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Structural Properties and Mechanical Characterizations of Graphene Based Cobalt-ferrites Nanocomposites for Load Baring Applications

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Abstract— in this study we developed graphene based cobalt ferrites composites by in situ co-precipitation route. Four samples were prepared with 0%, 0.1%, 0.5% and 1% graphene sheets to cobalt ferrites. The samples were characterized by XRD, and FTIR, while SEM was used to observe the hybrid structure of embedded graphene sheets in cobalt ferrites. SEM confirms the successful adhesion of cobalt ferrites particles (10-20 nm) on graphene nano sheets, which are dispersed in metal oxide matrix. Mechanical characterizations reveal that our composites samples have higher flexural strength (19.92 MPa for 1 % loading) and improved toughness (>6000 J/mm^2) compare to pure cobalt ferrites (10.28 MPa, 1000 J/mm^2).

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Keywords— *GO, RGO, Cobalt-Ferrites, Toughness, Flex-Strength and Micro Vickers hardness*

1 Introduction

After the discovery of graphene in 2004 by Giem and novasolve [1], Scientist extensively started interest in the study and applications of this important material to cope with modern scientific challenges [2, 3, 4]. In short span of time, so many educational and industrial organizations put their efforts to explore its properties for useful applications. Individual graphene sheet is thought to be a potential candidate for future electronics such as FETs and flexible displays [5, 6].

Besides pure graphene sheet, functionalized graphene (RGO) which is obtained through chemical synthesis routes by reducing graphene oxide is also equally important due to ease of preparation and application[7,8]. Due to different groups attached with graphene sheet in RGO, its conductivity is not remaining as in pure form but reduces several times [9]. Although the properties of RGO is totally different from single graphene sheet but still having some tremendous properties such as good conductivity high mechanical strength and transparent nature [10, 11].

Peoples are trying to improve the mechanical and electrical properties of other materials by making composites of it with RGO as well as to make devices from pure RGO for different applications [12, 13]. Due to high surface area and sheet like morphology nanoparticles are efficiently dispersed on it to make good adhesion and hence best results can be obtained.

Ferrites are the magnetic mix metal oxides comprising the ferric ions as an essential constituent, while in mineralogy or in metallurgy the term ferrites refer to that material having a cubic crystal structure of spinal mineral[14,15]. The ferrites application has been known from ancient times for multiple centuries. Magnetite or ferrous ferrite is a naturally occurring ferrite. Almost all cobalt ferrites are also a promising candidate for medical treatment, electronic circuit's telecom and RF applications [16-18].

Many efforts have been done to make microwave absorbing materials from ferrites, but such materials are facing obstacles to perform efficiently, due to heavy weight and poor mechanical properties [19, 20]. To overcome these problems researchers started to make its composites with different matrix materials and to develop materials for specific area of application [21]. To get flexible and light weight sheets, ferrites are used to mixed with different polymers to improve its mechanical properties but rise the problem of low thermal conductivity and caused heat accumulation in the covered device as well as within the sheet itself which may

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lead to severe problems and degradation of these absorbing sheets [22, 23].

In present work we have tried to make cobalt ferrites composites with graphene nanosheet, to overcome the problem stated above.

2 Materials and Methods

Composites of graphene with cobalt ferrites were synthesized by in situ Co-precipitation mechanism [24]. In typical method 0.02 mol of Fe $(NO_3)_3.9H_2O$ salt along with 0.1 mol Co $(NO_3)_2.6H_2O$ was added to 200 ml DI water and mixed to form homogeneous solution. Appropriate amount of GO was mixed with 4 gm NaOH to achieve the GO loading upto 0 % , 0.1 %, 0.5 % and 1 % to compare with ferrites salts precursors. Ferrites- salt containing mixture was heated up to 90 ◦C and stirred vigorously, while NaOH contain GO was added drop by drop. The one pot mixture was left for 3 hours stirring without lowering the temperature. The precipitate formed was filtered and washed thoroughly with water until we got neutral pH. Powder obtained was dried in oven and ground with the motor and pestle, the sintered for 3 hrs at 800 ◦C in the furnace. Sintered samples were named S_0, S_1, S_2 and S_3 respectively.

3 Characterizations

The phase identification of all the composites samples were performed in X-ray Diffractometer (2002 model) using Cu-Kα radiation (λ=1. 54 Å) in the 2θ range from 8 to 80 degrees. The presence of characteristic chemical bonding of RGO, cobalt ferrites and its composites were studied by Fourier transform infrared spectroscopy (FTIR) analysis using a FTIR spectrophotometer [Nicolet 6700]. For FTIR analysis, small amount of sample was mixed with KBr and then pressed to make pellets for FTIR analysis. Morphology, dispersion and adhesion of cobalt ferrites particles with graphenenanosheet, were further studied by scanning electron microscope [JSM_6490A] on powder samples.

To evaluate the mechanical properties we performed two types of tests, micro Vickers and Flexural compressive strength test. Both of these tests were performed on the pressed pellets according to ASTM standards [C 1327 – 03]and [C 1161 – 02c] respectively. Vickers hardness was performed by applying a load of 0.5 kg. A Flexural compressive test was performed with the help of Designed Die with the same dimensions as the pellet, in a universal testing machine.

4 Results and Discussion

4.1 Phase Identification of Composites

The ferrite powder obtained was sintered at 800°C for 3 hours in a furnace, and then analyzed by X-ray diffraction instrument to get the characteristic spectra for all the prepared samples, as shown in figure.1 For these samples characteristic planes (111), (220), (311), (222), (400), (422), (511), (440), and (531) are observed in all the samples. And these planes correspond to pure crystalline phase of cobalt ferrites matched with reference card no (JCPDS, 03-0867) of XRD. High intensity with respect to background signals and sharpness of these characteristic peaks is the evidence for good quality crystalline cobalt ferrite formation.

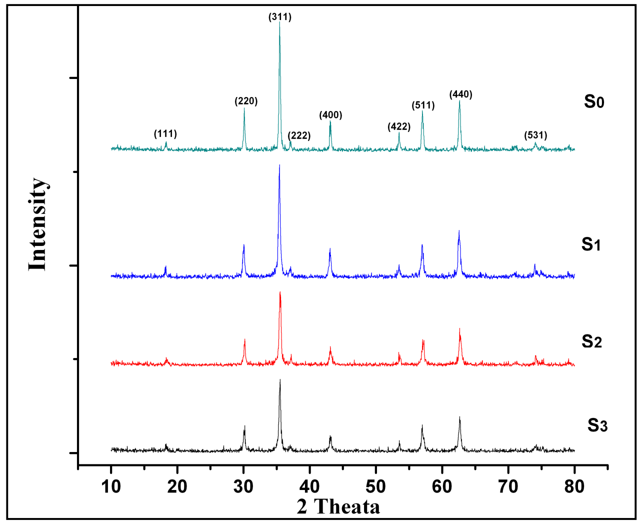

Figure 1. XRD spectra for cobalt ferrites and its composites samples with graphene.

As we can see that impurity phase is present only for 1 % doping of graphene into cobalt ferrites at 28 degrees, so for other samples 0.1 and 0.5 % doping, graphene amount is not enough to incorporate in XRD spectra [25-26].

4.2 Functional Group Analysis

FTIR spectra are shown for cobalt ferrites as well as for three composite samples in Figure.2.It are clearly shown that there are only two characteristic peaks at 425 cm^{-1} and 590 cm^{-1} along with a broad downhill after 3000 cm^{-1} for S_0 sample. Peak at 425 cm^{-1} attributes to Fe-O group and 590 cm^{-1}peak is due to the presence of Co-Ogroup, while broad peak after 300 cm^{-1} is due to incorporated water molecules.

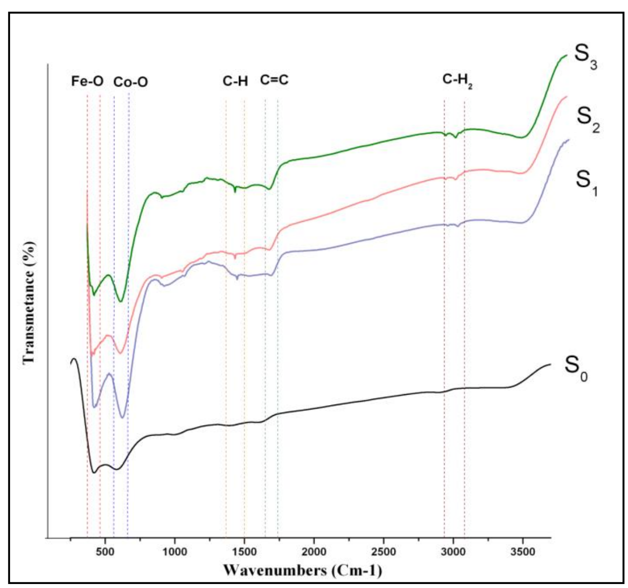

Figure 2. FTIR for cobalt ferrites and its composites samples with different percent loading of graphene

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For composite samples we have extra peaks at 1380-1390 cm^{-1}, 1620-1680 cm^{-1} and at 2920-2930 cm^{-1} attributes to C-H, C=C and $C\text{-}H_2$ deformation respectively.

All this data is in agreement with literature for cobalt ferrite formation as well as graphene-cobalt ferrites composites [27-28].

4.3 SEM Analysis

Figure.3 shows the micrographs of cobalt nano particles (S_0) synthesized by co-precipitation technique and all the three samples (S_1, S_2, S_3) respectively.

S_0 sample was analyzed via making suspension in water without sonication, and hence we see the cobalt ferrite particles upto 15 nm by size, along with agglomeration of these particles in the form of an island.

The composite samples were analyzed by SEM in bulk-powder form putting on the clean glass substrate. As shown from figure, for very low concentration (0.1%), there is no graphene flake to see within cobalt ferrites, while for another two samples S_2 (0.5%) and S_3 (1%) we have graphene flakes embedded with in cobalt ferrites.

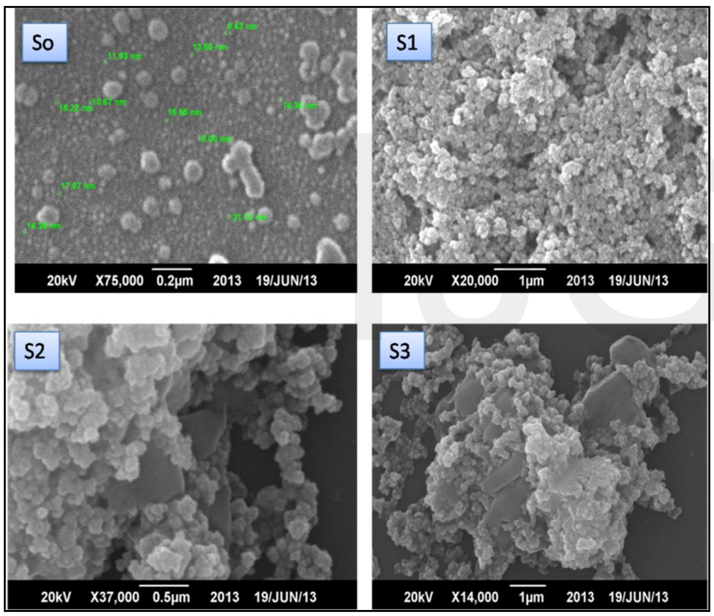

Figure 3. SEM images of cobalt ferrites and graphene based composites

5 Mechanical Characterization

5.1 Stress versus Strain Behavior

Stress versus strain curves are given for all the composites and RGO sample are given in figure.7 , As the loading of graphene in cobalt ferrites is very low (up to 1 %), so all the composite samples behave like ceramics as reported for ferrites samples [30]. While for RGO, the deformation behavior is somehow like poor polymer as shown in Figure 4. This behavior is much expected from the RGO sample as it has a flaky morphology along with flexible nature. Further it is clear from the figure 4, that time before failure is much increased by increasing the percent loading of graphene in cobalt ferrite matrix. The UTS for all the samples and RGO is given in the Table1.

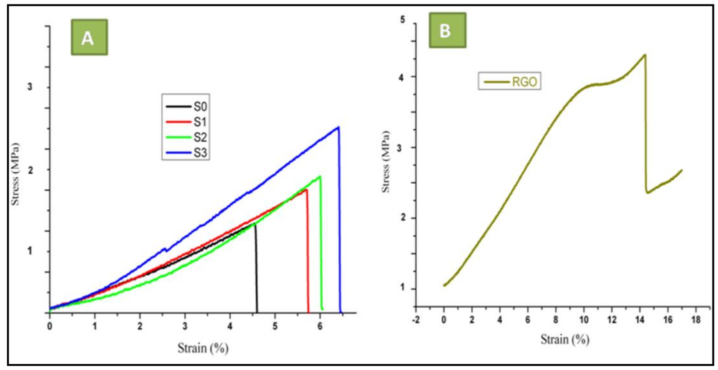

Figure 4.Stress strain curves for composites and RGO samples

5.2 Toughness

In this study our aim was to improve the toughness of the ferritic material by the addition of graphene to it. So here we evaluated the overall relative toughness of our samples by a simple method. As the overall toughness of the material can be measured by calculating the area under the stress strain curve. So all these areas were calculated via origin approximation and compared with each others. Relative toughness versus graphene loading to cobalt ferrites are illustrated here in the form of bar graph is shown in Figure.5.

It can be seen from the graph that ferrites having strong brittle nature with very low toughness upto 10,000 J/m³ which increased up to 32,000 J/m³ by only 1 % graphene addition. We got very high toughness up to 63,000 J/m3 for RGO sample.

S.No	Sample	UTS (N/mm2)
1	S0	1.08
2	S1	1.34
3	S2	1.96
4	S3	2.32
5	RGO	4.45

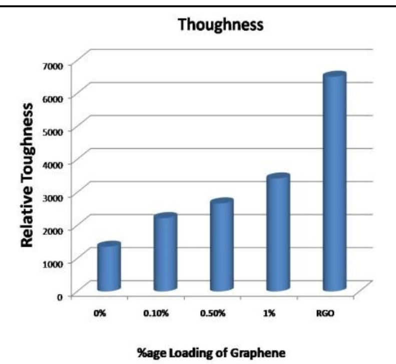

Figure 5. Bar graph of relative toughness for Co-composites and RGO samples.

So it is revealed from this experimental data that there is definitely a possibility to improve the toughness of cobalt ferrites by doping with graphene, which may lead to solutions for problems such as achieving flexible devices of ferrites composites for different microwave applications.

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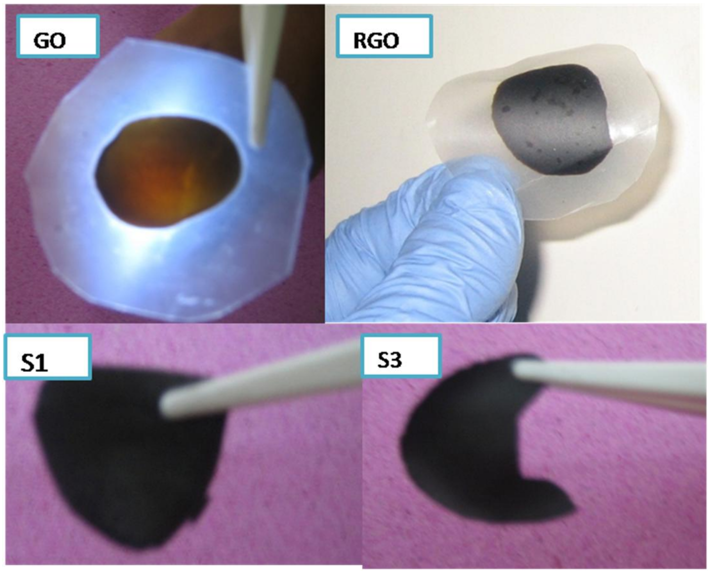

Above are the camra images of GO, RGO composite sample S1 and S2 respectively, as shown that GO yellowish colur changed to dark black on reduction. The RGO sample is still flexible over a plastic sheet and images of composites (S1 and S2) reveals that flexible sheets are obtained of ferrites (pure ceramics) with the help of graphene.

5.3 Flexural Strength

Biaxial flexural strength is plotted for each sample as shown in Figure.6. The trend remains the same as UTS, explained above from the stress - strain curve. We have 10.28 MPa for pure cobalt ferrites which is improved up to 19.92 MPa for only 1 % loading of graphene, while for RGO is so high up to 32.17 MPa.

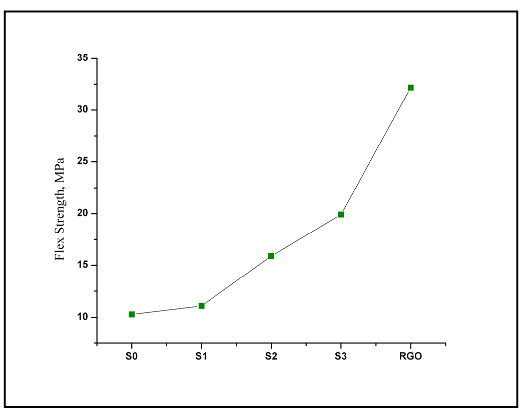

Figure 6.Graph of flexural strength for all Co-ferrites and RGO samples on ring pellets.

5.4 Vickers Hardness

The micro Vickers hardness test was performed on sintered pellets of composites samples, according to ASTM standard C 1327 – 03[31]. Micro indents were applied to a load of 0.5 kg for 5 sec. five indents were made on each pellet. For reliable results the diagonal measurements were performed by JEOL SEM. Vickers Hardness no (Hv) were calculated by the formula [32],

$$HV=1.8544\,(P/d^2)$$

Where
P = load in kgf, and
D = average length of the two diagonals of the indentation in mm.

Figure 7, shows that the Hv No lowered with increasing graphene loading.

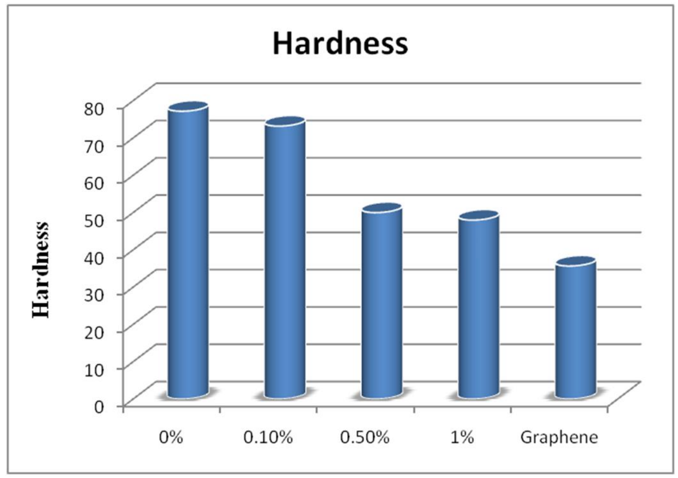

Figure 7. Bar graph of Vickers hardness for all samples

Cobalt ferrites have Hv.No up to 77, which decreased up to 48 for 0.5 % loading .This decrease in hardness is due to the incorporation of flexible sheets of graphene, which promote the penetration and slipping of cobalt ferrite particles under the applied load by indent. Furthermore, graphene loading beyond 0.5 % negligible decrease in hardness reveal that after some optimum limit the graphene loading will act as a reinforcing agent in cobalt ferrite matrix and may increase its hardness.

Conclusions

A simple and facile method is used to make graphene-Co-ferrite composite structure. Due to high surface energy of graphene sheets, the Cobalt ferrites nano particles are embedded with it to form a homogeneous structure. The mechanical characterizations of these composites samples reveal that graphene enhanced both the strength and toughness of Cobalt ferrite samples.

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