs tend to interact with epoxy molecules, forming CNT/epoxy interfaces. These interfacial regions act as reinforcements within the matrix, hindering crack propagation through the polymer network by effectively bridging the gaps between epoxy molecules

CONCLUSION

Three carbon nanostructured compounds and a super-paramagnetic material were successfully prepared with the help of hydrothermal methods. Ultrasonic waves were used in all stages of synthesis and dispersion in the polymer. The results showed that carbon nanostructures were effective for improving thermal resistance, but they alone did not show great flame resistance. Conversely, magnetic nanoparticles were successful and effective against flame, but not so great against heat. By combining and adding both magnetism and nanocarbons, both properties of slow burning and heat resistance were improved. Among carbon nanostructures, as expected, zero-dimensional carbon dots, compare to carbon nanotubes had better dispersion and subsequently better thermal performance. And finally, graphene sheets showed the weakest thermal resistance results and the worst dispersion in comparison to nanotubes and carbon dots.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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