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Studies on Electroless Co-P alloy Coated Nano Cenosphere/Polymer for EMI shielding Application

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ABSTRACT

Electromagnetic interference (EMI) is an escalating concern in the modern electronic climate. As such it has become a critical area to consider when designing and packaging electronics. In this context, electroless cobalt-phosphorous alloy coated nano cenosphere (CPCNC) in polymethyl methacrylate (PMMA) and acrylonitrile butadiene styrene (ABS) composites have been tried for their EMI shielding effectiveness (SE). The strategy is to render the polymer conductive by dispersing CPCNC in various proportions in these polymers separately and to promote wave absorption by making sheet of the polymer-based composite. In our study, energy dispersive X-ray analysis confirmed the presence of Co-P on the coated nano cenosphere. This was further, confirmed through phase analysis by X-ray diffractometer pattern. Scanning electron microscope analysis was conducted to see the size, shape, and adherence of the Co-P alloy on nano cenosphere particles and to observe the distribution of these particles in polymer matrix in the composite sheet. BET surface area of electroless coated powders was quite high indicating good surface properties. The processing methods, electrical properties (surface resistivity), and electromagnetic behavior (EMI SE) were investigated. SE values of approximately 25 dB at a frequency of 1 GHz was obtained for coatings of electroless CPCNC in ABS polymer which can further be increased by adding other conductive nano fillers along with coated cenospheres.

Key words: *Nano cenosphere, Electroless coating, Electromagnetic interference.*

1. INTRODUCTION

Electromagnetic interference (EMI) is an important topic of interest in present times. As the technology is advancing, the importance to integrate a large amount of electrical and electronic devices in various engineering fields such as automobiles, space, and medical instruments is of utmost need. In an electronic system, EMI can very badly affect the performance of an integrated circuit internally and also on the other electronic components which are in close proximity. The interference sources may be internal or external to the electrical or electronic system, and they may propagate by radiation or conduction.

The word cenosphere literally means spheres which are hollow in structure. Cenospheres belong to ceramic family with light weight, inert, and hollow sphere which is typically made up of silica and alumina and hollow sphere is filled with air or inert gas, mainly produced as a by-product of coal combustion unit at thermal power plants. Cenosphere particles are hard and rigid in nature; they are also water repellant and insulative. Cenospheres are very easy to handle, and they easily flow and have a good surface area. Due to their inert properties, they are not affected by water, acids, alkalis [1,2], or solvents.

There are many methods which are available to coat ceramics such as electro plating, metal spraying, vacuum metalizing, hot dipping, and electroless plating. Among all these methods, an electroless plating method is considered to be more suitable for the present study involving fine particles, because the substrates are in the form of powder (nano cenosphere) and the coating method provides a thin, homogenized [3] and controllable coating [4]. In this study, electroless alloy coated cobalt-phosphorous combination was successfully studied for EMI shielding effectiveness (SE) [5].

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2. EXPERIMENTAL

2.1. Materials and Methods

Cenospheres, cobaltous sulfate, sodium hypophosphite, sodium acetate, sulfuric acid, nitric acid, hydrochloric acid, stannous chloride, palladium chloride, acrylonitrile butadiene styrene (ABS), poly methyl methacrylate (PMMA), acetone, chloroform, graphene, and multi walled carbon nano tube (MWCNT).

2.2. Development of Nano Cenosphere

About 50 g of acid washed cenosphere powder was milled using higher energy ball mill in a zirconia jar with zirconia balls of different sizes as grinding media in acetone medium for 50 h with 300 rpm. The particle size range of ground cenosphere powder was found to be 100-200 nm. Several batches of nano cenosphere were prepared.

2.3. Pre-treatment of Nano Cenospheres

The nano cenosphere powder was again washed for an hour with the solution of 5% sulfuric acid followed by filtering through fine filter paper and dried at 100°C.

2.4. Mechanism of Electroless Co-P Coating

The process involves sensitization of nano cenosphere particles followed by activation to create active negatively charged sites on nano cenosphere particle surfaces and then electroless coating process consisting of Cobaltous sulfate used as the source of cobalt ions while sodium hypophosphite as the reducing agent as well as source of Phosphorus ions, Sodium acetate for adhesion of cobalt-phosphorous on nano cenosphere surface. The bath is prepared by adding the constituents in the appropriate sequence. The pH of the solution is maintained between 7.5 and 8.0 [4].

2.5. Preparation of Cobalt-Phosphorus Coated Nano Cenosphere (CPCNC)/Polymer/Filler Composite Sheet

2.5.1. Preparation of CPCNC/PMMA composite

Weighed quantity PMMA was dissolved in chloroform. After the complete dissolution of PMMA polymer, CPCNC was added to the solution and was stirred continuously for 1 hr followed by ultrasonication in a high-frequency sonicator for 30 min. The different weight percentage of the polymer and CPCNC is as shown in Table 1. Similarly, CPCNC/ABS composite was prepared.

Preparation of CPCNC/polymer/filler composite sheet graphene/MWCNT was used as the filler materials along with CPCNC. Initially, the polymer was completely dissolved in the solvent followed by the addition of CPCNC along with filler materials, *viz.*: Graphene or MWCNT in different percentages ranging from 5 to 10. The different weight percentage used is as shown in Table 2.

Table 1: Weight percentage list of CPCNC/polymer composite.

% CPCNC in composite sheet	Weight of CPCNC (in grams)	Weight of polymer-ABS/PMMA (in grams)
5	0.5	9.5
10	1	9
15	1.5	8.5
20	2	8
25	2.5	7.5
30	3	7
35	3.5	6.5

CPCNC=Cobalt-phosphorous alloy coated nano cenosphere

3. CHARACTERIZATION

Phase analysis by X-ray diffraction (XRD): Phase analysis by XRD was carried out after the coating of powder. Figure 1 gives the XRD pattern of CPCNC. It can be seen that the coated powder is semi crystalline in nature with peaks pertaining to coated species cobalt and phosphorous along with those of cenosphere base phases (mullite, alumina, and quartz).

EDAX was carried out to know the chemical composition of the nano cenosphere particles, after pressing it in the form of a pellet. The composition reveals the presence of cenosphere constituents which is shown in Figure 2. Further, EDAX of CPCNC revealed the presence of elements Co and P on the surface of the pellet apart from those of the cenosphere constituents which has been shown in Figure 3. Tables 3-6 summarize the chemical compositions of nano cenosphere and CPCNC.

Figure 4 shows the scanning electron microscope image of nano cenosphere. Particles were found to be agglomerated as shown in Figure 4 and the average particle size was measured to be around 100-200 nm.

Figure 5 represents the scanning electron microscope (SEM) image of CPCNC in which Co-P is uniformly distributed all over the surface of cenosphere. However, due to extensive agglomeration, the exact particle size could not be measured. The complete coating of Co-P on the surface of nano cenosphere particles was supported by EDAX analysis which is shown in Figure 3.

Further, the CPCNC powder was mixed with conducting nano fillers, and again composite sheets were prepared and characterized. SEM photographs of 30% concentration of nano powder in the polymer matrix are shown in Figure 6.

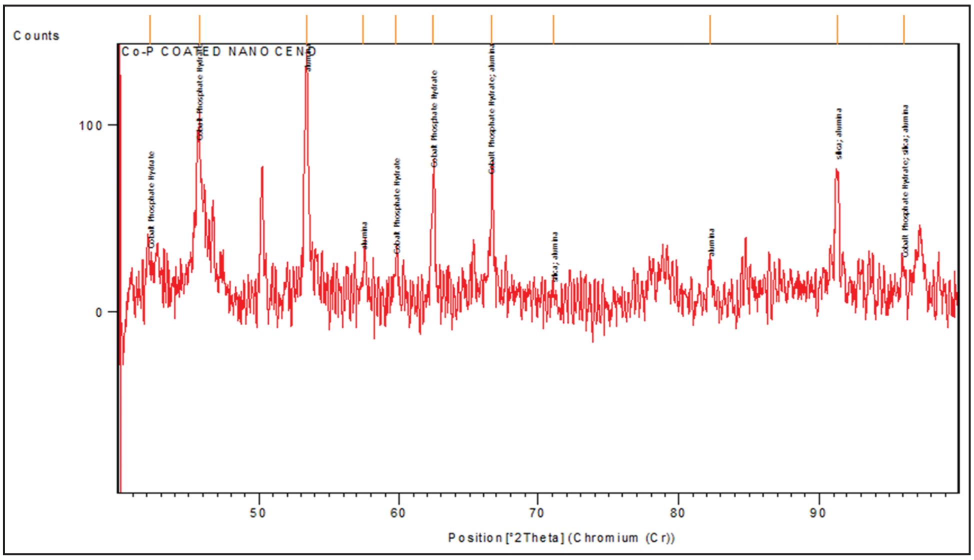

Figure 1: X-ray diffraction pattern of cobalt-phosphorous alloy coated nano cenosphere powder.

Table 2: Weight percentage list of Co-P CPCNC/polymer/filler composite.

%conductive nano filler in polymer/CPCNC composite material	Weight % of polymer-PMMA/ ABS (grams)	Weight % of Co-P CPCNC (in grams)	Weight % filler material-graphene/ MWCNT (grams)
5.0	7	2.50	0.50 (1)
10.0	7	2.00	1.00
15.0	7	1.50	1.50

CPCNC=Cobalt-phosphorous alloy coated nano cenosphere

Table 3: X-ray diffraction pattern list (phases) of CPCNC powder sample.

Reference code	Score	Compound name	Scale factor	Chemical formula
00-033-0432	20	Cobalt phosphate	1.465	Co-P
00-033-1161	23	Silica	0.902	$Si\ O_2$
00-042-1468	27	Alumina	0.603	Al_2O_3
	30	Mullite	0.900	$Al_6Si_2O_{13}$

CPCNC=Cobalt-phosphorous alloy coated nano cenosphere

Table 4: Chemical composition of nano cenosphere.

Element	Weight %	Atomic %
OK	52.66	66.55
AIK	13.90	10.42
SiK	29.65	21.35
CiK	0.49	0.28
KK	0.46	0.24
Ca K	0.61	0.31
Ti K	0.78	0.33
Fe K	1.44	0.52

The cobalt-phosphorous alloy coated nano cenosphere (CPCNC) particles were then uniformly distributed in the ABS/PMMA polymer matrix in the range of 5-35% concentration through ultrasonication and allowed to dry overnight. The resultant composite sheets thus obtained were characterized for SEM, EDAX, XRD, conductivity and finally taken for EMI SE measurements.

From the above, it can be concluded that the composite sheet comprises the phases of base material along with the coated alloy of Co-P. However, the sample is glassy as can be seen from the XRD spectrum which is the basic nature of the raw material on which coating has been carried out (Nano cenosphere). Further, the peaks due to the coated phase (Co-P) are too small because the coating is in the nano range. Further, it was also observed that the thickness of the composite sheet as measured was found to be approximately 500 µm from the SEM photographs taken at 500

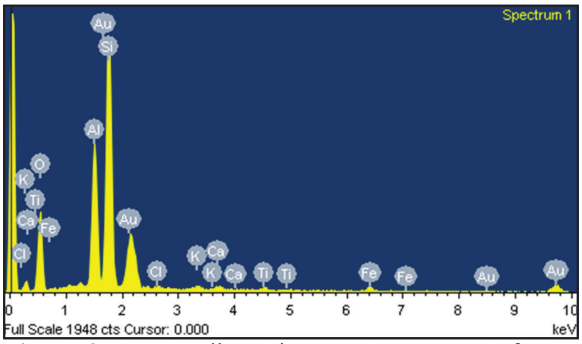

Figure 2: Energy dispersive X-ray spectrum of nano cenosphere.

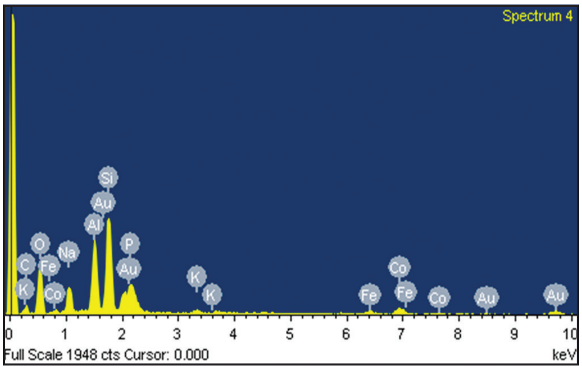

Figure 3: Energy dispersive X-ray spectrum of cobalt-phosphorous alloy coated nano cenosphere powder.

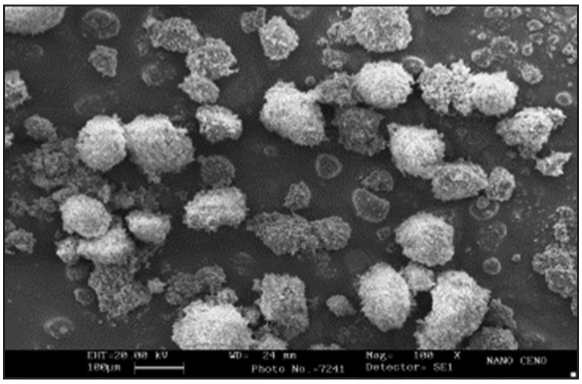
Figure 4: Scanning electron microscope image of nano cenosphere.

magnification it can be observed that the uniformity of distribution of particles was quite uniform and was very uniform in the 20% CPCNC and 10% nano filler in ABS polymer matrix sheet which resulted in the higher conductivity and good SE at 1.0 GHz frequency.

4. RESULTS AND DISCUSSION

The CPCNC powder was subjected to surface area measurements before and after electroless coating. The BET surface area was around 250 m^2/g. The surface area was found to be quite significant which means that the powder has good surface

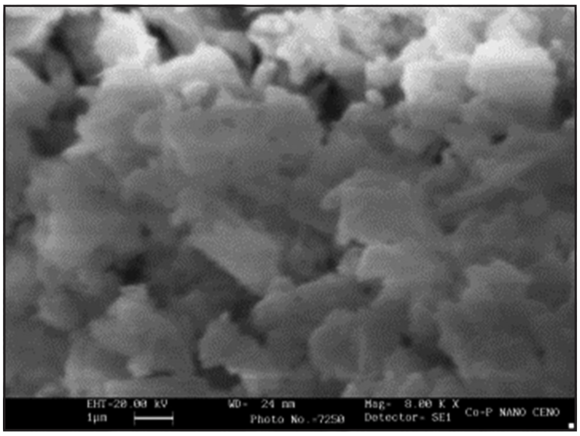
Figure 5: Scanning electron microscope image of cobalt-phosphorous alloy coated nano cenosphere.

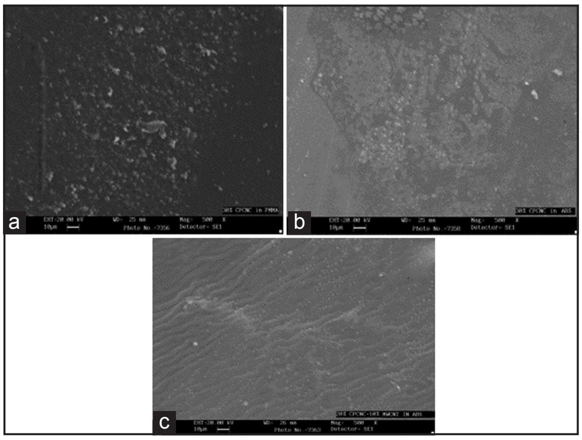

Figure 6: Scanning electron microscope photographs of composite AT 500X, (a) 30% cobalt-phosphorous alloy coated nano cenosphere (CPCNC) in PMMA, (b) 30% CPCNC IN acrylonitrile butadiene styrene (ABS), (c) 20% CPCNC/10% MWCNT IN ABS.

characteristics such as higher surface energy and surface reactivity.

4.1. Resistivity of the Composite Sheet after Dispersion of CPCNC in the Polymer Matrix

The resistivity of the composite sheet was measured by four probe technique, and it was ranging between 40 and 200 ohms at different wt% of CPCNC in the polymer matrix, and filler added CPCNC in the polymer matrix. This low resistivity indicates that the composite sheet has reasonably good conductivity and suitable for the lower range EMI shielding applications and the conductivity versus wt% graph is as shown in Figure 7.

The conductivity of CPCNC particles in ABS matrix was higher than in the case of PMMA polymer due to the higher uniformity of distribution of the particles in the composite sheet. Thus, the EMI SE (Figure 8)

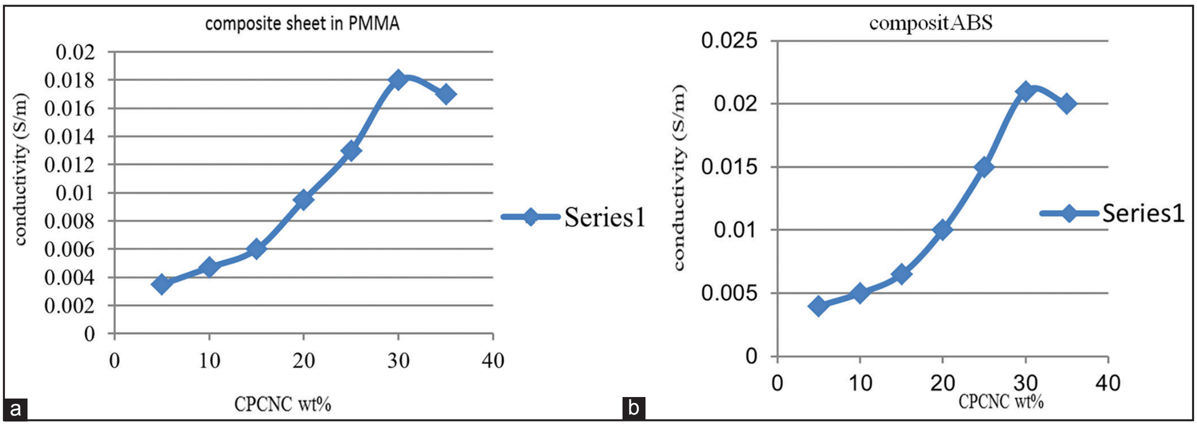

Figure 7: (a and b) Conductivity of composite of poly methyl methacrylate and acrylonitrile butadiene styrene.

is higher in the case of CPCNC distributed composite sheet.

The conductivity of composite sheets after incorporating the nano conductive fillers (MWCNT and graphene in percentages ranging 5-15) with 15% CPCNC in ABS polymer matrix resulted in further increased the conductivity of maximum conductivity was observed to be about 0.03 S/m for 15% graphene/ MWCNT along with 15% CPCNC. The total percentage of filler and CPCNC was restricted to 30% since beyond this percent the conductivity tends to decrease as can be seen from Figure 9. The increased conductivity after incorporation of conductive nano fillers along with CPCNC in ABS polymer matrix resulted in higher SE of the composite sheet.

As a result of the lower uniformity in distribution of CP CNC particles (30%) in PMMA, there is decrease in conductivity of the composite sheet (Figure 8) which resulted in the EMI SE of around 23dB at 1 GHz (Figure 9). 30% CPCNC composite sheet was taken for EMI measurements since this composition showed the highest conductivity whereas in the case of CPCNC in ABS matrix the conductivity of the composite sheet was higher for the same 30% composition which resulted in the higher SE of around 25 dB (Figure 9).

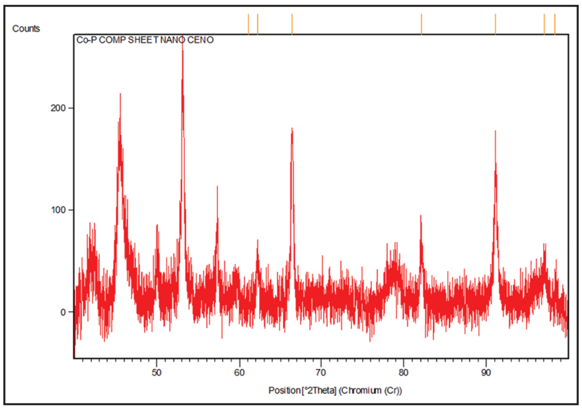

Figure 8: X-ray diffraction spectrum of composite sheet.

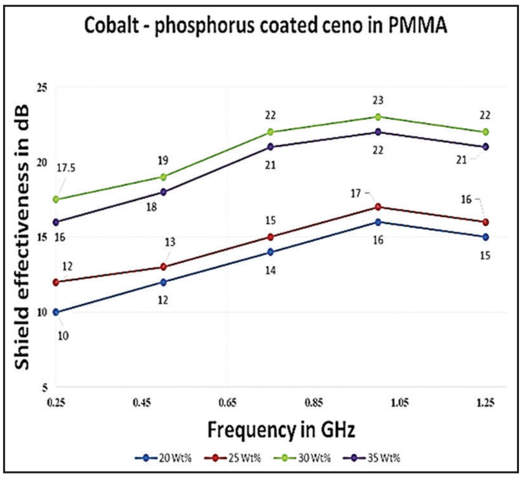

Figure 9: Electromagnetic interference of composite sheet (in poly methyl methacrylate).

4.2. EMI SE Measurements

Further, EMI measurements were carried out on conductive filler incorporated ABS polymer composite sheet (15% CPCNC with 15% graphene/MWCNT nano conductive fillers), and the following figures show the SE. A SE of about 35 dB was obtained for conductive filler incorporated CPCNC ABS composite sheet material (Figures 10 and 11).

5. CONCLUSIONS

- Electroless method has been successfully adopted for coating Co-P alloy on nano cenospheres particles which can be observed through SEM, XRD, and energy dispersive X-ray.
- The processing of particles distribution in ABS matrix is quite uniform which can further be improved.
- Conductivity was found to be 0.02 S/m for 30Wt% of CPCNC/ABS composite and 0.03 S/m for nano filler (MWCNT/Graphene) mixed CPCNC composite [15+15] %) sheet in ABS

Table 5: Chemical composition of cobalt-phosphorous alloy coated nano cenosphere.

Element	Weight %	Atomic %
CK	5.93	9.90
OK	45.28	56.81
Na K	7.48	6.53
AlK	11.58	8.61
SiK	17.71	12.66
PK	3.98	2.58
KK	0.75	0.39
FeK	2.07	0.74
CoK	5.21	1.78
Total	100.00	

matrix. There is a scope for further improvement in conductivity by addition of nano fillers along with CPCNC in the higher percentages. However, uniform distribution of the mixed nano powders in polymer matrix needs to be ensured.

- SE is found to be appreciable of 25 dB at 1GHz for 30 wt% of CP CNC/ABS composite. The SE further increases to about 35 dB at 1.0 GHz frequency which can further be improved by further optimization of CPCNC/conductive nano filler/polymer combinations.

6. ACKNOWLEDGMENTS

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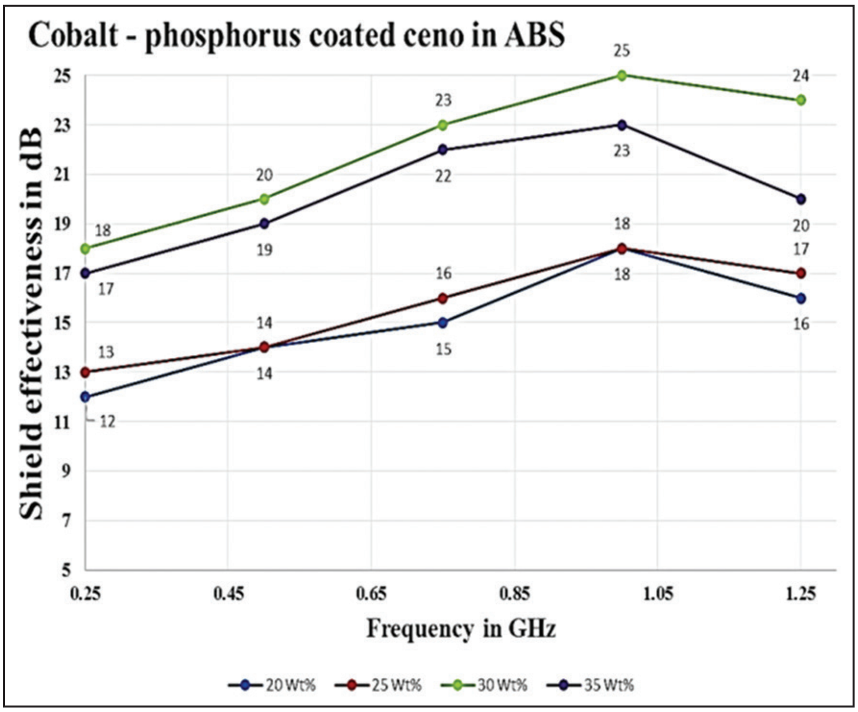

Figure 10: Electromagnetic interference of composite sheet (in acrylonitrile butadiene styrene).

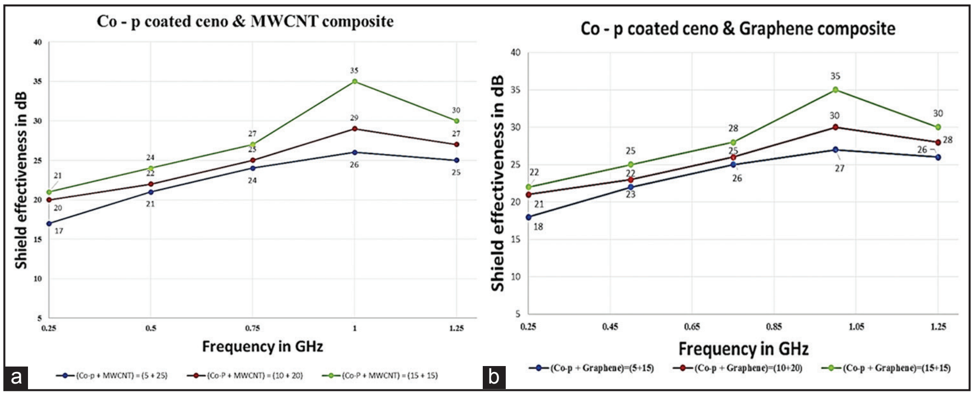

Figure 11: (a and b) Electromagnetic interference of composite with nano fillers.

Table 6: X-ray diffraction pattern list of CPCNC distributed over composite.

Pattern list: Phases present in the composite sheet			
Compound name	**Displacement [2Th.]**	**Scale factor**	**Chemical formula**
Alumina	0.000	0.349	Al_2O_3
Stishovite	0.000	0.560	$Si\ O_2$
Senegalite	0.000	4.421	$Al_2\ (PO_4)$ $(OH)_3$! H_2O
Cobalt-phosphorous	0.000	1.256	Co-P

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Bibliographical Sketch

Shri. S. Vynatheya Joined the CPRI during Feb. 1986 and presently he is continuing in the Materials Technology Division as Joint Director. He is presently pursuing his PhD degree in Chemistry at Dr. AIT, Bangalore, under VTU, Belgaum. He has over 50 technical papers to his credit published in national and international journals, presented at seminars and conferences, six technical reports and two patents.