



Synthesis, Characterization and Electrical Conductivity Studies on Poly (2-Chloroaniline-Co-2-Methoxyaniline)- Fe₂O₃ Nanocomposites with Varying Weight Percentages of Fe₂O₃

P. Lakshmi^a, G.Vania^a, Julia Sebastian^a and S. Jhancy Mary^{b*}

^a Research Scholars, Auxilium College, Vellore-632006, Tamilnadu, India

^bAsso. Prof. of Chemistry, Auxilium College, Vellore-632006, Tamilnadu, India

Received: 12 Oct 2020 / Accepted: 6 Nov 2020/ Published online: 01 Jan 2021

*Corresponding Author Email: jhancy2011@gmail.com

Abstract

Poly (2-chloroaniline-co-2-methoxy aniline)/Fe₂O₃ nano composites with various weight percentages of Fe₂O₃ (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.

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 (Fe₂O₃ and Fe₃O₄) 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 mortar 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.

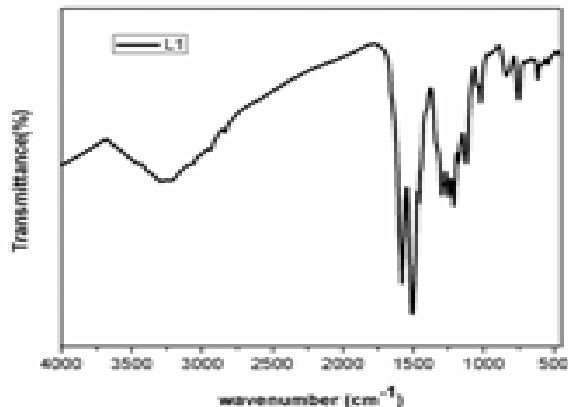


Fig.1. IR spectrum of the copolymer

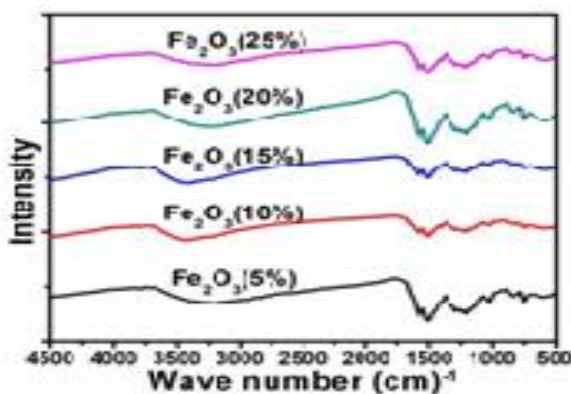


Fig.2. IR spectra of the nanocomposites

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 $\pi-\pi^*$ transition of the benzenoid and quinonoid rings [41]. The band at 303 nm is due to $n-\pi^*$ 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 $\pi-\pi^*$ transition and the polaron transition in the composites of varying composition and the broadening of the $n-\pi^*$ 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.

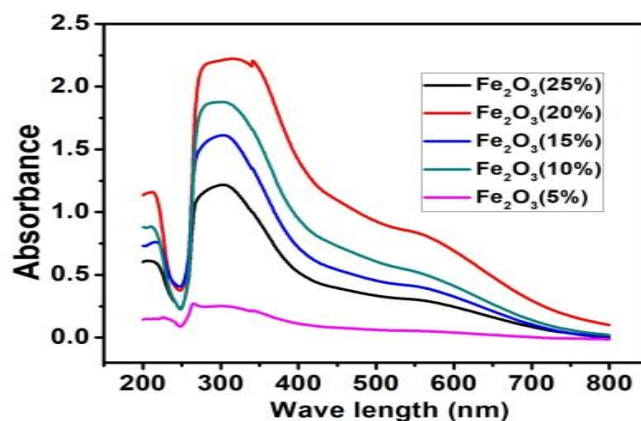


Fig.3. UV –Visible spectra of the composites

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.

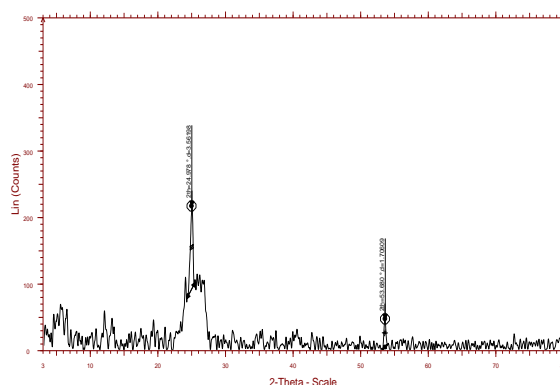


Fig.4. XRD pattern of the copolymer

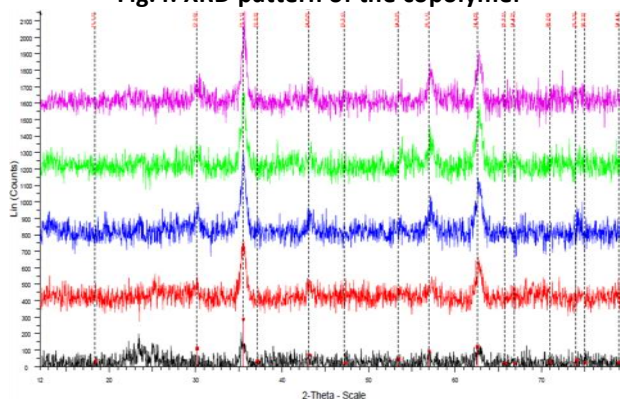


Fig.5. XRD patterns of the copolymer composites

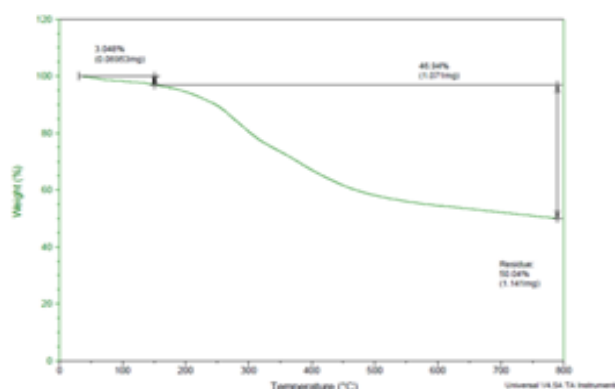


Fig.6. TGA of the copolymer composite (5%)

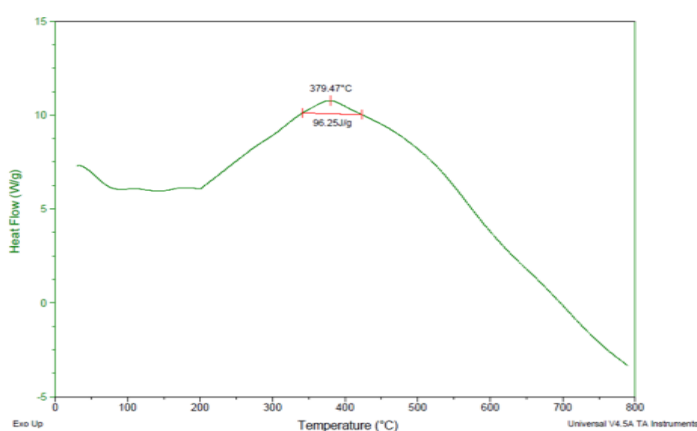


Fig.7. DSC of the copolymer composite

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 °C is due to the loss of volatile impurities and moisture. The loss of the dopant take place at 300°C and the decomposition of the copolymer composite takes place around 400°C. 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*, *Mucor* and *Aspergillus fumigates* as shown in Table 3 and Plate 2. It is inactive against *Mucor*.



Plate 1: Antibacterial activity of copolymer and copolymer composite: L₂ – Copolymer; L₇- Copolymer composite

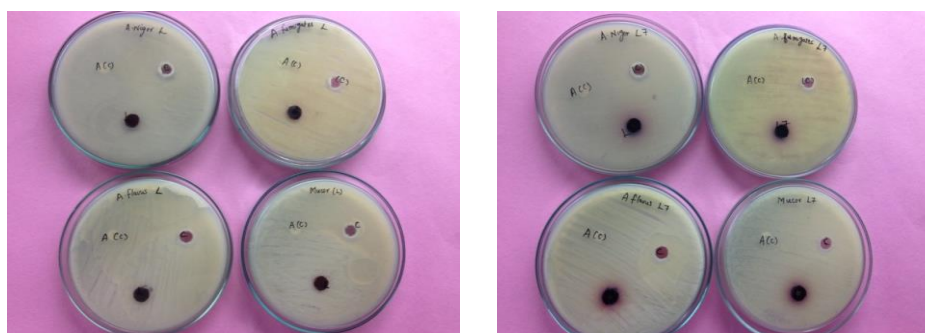


Plate 2: Antifungal activity of copolymer and copolymer composite: L₂ – Copolymer; L₇- Copolymer composite

Table 1: The electrical conductivity values of the copolymer composites

Fe ₂ O ₃ (weight %)	Area (cm ²)	Thickness (cm)	Bulk Resistance (S)	Conductivity (S/cm)
5	1	0.005	47.7	1.04 X 10 ⁻⁴
10	1	0.005	51.5	0.97 X 10 ⁻⁴
15	1	0.005	39.6	1.26 X 10 ⁻⁴
20	1	0.005	30.5	1.63 X 10 ⁻⁴
25	1	0.005	34.6	1.44 X 10 ⁻⁴

Table 2 Zone of inhibition (mm)

Bacteria	Copolymer	Copolymer composite	Control
Code No	L ₂	L ₇	C
<i>Pseudomonas aeruginosa</i>	—	14	13
<i>Staphylococcus aureus</i>	—	12	12
<i>Shigella</i>	—	13	12

Table 3 Zone of Inhibition (mm)

	Copolymer	Copolymer composite	Control
Code No	L ₂	L ₇	C
<i>Aspergillus flavus</i>	1.6	1.7	1.2
<i>Aspergillus niger</i>	2	2.3	1.6
<i>Aspergillus fumigates</i>	2.1	2	0.9

CONCLUSION

Poly (OMA-co-OCA / Fe₂O₃ 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 Fe₂O₃ 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 Fe₂O₃ 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 / Fe₂O₃ 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.

REFERENCES

- G. Kumar, A. Sivashanmugam, N. Muniyandi, S.K. Dhawan and D.C. Trivedi., Polyaniline as an electrode material for magnesium reserve battery. *Synth. Met*, 80., 279 -282 (1996).
- M.K. Song, I.J. Won and H.W. Rhee., Flexible Polymer Battery with Conducting Polymer as a Cathode. *Mol. Cryst. Liq. Cryst*, 316- 337 (1998).
- M. Kurian, M.E. Galvin, P.E. Trapa, D.R. Sadoway and A.M. Mayes., Single-ion conducting polymer-silicate nanocomposite electrolytes for lithium battery application. *Electrochim. Acta*, 50., 2125-2134 (2005).
- S. Koul, R. Chandra and S.K. Dhawan., Conducting polyaniline composite: a reusable sensor material for aqueous ammonia. *Sens Actuators B*, 75., 151-159 (2001).
- X.B. Yan, Z.J. Han, Y. Yang and B.K. Tay., NO₂ gas sensing with polyaniline nanofibers synthesized by a facile aqueous/organic interfacial polymerization. *Sens Actuators B*, 123., 107- 113 (2007).
- C.P. de Melo, B.B. Neto, E.G. de Lima, L. F.B. de Lira and J.E.G. de Souza., Use of conducting polypyrrole blend as gas sensors. *Sens Actuators B*, 109., 348-354 (2005).
- S.K. Dhawan, N. Singh and D. Rodrigues., Electromagnetic shielding behaviour of conducting polyaniline composites. *J. Sci. Technol. Adv. Mater*, 4., 105-113(2003).
- N. F. Colaneri and L.W.IEEE. Shacklette., EMI Shielding measurements of conductive polymer blends. *Trans. Instrum. Meas*, 41., 291-297(1992).
- N.C. Das, D. Khastgir and T.K. Chaki., Electromagnetic Interference Shielding Effectiveness of Hybrid Conductive Polymer Composite. *J.Elastomers. Plast*, 34., 199-223(2002).
- Y. Wang and X. Jing, Polym., Intrinsically conducting polymers for electromagnetic interference shielding. *Adv. Technol*, 16.,344-351(2005).
- Wycisk, R.Pozniak and A.Pastemak., Conductive polymer materials with low filler content. *J. Electrostatics*, 56.,1, 55-66(2002).
- S. Koul, R. Chandra and S.K. Dhawan., Conducting polyaniline composite for ESD and EMI at 101 GHz. *Polymer*, 41.,26, 9305- 9310 (2000).
- L. Kumar, S.K. Dhawan, M.N. Kamalasannan, S.Chandra and L.Kumar., Bright-orange organic light emitting diodes fabricated using benzene-naphthalene co-polymer. *Thin Solid Films*, 441., 243 (2003).
- S.R. Forrest., The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature*, 428, 911 (2004).
- W.H. Kim, A.J. Makinen, N. Nikolov, R. Shashidlar, H.Kim and Z.H. Kafafi., Molecular organic light-emitting diodes using highly conducting polymers as anodes. *Appl. Phys. Lett*, 80., 3844(2002).
- S.Tokito, M. Suzuki and F. Sato., Improvement of emission efficiency in polymer light-emitting devices based on phosphorescent polymers. *Thin Solid Films*, 445., 353-357(2003).
- S.C. Jain, T. Aernout, A.K. Kapoor, V. Kumar, W. Greens, J. Poortmans and R. Mertens., I-V characteristics of dark and illuminated PPV-PCBM blends solar cells. *Synth Met*, 148.,245-250(2005).
- H. Etti, X. L. Jin, T. Yosudha, S.Mataka and T. Tsutsui, Spirobifluorene derivatives for ultraviolet organic light-emitting diodes. *Synth. Met*, 156., 1090-1096(2006).
- C.K. Tan and D.J. Blackwood., *Corrosion* protection by multilayered conducting polymer coatings. *J.Corros Sci*, 45(3), 545-547(2003).
- S.Sathyanarayanan, K. Balakrishnan and S.K. Trivedi., Prevention of corrosion of iron in acidic media using poly (o-methoxy-aniline). *Electrochim. Acta*, 39., 831(1994).
- J. E. P. Da Silva, S. I. C. de Torresi, R. M. Torresi., Polyaniline acrylic coatings for corrosion inhibition: the role played by counter-ions. *Corros. Sci*, 47., 811(2005).
- N. Plesu, G. L. lia, A.Pascraiu and G.Vlase., Preparation, degradation of polyaniline doped with organic phosphorus acids and corrosion essays of polyaniline-acrylic blends. *Synth. Met*, 156., 230 (2006).
- E. Sahin, P.Camurlu and L.Toppare, Dual-type electrochromic devices based on both n- and p-dopable poly(dithieno[3,4-b,3',4'-e]-[1,4]-dithiine). *Synth Met*, 156., 1073(2006).
- W.A. Gazotti, G. Casalbore-Miceli, S. Mitzakoff, A. Geri, M.C. Gallazzi and M.A. de Paoli., Conductive polymer blends as electrochromic materials. *Electrochim Acta*, 44., 1965 (1999).
- J.C. Gustafson, O. Inganaes, A.M.Andersson., Conductive Polymers as Electrochromic Materials in Solid State Electrochromic Devices. *Proc SPIE-Int.Soc. Opt.Eng*. 42.,1728(1992).
- S.K. Dhawan, N. Singh and S. Venkatachalam., Shielding behaviour of conducting polymer-coated fabrics in X-band, W-band and radio frequency range. *Synth. Met*, 129.,3,261-267(2002).
- L.F. Chen, C.K. Ong, C.P.Neo, V.V. Varadan and V.K. Varadan, *Microwave Electronics: Measurement and Materials Characterization*. Microwave electronics, England: John Wiley & Sons, (2004).
- P. Dutta, S.Biswas, S. Ghosh, S.K. De, and S. Chatterjee S., The dc and ac conductivity of polyaniline-polyvinyl alcohol blends. *Synth. Met*, 22., 455(2001).
- R. Gangopadhyay, A. De, and G. Ghosh., Polyaniline-poly(vinyl alcohol) conducting composite: material with easy processability and novel application potential. *Synth. Met*, 123., 529 (2001).
- A.A. Saad, W. Khan, P. Dhiman, and A.H. Naqvi., Structural, optical and magnetic properties of perovskite (La_{1-x}Sr_x)(Fe_{1-x}Ni_x)O₃, (x = 0.0, 0.1 & 0.2) nanoparticles. *Electronic Materials Letters*, 9., 77(2013).

31. Ritu Saharan, Amarjeet kaur & K.Sundeeep and Dhawan., Synthesis and characterization of poly(*o*-methoxy aniline) and its copolymer for electrochromic device energy applications. *Indian Journal of Pure & Applied Physics*, 53., 316-319 (2015).
32. Arunachalam Mahudeswaran, Devarajan Manoharan, Joseph chandrasekaran, Janakiramam Vivekanandar and Pachanoor subbian vijayanand., CSA Doped Poly(aniline-co-*o*-toluidine) and Dispersed Zinc Oxide Nanoparticles: a Promising Material for Photovoltaics. *Materials Research*, 18(3), 482-488 (2015).
33. A.D. Borkar., Effect of copolymer composition on solubility and electrical conductivity of poly(aniline-co-*o*-chloroaniline). *J. of Chem.and Pharm. Res*, 4(7), 3526-3528(2012).
34. Omar Melad, Hussein Alhendai and Mohammed Fayaad., The Influence of organic solvents on the polymerization of polyaniline. *Research and reviews: J. of Mat. Sci.*, 2., 3(2014).
35. A. Kuestan and Ibrahim., Synthesis and characterization of polyaniline and poly(aniline-co-*o*-nitroaniline) using vibrational spectroscopy. *Arab. J. of Chem*, 10., 2668-2674(2013).
36. R. Marija, Gizdavic-Nikolaidis. D. Zoran, Zujovic, Sudip Ray, J.Allan, Easteal, A.Graham and Bowmaker., Chemical synthesis and characterization of poly(aniline-co-ethyl 3-aminobenzoate) copolymers. *J. of Polym. Sci*, 48., 1339-1347(2010).
37. Bidhan C Roy, Maya Dutta Gupta, Leena Bhowmik and Jayanta K Ray., Synthesis and characterization of poly(2,5-dimethoxyaniline) and poly(aniline-Co-2,5-dimethoxyaniline): The processable conducting polymers. *Bull. Mater. Sci*, 24., 4, 389-396(2001).
38. G. Devi, L. Porselvi and S. Jhancy Mary., DC-AC conductivity behaviors of Poly (2-methoxy aniline-co-2-chloro aniline) and Poly (2-methoxy aniline-co-2-chloro aniline)-composite-clay. *Journal of Applied Chemical Science International*, 6(3), 119-131(2016).
39. P.K. Upadhyay and A. Ahmad., Synthesis, Characterization and Conductivity Study of Poly (*o*/*m*-toluidine-co-*o*/*m*-nitroaniline). *Analytical & Bioanalytical Electrochemistry*, 2(3), 139(2010).
40. P. Lakshmi and S.Jhancy Mary., A Comparative Study on the Electrical And Thermal Properties of The Chemically Synthesized Copolymer, Poly(2-Methoxyaniline-Co-2-Chloroaniline) And Its Nanocomposite, Poly(2-Methoxyaniline-Co-2-Chloroaniline) –Composite- Fe₂O₃. *ISOR Journal of Pharmacy*, 17-23(2017).
41. A.G. Mac Diarmid, J.M Ginder, and A.J. Epstein., Optical Studies of Polyanilines: Effects of Alkyl Ring-Substitution and Solvent Environment. *Proc. Mat. Res. Soc*, 173., 353(1990).