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STRUCTURAL CHARACTERIZATION AND MAGNETIC PROPERTIES OF RUBBER FERRITE COMPOSITES

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Abstract

Rubber ferrite composites (RFCs) were prepared by incorporating ferrites in rubber matrixes has the advantage of easy flexibility. The loading of barium ferrite and nickel ferritein natural rubber matrices(120 phr) have been prepared with rubber accelerator chemical agents and using the processes of mixing, stirring and milling. The dielectric constant of the composite as well as the ferrite filler and natural rubber vulcanization was analyzed by Instek GW 821 LCR meter. The dielectric constant decreased with increase of frequency for ceramic samples of NFO and BFO, natural rubber vulcanisate and for the RFC samples. Magnetic hysteresis was measured by using a Permagraph L apparatus at room temperature. The remanence (B_r) and coercivity (H_c) were derived from the hysteresis loops. From the magnetic behaviour results, a rather low density, high coercivity, large stored energy and high flexibility rubber ferrite composites was successfully obtained.

Keywords: Hysteresis; magnetic properties; natural rubber; remanence; coercivity; Permagraph L; XRD; Grain size; composites.

Introduction

Ferrites represent an important category of materials, which are largely used, due to their numerous practical applications, as for example magnetic devices in electronic, optical and microwave installations. The M-type of ferrites with general formula $MeO.6Fe_2O_3$, where Me is divalent metal such as Ba, Sr or Pb, have been extensively used as permanents magnets due to their low cost, high coercivity and remanent magnetic induction.

Ferrospinel compounds are a very important group of magnetic materials due to their extensive use in a wide range of applications from low to high permeability devices including electronics, ferrofluid, magnetic drug delivery microwave devices and high density information storage devices.

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Polymers and polymer based composites are playing a crucial role in the day to day life of human beings. With the advent of nanotechnology aided by the capacity to modify the electrical, mechanical and magnetic properties of polymers, polymer composites are increasingly playing a lead role in everyday life. The magnetic polymer composites especially rubber ferrite composites is one of the many composite materials in which the scientist and engineers are interested and find scope for possible exploitation of commercial applications. High flexibility, chemical resistance and easy moudability are the main attributes of rubber magnetic composites.

The main focus of this research work was to synthesis, characterize and investigate the magnetic, dielectric properties of Nickel ferrite, Barium ferrite and rubber-Ni/Ba ferrite composites. The natural rubber is chosen as one of the polymer matrixes because of its easy availability and low cost.

Materials and Experimental Methods

Natural Rubber

Natural rubber (NR) is obtained from the sap of a tree caned 'caoutchou' or 'weeping wood' and is botanicalty known as 'Hevea Brasiliensis', named after the large forest tree, which is its outstanding source. The chemical name of natural rubber is polyisoprene, since it is a polymer of isoprene. Rubber is a poor conductor of electricity and hence it is very valuable as an electrical insulator. Some of the applications include the manufacture of automobile tyres, mechanical goods, footwear, hoses, beltings, adhesives and latex based products like gloves, foam rubber and thread. Rubber in this research work was collected from Mawlamyine district, Mon state (Myanmar).

Preparation of Nickel ferrite

Nickel nitrate $Ni(NO_3)_2{\cdot}7H_2O$, ferric nitrate $Fe(NO_3)_3{\cdot}9H_2O$, citric acid and liquor ammonia have been used as starting materials. The polycrystalline nickel ferrites were prepared by the sol-gel combustion method. Stoichiometricamounts of cationic salts were weighed separately and dissolved in minimum amount of deionised water to make clear solution; they are mixed and stirred for 1 hr to get ahomogenous solution. Citric acid solution is prepared in deionised water and 1 : 1 molarratio of metal nitrates to citric acid solutions were mixed and stirred. A small amount of liquor $NH_3$was added to the solution to adjust the pH value at 7.0. The solution was heated, stirred continuously to transform into a highly viscous gel. The gel was heated gradually up to 90°C, to evolve reddish brown color gases and finally the dried gel was finally burnt-out completely to form loose powders. These particles are further purified by acetone and toluene to get dark brown precipitate or black precipitate. Finely powdered materials were annealed at 800°C for 2 h for further crystallization. The sizes of particles were calculated by X-ray diffraction patterns.

Preparation of Barium ferrite

Barium ferrite ($BaFe_{12}O_{19}$) is a magnetic material, in the form of nanoparticles, having a hexagonal crystal structure, resistance to high temperature, resistance to corrosive and oxidative environments. Nanostructured barium hexaferrite powders were synthesized using the sol–gel combustion method. The starting materials were iron nitrate, barium nitrate, citric acid and ammonia, all of analytic purity. Appropriate amount of $Fe(NO_3)_3{\cdot}9H_2O$ and $Ba(NO_3)_2$, in a molar ratio of 12:1, were dissolved in a minimum amount of deionized water. Citric acid was then added into the prepared aqueous solution to chelate Ba^{2+} and Fe^{3+} in the solution, thensonicated for 20 min. The mixed solution was neutralized to pH 7 by adding liquor ammonia. The neutralized solution was evaporated to dryness by heating at 100 °C on a hot plate with continuous stirring. As water evaporated, the solution became viscous and finally formed a very viscous brown gel. Increasing the temperature up to about 300 °C led to the ignition of the gel. The dried gel burnt in a self-propagating combustion manner until all gels are completely burnt out to form a loose powder. Finally, the as-burnt powders were calcined in air at 1000 °C for 2 h to obtain barium hexaferrite nanoparticles. The flow diagram of sol–gel combustion method for ferrites was shown in figure 1. The photo graph of preparation of ferrite powder samples were shown in figure 2.

Preparation of rubber ferrite composites

Rubber ferrite composites are magnetic polymer composites consisting of ferrite fillers and natural rubber matrix. Nickel ferrite and Barium ferrite prepared by sol-gel auto-combustion method wereincorporated in a natural rubber matrix at loadings of 120 phr to obtain rubber ferrite composites (RFCs). The incorporation of ferrite in a natural rubber matrix was performed by appropriate amounts of ZnO, Stearic acid, cyclohexyl-2-benothiazole sulphonamide (CBS) and sulphur. The mixing was carried out in a ceramic. The temperature of the mixing cup is controlled by magnetic stirred can bevaried up to 300°C. Sulphur plays the role of a cross linking agent, while zinc oxide is added for activation. Stearic acid, CBS act as accelerators. The mixing was performed at around 50°C and the mixing operation went on for around 7 minutes at a frequency of rotation of 50rpm was maintained throughout the course of mixing. The mixing is rolled by roller and compressed with hydraulic press of 20 tons for 30 min. The photo graph of preparation rubber ferrite samples were shown in figure 3.

Results and Discussion

Characterization of ferrite powders

Powder X-ray diffraction studies (XRD) for nickel ferrite and barium ferrite have been carried out on the powder sample sintered at 800°C and 1000°C temperatures for 2 hrs, respectively and these patterns were shown in figure 4(a) and (b). The XRD pattern of the NFO and BFO samples were recorded by using a powder X-ray diffractometer {Schimadzu model: XRD 6100 using CuKα (λ =1.54Å) radiation}, with a diffraction angle between 10^{o} and 70^{o} respectively. The figure 4(a) showed that the as prepared sample consisted entirely of nano-crystalline $NiFe_2O_4$ particles and it showed the formation of single phase cubic spinal crystal structure. Then the lattice parameter of NFO compound, a = 8.33Å was calculated assuming cubic symmetry by using the relation, $d = \frac{a}{h^2+k^2+l^2}$. The XRD patterns of BFO compound indicated that it was mono-phase and highly crystalline in nature, without any detectable impurities.XRD pattern indicates that all the crystal planes of the $BaFe_{12}O_{19}$ correspond to the 00-007-0276 standard cart related to the crystal structure of barium hexaferrite. The lattice parameter was observed a = b = 5.895 Å and c = 23.199 Å. According to the XRD pattern the nanoparticles were fully calcined and no carbonic phase, relating to the citric acid and cotton template, was found in the pattern.From the XRD data, the average particle sizes of particles were calculated by using Debye Scherrer formula $t = \frac{0.9\lambda}{\beta \cos\theta}$ where t is the particle sizeλ is the wavelength of X-ray radiation, β is the full width half maximum(FWHM = 0.299)of X-ray peak broadening peak (311) and θ is the Bragg angle35.5° in NFO compound and FWHM = 0.228 of X-ray peak (110), angle 31.31° in BFO compound. The particle size was estimated to be about56.99 nm and 71.17 nm respectively. This shows that the synthesized powder has nano-size crystalinity.

Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) was done to determine the calcinations temperature of the as prepared powders and has been carried out to study the mass changes the increase temperature. The mass loss of sample was due to the vaporization process occurred when the temperature increased until a certain high temperature. TGA was performed from 37.97°C to 601.28°C. Figure 5 presents TGA curves and the weight loss as a function of temperature of the as prepared of Nickel ferrite and Barium ferrite. The results of weight loss at 3% are important to understand the thermal behaviour at initial stage and to determine the thermal stability of nanoparticle. From this analysis, 474.23°C is chosen as the minimum calcinations temperature for these barium ferrite powders. Four distinct regions (70.57°C, 125.98°C to 195.12°C and 474.23°C) of weight loss are observed. The weight loss around 474.23°C is observed to saturate compared to other regions. It was observed that the weight loss of Barium ferrite sample was 5.812 mg (7.774%). The weight loss of this sample was due to the vaporization process occurred when the temperature increased until a certain high temperature.

SEM analysis

The morphology and the size distribution of the NFO, BFO and their rubber based composites were determined using SEM. Typical SEM images of these compounds are shown in Figure 6. SEM micrograph depicts that the samples contain micrometrical aggregation of tiny particles. The existence of high dense agglomeration indicates that pore free crystallites are present on the surface. The SEM images show the agglomerated form of $NiFe_2O_4$ compound. As the nanoparticles possess high surface energies, they tend to agglomerate and grow into larger assemblies.

Dielectric behaviour of rubber ferrite composites

A study of the dielectric nature of NFO and BFO compound could furnish useful information about the electric field allocation within these compounds. The dielectric studies of both ceramic and rubber ferrite composites were carried out using LCR meter of model Instek GW 821. Disc shaped samples were used to evaluate the dielectric constant. The capacitance and dielectric loss in the frequency range 1 kHz to 200 kHz were determined. Dielectric constant or relative permittivity were calculated using formula $\varepsilon_r = \frac{C \times d}{\varepsilon_0 A}$ where d is the thickness of the sample, C is the capacitance, A is the area of cross section of the sample and ε_0 is the permittivity of the free space. ε_r is the relative permittivity of the material which is a dimensionless quantity. It was noticed that the value of the dielectric constant decreased with increase in the frequency. In ferrite materials, it is very high dielectric constant at very low frequencies and fall in the order of tens around frequency 100kHz. From the dielectric studies it became evident that the frequency negatively impacted both the dielectric constant and the dielectric loss as decreased with increase in the frequency. The frequency dependence dielectric constant value of Rubber, NFO, BFO and their rubber ferrites are shown in figure 6. A decrease in dielectric constant with increase in temperature was observed for natural rubber. Almost similar behavior as that of the ceramic component present in the matrix was obtained in the case of rubber ferrite composites. The absolute values of the dielectric constant of the composites were found to be greater than that of the natural rubber, but less than that of the ceramic NFO and BFO.

FTIR Analysis of rubber ferrite composites

Chemical functional groups of rubber ferrite composites were characterized by FT-IR spectroscopy and shown in the figure 7. There have similarly the same peak was observed in all of rubber ferrite samples. The absorbing bands at 1076.22 cm^{-1} is assigned to the hexagonal positions of metal-oxide stretching vibrations. The peaks at 1374.95, 1447.82, and 1637.29 cm^{-1} are related to the O-H vibrations related to the adsorbed water. The peak at 3331.20 cm^{-1} is attributed to the adsorbed CO_2 on the surface of these samples. FT-IR result showed that all the carbonic functional groups related to the precursors were eliminated.

Magnetic properties of rubber ferrite composites

The magnetic measurement of all samples was measured by using PERMAGRAPH L apparatus and which shows that samples exhibited magnetic behavior. The high coercivity values account for the slower rate of growth of crystallite size that takes place during the heating process. It is not only the temperature but also the morphology that seems to significantly influence the magnetic properties. The increased value of the coercivity could be attributed to the magnetic spin orientation along the axis that eases magnetization. On account of the grain boundaries and free surface, the magnetic properties improved. Figure 6 showed the magnetic hysteresis loops of the Natural Rubber, NFO, BFO and their runbber ferrites at room temperature. The magnetic parameters, namely retentivity (or) remanence, coercivity, and saturation magnetization of the samples were measured are shown in table 1 and their B-H loops were shown in figure 8.

Conclusion

Nickel ferrite and barium ferrite powders having the particle size of 56.99 and 71.17nm were incorporated into a natural rubber with loading levels 120 phr to obtain RFCs. It was successfully produced the RFCs having a rather low density, high coercivity, large stored energy and high flexibility even at relatively low mass fraction of the filler. The dielectric constant decreased with increase of frequency for ceramic samples of NFO and BFO, natural rubber vulcanisate and for the RFC samples. Useful magnets can be made by bonding ferrite powders in various resins, natural rubber. If no special steps are taken, the material is isotropic and energy product is unlikely to exceed 5.5 kJ/m^3. If good flexibility is required the proportion of ferrite powder must not be too large and $(B\text{-}H)_{max}$ becomes considerably lower. These magnetic composites have a variety of applications as flexible magnets, pressure/photo sensors and microwave absorbers. One of the familiar applications of rubber magnets is the refrigerator door seal. They are lightweight, soft, elastic, stable, flexible, easy to be processed, energy saving and low cost.

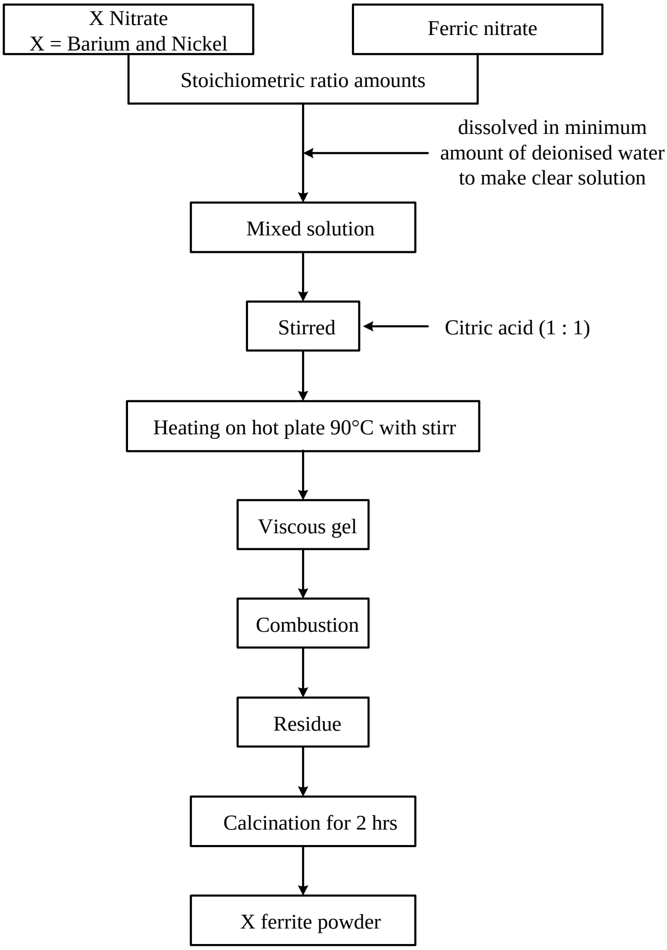


Figure 1: The flow chart of preparation of ferrites powder.

Figure 2 : The photograph of preparation of ferrites powder.

Figure 3 : The photograph of preparation of rubber ferrite matrices.

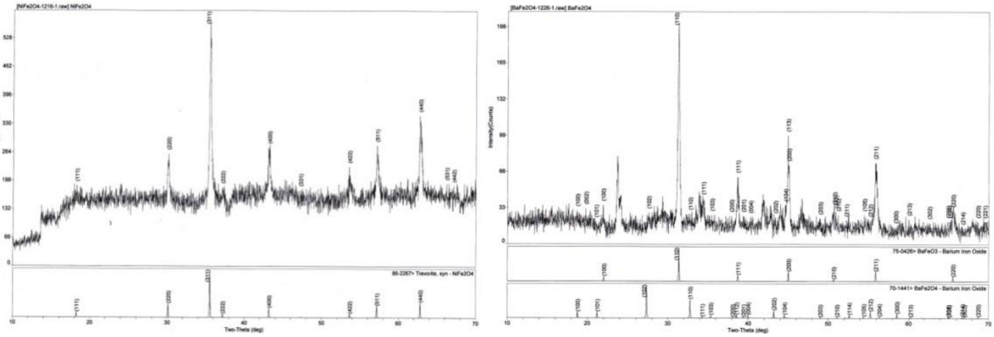


Figure 4:(a) The XRD pattern of Nickel ferrite compound and

(b) : The XRD pattern of Barium ferrite compound

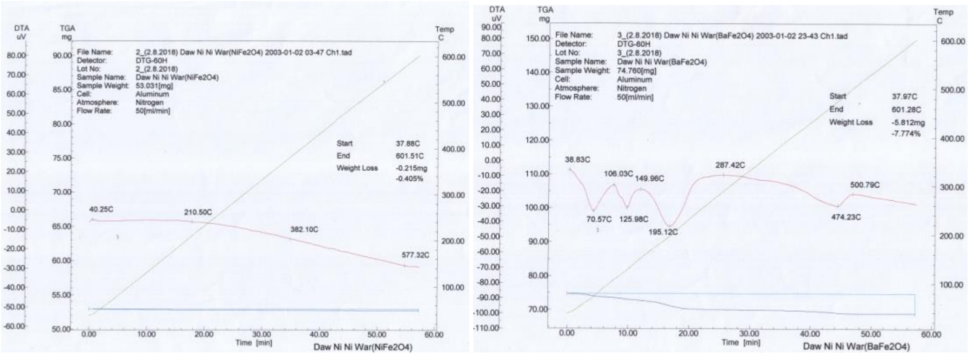


Figure 5: (a) TGA-DTA result of Nickel ferrite compound and

(b) TGA-DTA result of Barium ferrite compound

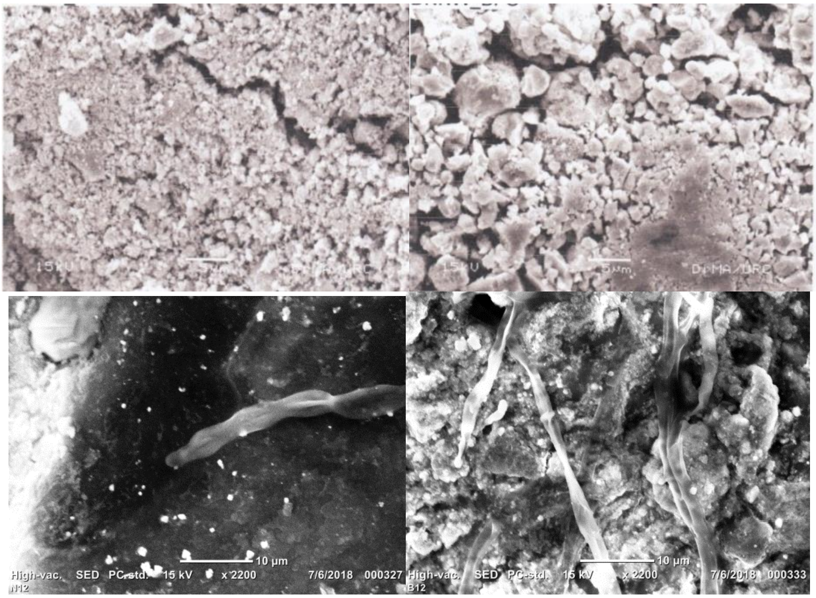
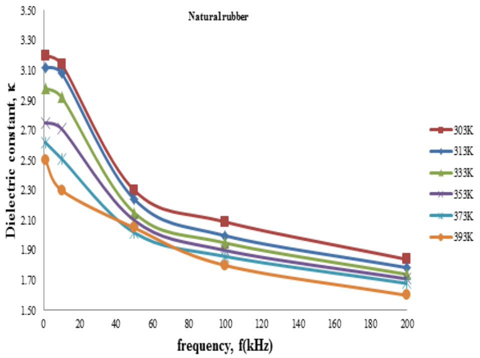
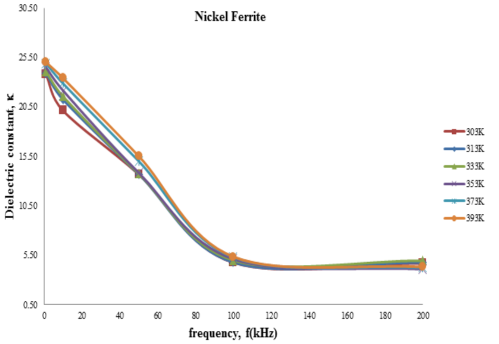
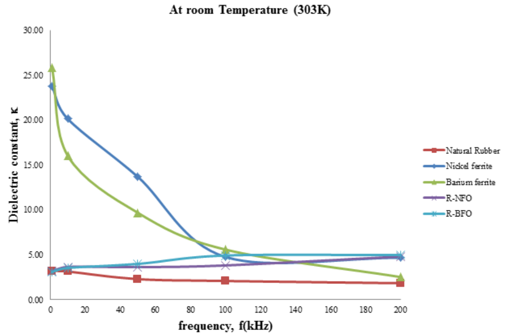
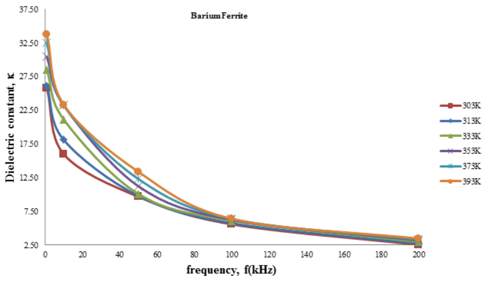


Figure 5: The SEM image of NFO, BFO and their rubber composites (120phr)









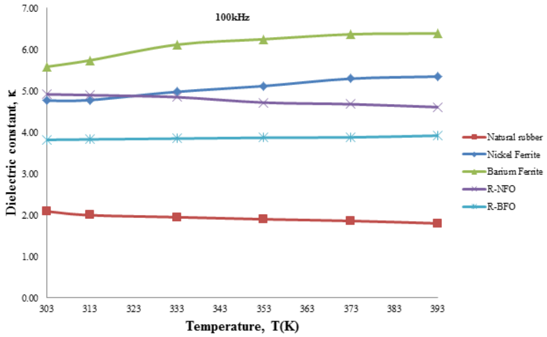


Figure 6 : The frequency dependence of dielectric constant of NFO, BFO and

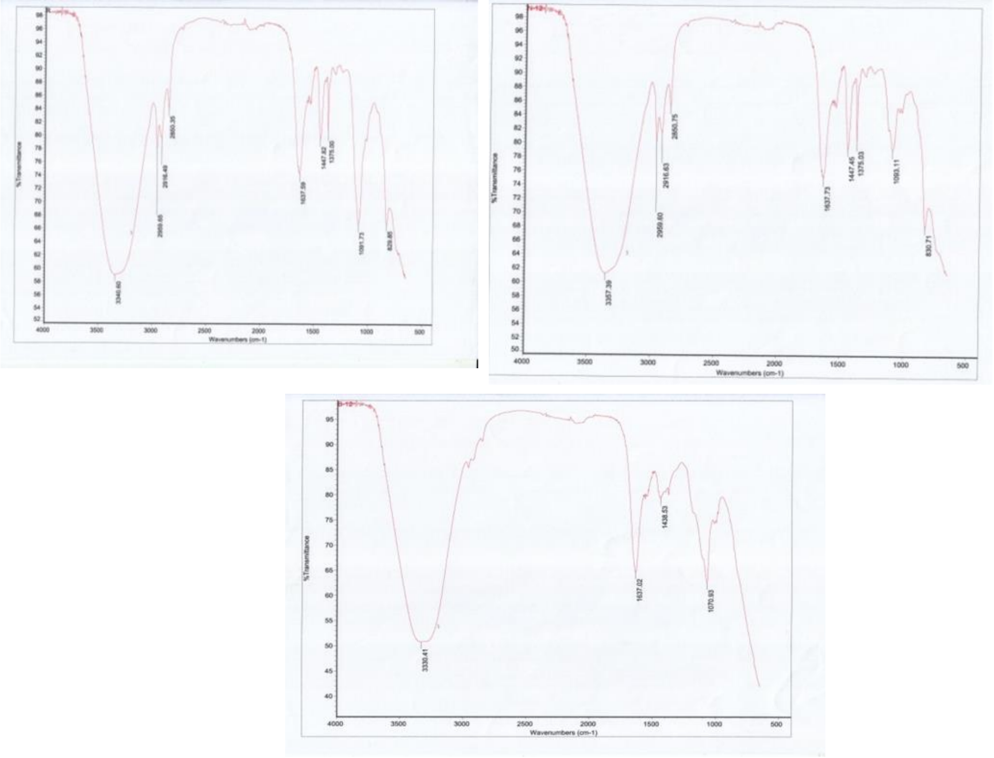


Figure 7: The FTIR results of pure rubber, Ni rubber ferrite and Ba rubber ferrite composites.

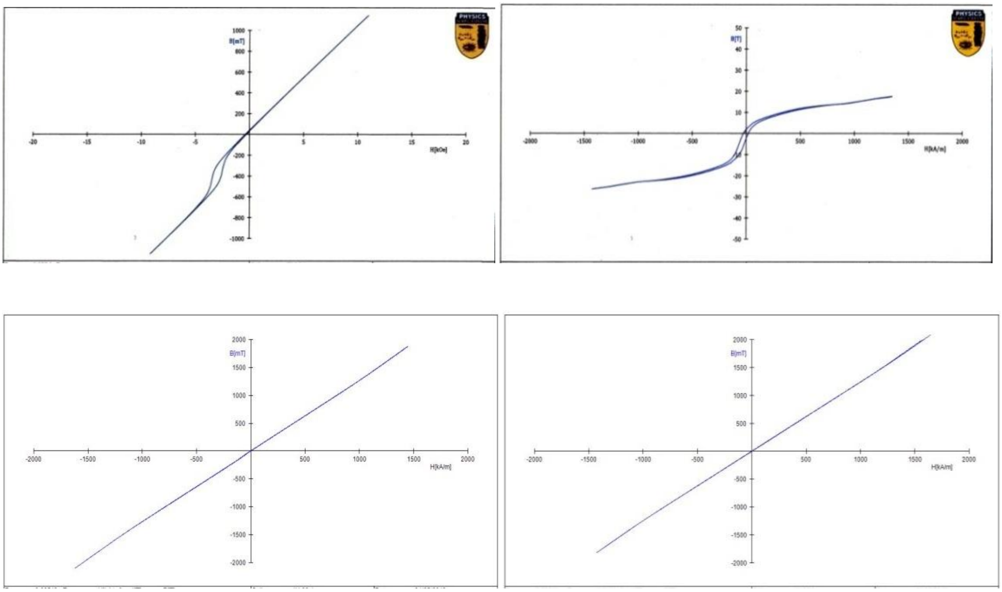


Figure 8: The B-H measurement of NFO, BFO and rubber ferrite composites with PERMAGRAPH L apparatus.

Table 1 : The magnetic parameters of RFC samples

Materials	**Remanence, B_r (T)**	**Intrinsic coercivity, H_{cJ} (kAm^{-1})**	**Energy Product, $(B\text{-}H)_{max}$ kJ/m^3**
Nickel ferrite	0.03060	31.8	0.120
Barium ferrite	0.00359	43.7	0.019
Rubber Ni ferrite	0.00543	76.2	0.028
Rubber Ba ferrite	0.00311	92.3	0.038

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