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Synthesis, Characterization and Electrical Conductivity Studies on Poly (2-Chloroaniline-Co-2-Methoxyaniline)- Fe_2O_3 Nanocomposites with Varying Weight Percentages of Fe_2O_3

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Abstract
Poly (2-chloroaniline–co-2-methoxy aniline)/Fe_2O_3 nano composites with various weight percentages of Fe_2O_3 (5%, 10%, 15%, 20%, and 25%) were prepared by mechanical blending of the copolymer which was synthesized by *in situ* chemical oxidative method with γ- ferric oxide nano particles, characterized and the electrical conductivities measured. The formation of the composites was confirmed by FTIR, UV-Visible spectroscopy, TGA, DSC and XRD. The electrical conductivities of the nano composites were of the semiconducting range (10^{-4} S/cm). The copolymer and the nanocomposite (5% by wt) were subjected to antibacterial and antifungal studies. The composite exhibits significant antibacterial activity and antifungal activity.

Keywords
copolymer, nanocomposite, semiconducting, antibacterial, antifungal.

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INTRODUCTION
Conducting polymers have become very popular in the field of material science due to their promising and novel electrical properties such as energy storage devices [1-3], gas sensors [4-6], EMI shielding [7-10], electrostatic charge dissipation [11-13], OLED and flexible display devices [14-18], anticorrosive materials [19-22], electrochromic materials [23-25] and electronic conducting fabrics [26]. The composite materials based on electrically conductive polymers have attracted the attention of many investigators for the development of new functional materials [27-30]. Among the ring substituted PANI derivatives, poly(2-chloroaniline) and poly(2-methoxyaniline) have been materials of interest in the recent past. With regard to polyaniline-based copolymers which show enhanced solubility, many papers have been published [31-38]. Copolymerization offers a way of improving the processability of PANI. The properties of the poly (substituted anilines) such as toluidine, anisidine, etc. depend on the type of substituents, whether electron withdrawing or electron donating groups and the presence of less affecting groups like alkyl groups. Electron withdrawing groups decrease the electron density in aniline, electron donating groups increase the electron density in the phenyl ring, whereas alkyl group may not affect the electron density much in aniline, only some mild positive inductive effect may increase the electron density [39]. There are few reports on the synthesis of copolymers of 2- chloroaniline and 2-methoxy aniline and their applications. Among the magnetic nanomaterials, iron oxides (Fe_2O_3 and Fe_3O_4) have been extensively investigated because of their excellent magnetic properties and biocompatibility. Due to the biocompatible nature of the iron oxide nano particles, it was chosen as the host material for the synthesis of the copolymer composites.

EXPERIMENTAL

Chemicals and Reagents

2-chloroaniline (Avra), 2-methoxyaniline (LOBA), ammonium per sulphate (SDFCL, 98% pure) and HCl were of analytical grade and used as received. γ-Fe_2O_3 nanoparticles of particle size 20-50 nm (99.9%) was purchased from SRL.

In situ Chemical oxidative polymerization of the copolymer and the composites

The poly(2-chloroaniline-co-2-methoxyaniline) was synthesized by in situ chemical oxidative polymerization technique as modified and reported in our earlier work [40]. The nanocomposites with varying weight percentages (5%, 10%, 15%, 20%, 25%) were prepared by mechanical grinding of the copolymer with ferric oxide nano particles on a morter and pestle for thirty minutes. The nanocomposites were insoluble in water, partially soluble in methanol and soluble in DMSO, DMF, chloroform and toluene.

RESULTS AND DISCUSSION

FTIR spectroscopy

The FTIR spectra of poly(2-chloroaniline-co-2-methoxy aniline) (Poly(OCA)-co-OMA) and poly(2-chloroaniline-co -2-methoxy aniline)/ Fe_2O_3 (Poly(OCA)-co-OMA)/ Fe_2O_3) are shown in Figure 1 and Figure 2 respectively. In the IR spectra of Poly (OCA)-co-OMA)/ Fe_2O_3 (5%), the N–H stretching frequency is observed at 3214 cm^{-1}. This frequency is shifted to higher wave numbers in the case of 10% and 15% copolymeric composites. The asymmetric and symmetric stretching frequencies of –CH present in methoxy groups are observed at 2937 cm^{-1} and 2839 cm^{-1}. The characteristic intense peaks due to the -C=C- ring stretching vibrations of the quinonoid and benzenoid rings occur at 1581 cm^{-1} and 1508 cm^{-1} respectively. The peak at 1293 cm^{-1} is due to aromatic C–N stretching vibration. The peak at 834 cm^{-1} is attributed to the para coupled phenyl rings in the copolymer chain. The peak at 1126 cm^{-1} confirms the charge delocalization due to the presence of charged structure and hence confirmed the emeraldine salt structure. The peak at 747 cm^{-1} corresponds to the chloro group attached to the phenyl ring. The Fe-O stretching is observed around 587 cm^{-1}. The above peaks confirm the formation of the composite and suggest a van der Waals kind of interaction between the polymeric chain and Fe_2O_3 nanoparticles. The same results were found in the polymer composites with 10%, 15%, 20%, and 25% of Fe_2O_3 which confirm the formation of poly (2-chloroaniline-co-2-methoxy aniline)/ Fe_2O_3 composites.

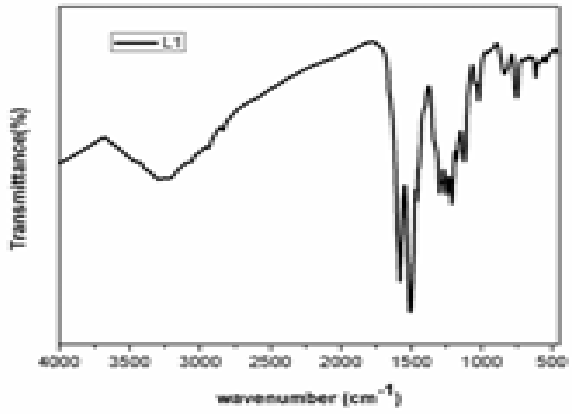

Fig.1. IR spectrum of the copolymer

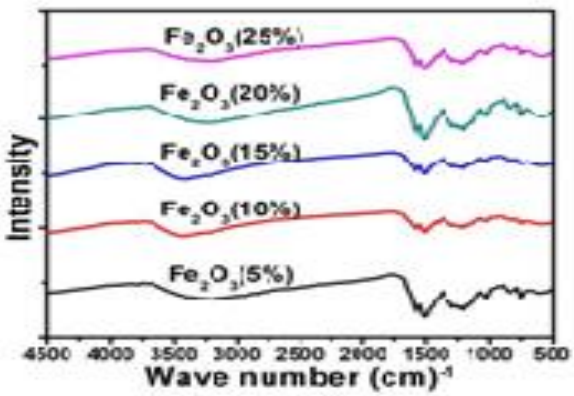

Fig.2. IR spectra of the nanocomposites

UV Visible spectroscopy

The UV-Visible spectra of Poly (OCA)-co-OMA)/ Fe_2O_3 dissolved in DMSO are shown in Figure 3. The absorption band at 208 nm is due to π-π* transition of the benzenoid and quinonoid rings [41]. The band at 303 nm is due to n-π* transitions. The band at 551 nm is due to the electron transition between the highest occupied molecular orbital of the benzenoid ring to the lowest unoccupied molecular orbital of the quinonoid ring. The slight red shift observed in the π-π* transition and the polaron transition in the composites of varying composition and the broadening of the n-π* bands are attributed to the increase in the weight % of Fe_2O_3 embedded into the polymer chains. This type of interaction may be due to the hydrogen bonding (N–H- - - -O) between the polymer chains and Fe_2O_3 particles.

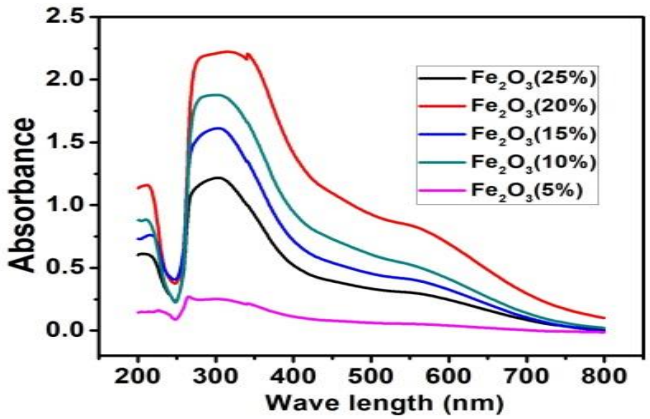

Fig.3. UV –Visible spectra of the composites

X-Ray diffraction studies.

The XRD of poly (OMA-co-OCA) and poly (OMA-co-OCA / Fe_2O_3 composites are given in Figure 4 and Figure 5, respectively. The nanocomposites are found to be partially crystalline in nature. The crystallinity of the pure polymer is increased due to the composite formation.

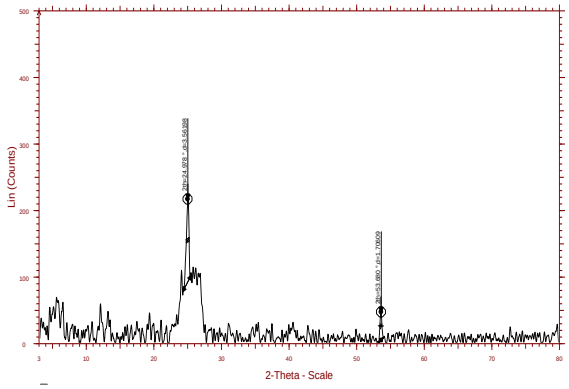

Fig.4. XRD pattern of the copolymer

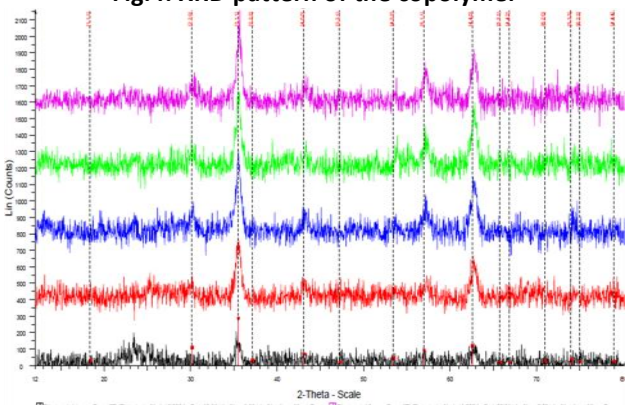

Fig.5. XRD patterns of the copolymer composites

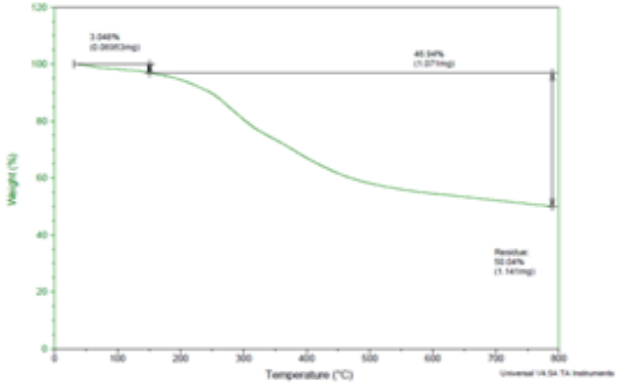

Fig.6. TGA of the copolymer composite (5%)

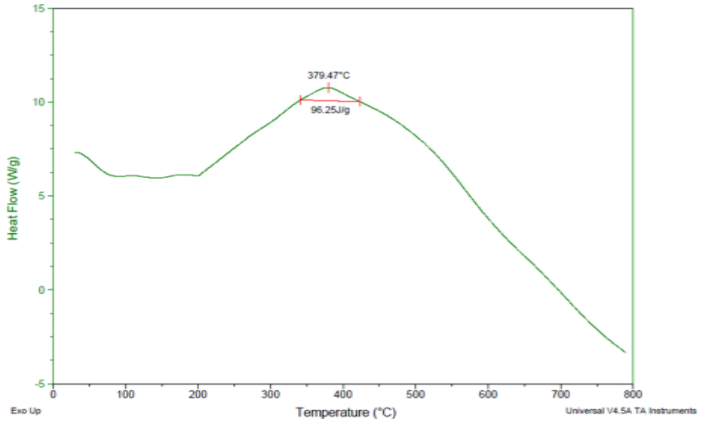

Fig.7. DSC of the copolymer composite

TGA/DSC

The TGA and DSC of poly (OMA-co-OCA / Fe_2O_3 (5%) are shown in Figure 6 and Figure 7, respectively. The polymer composite undergoes weight loss in three steps. The weight loss around 100 ℃ is due to the loss of volatile impurities and moisture. The loss of the dopant take place at 300℃ and the decomposition of the copolymer composite takes place around 400℃. 50.04% residue is left behind due to the presence of iron oxide nano particles. The DSC shows a broad exothermic melting at 379°C.

Electrical Conductivity Studies

The electrical conductivity values are tabulated in Table 1. The poly (OMA-co-OCA / Fe_2O_3 nano composites exhibit electrical conductivity in the order of 10^{-4} S/cm which is in the semiconducting range. The electrical conductivity of the copolymer reported in our earlier work is 2.57×10^{-5} S/cm and the incorporation of ferric oxide nano particles has significantly improved the electrical conductivity.

Antibacterial activity of the copolymer and its composite (5% by wt)

The antibacterial properties of the composites were evaluated against three Gram negative bacteria, *Pseudomonas aeruginosa, Staphylococcus aureus* and *Shigella* using agar well diffusion method. The zone of inhibition with the concentration 1000 µg per well is as shown in Plates 1. The data of the zones of inhibition is depicted in Table 2.

The poly (OMA-co-OCA / Fe_2O_3 shows good inhibition for the bacteria *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Shigella*.

Antifungal activity of the copolymer and its composite (5% by wt)

The antifungal activities of the composite and pure ferric oxide nano particles were also studied against *Aspergillus flavus, Aspergillus niger, Mucor and Aspergillus fumigates*.

The composite as well as the ferric oxide nano particles exhibit antifungal activity against *Aspergillus flavus, Aspergillus niger, Mucorand Aspergillus fumigates*as shown in Table 3 and Plate 2. It is inactive against Mucor.

Plate 1: Antibacterial activity of copolymer and copolymer composite: L_2 – Copolymer; L_7- Copolymer composite

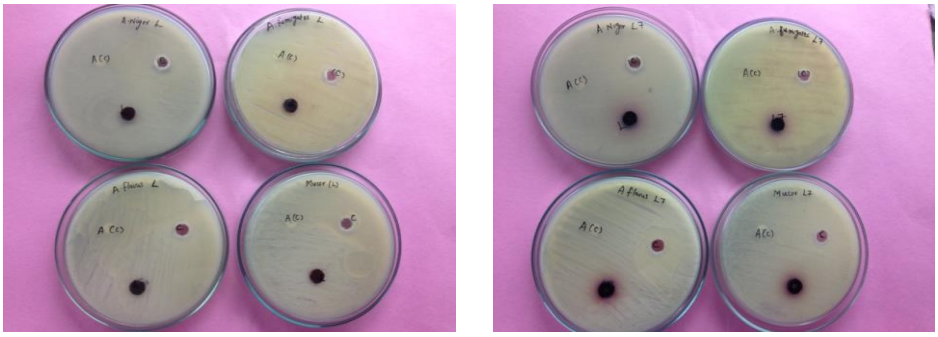

Plate 2: Antifungal activity of copolymer and copolymer composite: L_2 – Copolymer; L_7- Copolymer composite

Table 1: The electrical conductivity values of the copolymer composites

Fe_2O_3 (weight %)	Area (cm^2)	Thickness (cm)	Bulk Resistance (S)	Conductivity (S/cm)
5	1	0.005	47.7	1.04×10^{-4}
10	1	0.005	51.5	0.97×10^{-4}
15	1	0.005	39.6	1.26×10^{-4}
20	1	0.005	30.5	1.63×10^{-4}
25	1	0.005	34.6	1.44×10^{-4}

Table 2 Zone of inhibition (mm)

Bacteria	Copolymer	Copolymer composite	Control
Code No	L_2	L_7	C
Pseudomonas aeruginosa	_	14	13
Staphylococcus aureus	_	12	12
Shigella	_	13	12

Table 3 Zone of Inhibition (mm)

	Copolymer	Copolymer composite	Control
Code No	L_2	L_7	C
Aspergillus flavus	1.6	1.7	1.2
Aspergillus niger	2	2.3	1.6
Aspergillus fumigates	2.1	2	0.9

CONCLUSION

Poly (OMA-co-OCA / Fe_2O_3 composites were prepared and characterized. The IR spectra with shifts in the wavelength of N-H stretching in the composites confirm that there is interaction between the copolymer and Fe_2O_3 nanoparticles. The broadening of the peaks was also observed in the UV-Visible spectra, indicating that the absorption bands of the copolymer were influenced by Fe_2O_3 nanoparticles present in the polymer chain. The crystallinity was increased as shown by XRD. The composite melts at 379°C. The poly(OMA-co-OCA / Fe_2O_3 nano composites show electrical conductivity in the order of 10^{-4} S/cm. The copolymer does not

exhibit antibacterial activity but shows antifungal activity whereas the nanocomposite shows both good antibacterial and antifungal activities.

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