International Journal of Pharmacy and Biological Sciences
ISSN: 2321-3272 (Print), ISSN: 2230-7605 (Online)
IJPBS | Volume 9 | Special Issue 2 | 2019 | 208-215
| Research Article | Biological Sciences |Open Access |MCI Approved|
|UGC Approved Journal|

Synthesis, Characterization and Electrical Conductivity Studies on Poly (2-Chloroaniline-Co-2-Methoxyaniline)-Composite-Na Bentonite Clay

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Received: 29 Jan 2019 / Accepted: 25 Feb 2019 / Published online: 01 Apr 2019
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Abstract
The poly(2-chloroaniline-co-2-methoxyaniline)/Na-Bentonite nanocomposite was prepared by *in situ* chemical oxidative polymerization method using ammonium persulphate (oxidant), HCl (dopant) and sodium lauryl sulphate(surfactant). The material was characterized with FTIR and UV-Visible spectroscopic techniques, TGA/DTA analysis and conductivity measurements. The crystallinity of the copolymer composite was reduced when compared to pure copolymer. The conductivity of the copolymer composite was 2.305 x 10^{-6} S/cm and it was greater than the conductivity of the pure copolymer. The electrical conductivity measurements have been discussed in detail using dielectric constant, dielectric loss spectra, modulus spectra and tangent loss spectra.

Keywords
copolymerization, electrical conductivity, Na- Bentonite, poly(2-chloroaniline-co-2-methoxyaniline), dielectric constant.

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INTRODUCTION:

Conducting polymers are named as “synthetic metals” due to their electric, electronic, magnetic and optical properties inherent to metals or semiconductors. [1-3] The conductivity of conducting polymers assigned to the delocalization of π- bonded electrons over the polymeric backbone, show electronic properties, such as low ionization potentials and high electron affinities.[4,5] Use of conducting polymers gives us impedence type gas sensors[6,7] for low cost, which are highly sensitive and selective at room temperature.[8] Recently, conducting polymer nano materials have offered a great possibility for novel applications.[9-13] Polymer based composites with electroconductive properties have been used in numerous high technology applications such as inorganic light emitting diodes (OLED), polymer solar cells, sensors, energy storage, electro-optical devices wireless communication, satellite television, heating systems and electromagnetic shielding [14-16]. Among organic-inorganic nano composites, polymer-clay nano composites are most prevalent and interesting due to their unique properties as well as wide applications, abundance, low cost and attractive features such as large surface area and ion-exchange properties. [17]

This paper focuses on the chemical synthesis and characterization of poly (2- chloroaniline-co-2-methoxyaniline)/Na-Bentonite nanocomposite in the presence of sodium lauryl sulphate (SDS), by in *situ* chemical oxidative polymerization technique.

MATERIALS AND METHODS:

2-chloroaniline (Avra), 2-methoxyaniline (LOBA), ammonium per sulphate (SDFCL, 98% pure) and HCl were of analytical grade and used as received. Nano clay was purchased from Sigma Aldrich. The experimental techniques used in the characterization of the synthesized copolymer composite were FTIR spectroscopy, UV- Visible spectroscopy and XRD. The thermal stability of the copolymer composite was studied using TGA/DTA/DSC. The impedance measurement was used to calculate the electrical conductivity of the copolymer composite.

Chemical synthesis of poly(2-chloroaniline-co-2-methoxyaniline)/Na-bentonite nano composite:

2-chloroaniline (1ml,0.1 mol), 2-methoxy aniline (1ml, 0.1 mol), SDS (0.72 g in 50ml, 0.1 M) and 0.05 g nano clay (5% by weight) were stirred in a glass beaker maintained in the freezing mixture bath to obtain a suspension. HCl (1M,50ml) and ammonium per sulphate (5.7g,0.2 mol in 50ml) were added dropwise with constant stirring over a period of four hours. It was kept at 0°C overnight, filtered, washed with deionized water and finally with acetone to remove the oligomers. The product was again transferred and suspended in deionized water and stirred for an hour on a magnetic stirrer and filtered. The washing of the product was continued till the filtrate was free of acid, dried in air and powdered. 1.7464 g of the copolymer composite, poly (OMA-co-OCA)/ Na-bentonite was obtained. It was soluble in DMSO, DMF, Acetone, Methanol and $CHCl_3$.

RESULTS:

FT-IR spectroscopy:

The FTIR spectrum of poly (OCA-co-OMA)/ Na-bentonite (Fig 1) confirms the appearance of characteristic stretching frequencies which are tabulated in Table 1.

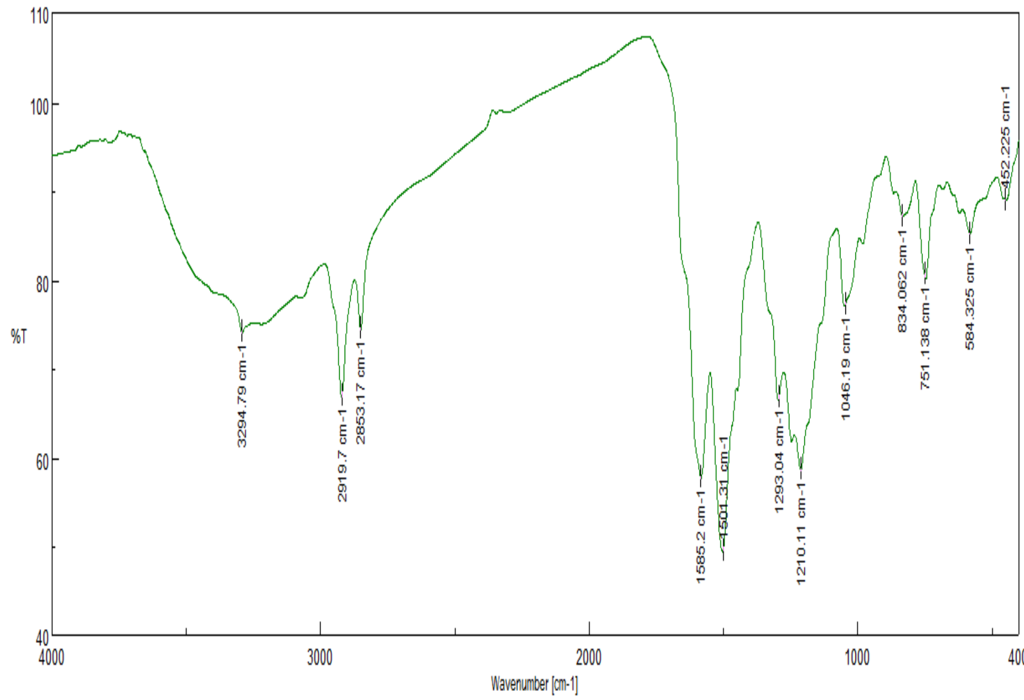

Figure 1: FTIR spectrum of poly (OCA-co-OMA)/ Na-bentonite.

Table 1: Assignments of the frequencies in the IR spectrum of poly (OMA-co-OCA)/ Na-bentonite

Vibrational assignments	Poly (OCA-co-OMA)/*Na- bentonite* (cm^{-1})
N-H stretching	3294
-C=C- stretching of Quinonoid	1585
-C=C- stretching of Benzenoid	1501
C-H asymmetric &symmetric stretching	2919 & 2853
1,2,4 trisubstituted benzene rings	834
C-Cl stretching	751
C-H stretching of OCH_3	1018
C-N stretching	1293
Na Bentonite stretching in the composite	1046

The N-H stretching frequency occurs at 3294 cm^{-1}. The asymmetric and symmetric stretching frequency of –CH present in SDS are observed at 2919 cm^{-1} and 2853 cm^{-1}. The characteristic peaks due to quinonoid and benzenoid rings occur at 1585 cm^{-1} and 1501 cm^{-1}.[18] The peak at 1293 cm^{-1} is due to aromatic C-N stretching vibration. The band at 834 cm^{-1} is due to –CH out of plane bending vibration of 1, 2, 4 tri substituted aromatic rings.[19] The characteristic band corresponding to Na-Bentonite is shown at 1046 cm^{-1} for Si-O-Si linkage. The ratio of the intensities of benzenoid and quinonoid peaks and dark green colour suggested that the polymer composite is in emeraldine salt structure.

UV-Visible spectroscopy:

The UV-Visible spectrum (Fig 2) shows absorption bands at 280nm and 315nm due to π-π* transition of benzenoid ring and n-π* transition of quinonoid ring respectively.[20,21] The band around 575 nm is due to quinonoid ring transition between transfer from the highest occupied molecular orbital of the benzenoid ring to the lowest unoccupied molecular orbital of the quinonoid ring.

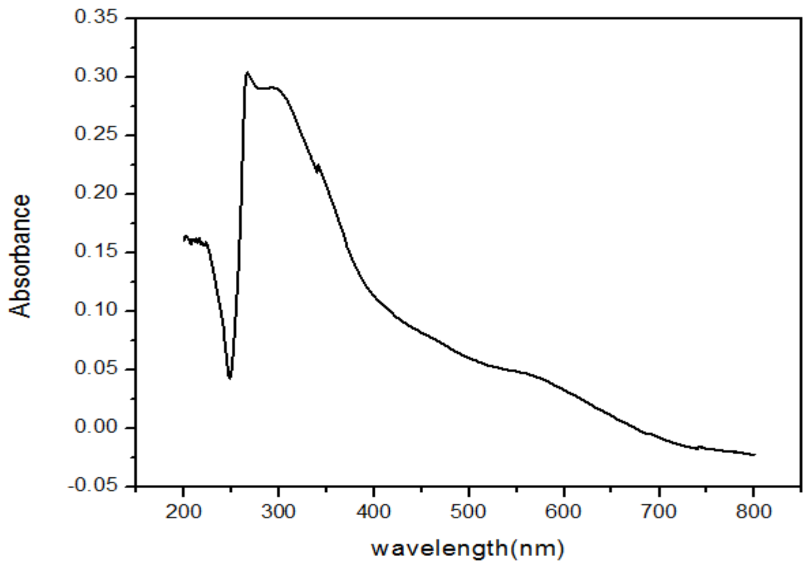

Figure 2: UV-Visible spectrum of poly (OCA-co-OMA)/ Na-bentonite.

Thermo Gravimetric Analysis/ Differential Scanning Colorimetry:

Thermal degradation pattern (Fig 3) shows two step weight loss.

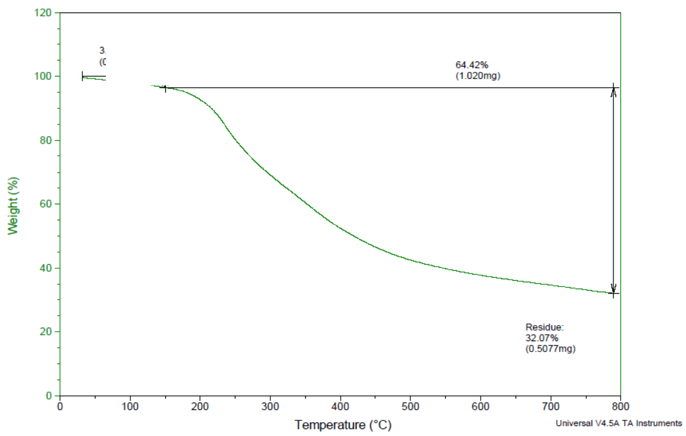

Figure 3:TGA curve of poly (OCA-co-OMA)/ Na-bentonite.

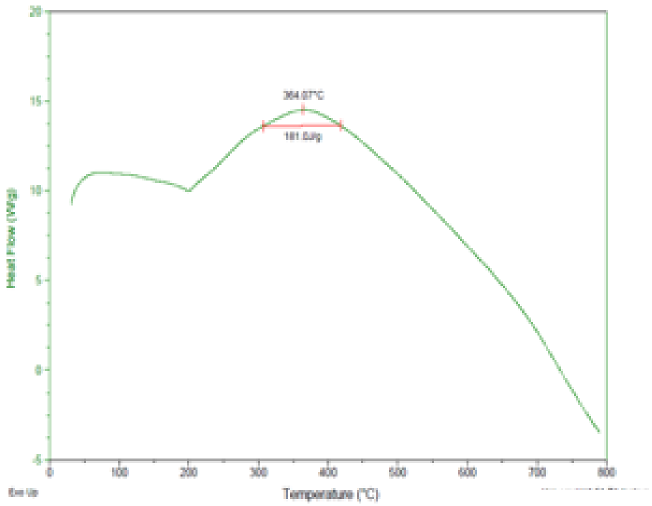

Figure 4: DSC curve of poly (OCA-co-OMA)/ Na-bentonite.

The weight loss around 100 ^{0}C is due to the loss of moisture, second weight loss starts at 200 ^{0}C due to structural decomposition of the copolymer along with the loss of the dopant. The DSC (Fig 4) shows two exothermic peaks around 150 ^{0}C and 364.07 ^{0}C respectively. The melting temperature of the composite is 364.07 ^{0}C.

X-Ray diffraction Studies:

The XRD pattern (Fig 5) exhibits a broad peak at 2θ= 26.85° representing the (1 1 0) reflection of emeraldine salt.[22]

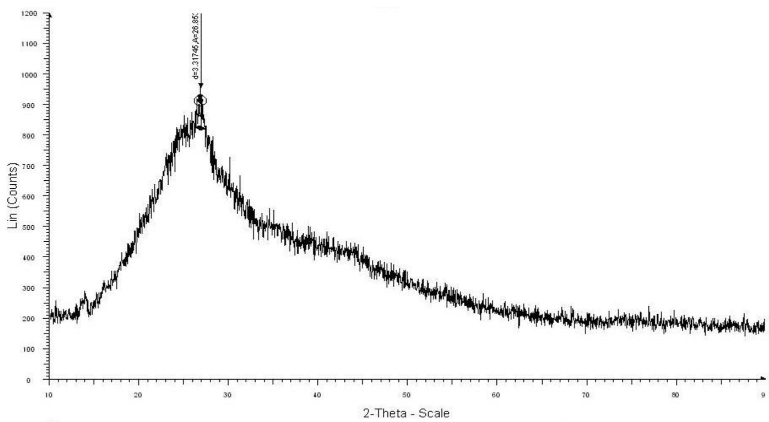

Figure 5: XRD Pattern of poly (OCA-co-OMA)/ Na-bentonite.

Electrical conductivity studies:

The poly (OCA-co-OMA)/ Na-bentonite was finely powdered and pressed into a pellet using IR sample press using model AVATAR-370 Thermo Nicolate with a maximum pressure of 15 tons/cm^2 to form circular pellets of 1.2cm diameter. The thickness of pellet was measured using screw gauge. The measurement was done by placing the pellet between two silver electrodes and the bulk resistance(R) was measured using computational analysis using HPVEE programme. The electrical conductivity was calculated using the formula

$\sigma = t/R_bA$

where t is the thickness of the pellet, A is the area of the cross- section and R_b is bulk resistance of the sample (Fig 6).

The electrical conductivity is 2.355 X 10^{-6} S/cm which is in the semiconducting range.

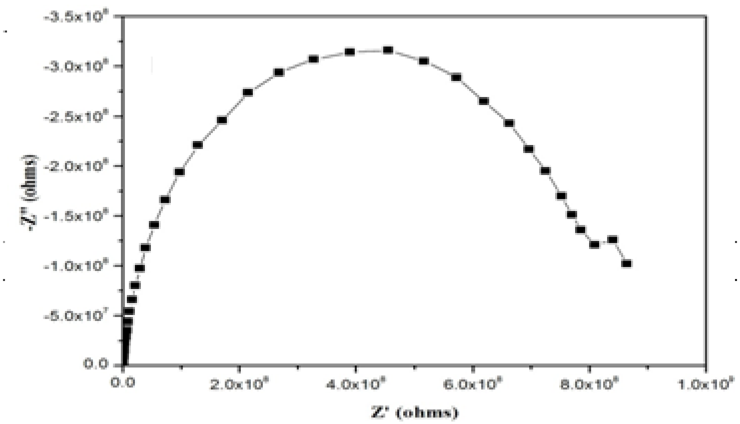

Figure 6: Complex Impedence plot of poly (OCA-co-OMA)/ Na-bentonite.

Dielectric spectra:

The dielectric constant(έ) has been calculated from the measured values of capacitance using the given expression[23].

έ = Cd

ε_0A

where C is the measured capacitance of the sample, d is the thickness of the medium, A is the area of the pellet and ε_0 is the permittivity of free space. The imaginary part (ἔ) of the complex impedence has been measured as

ἔ= έ tanδ

where tanδ is the dissipation factor.

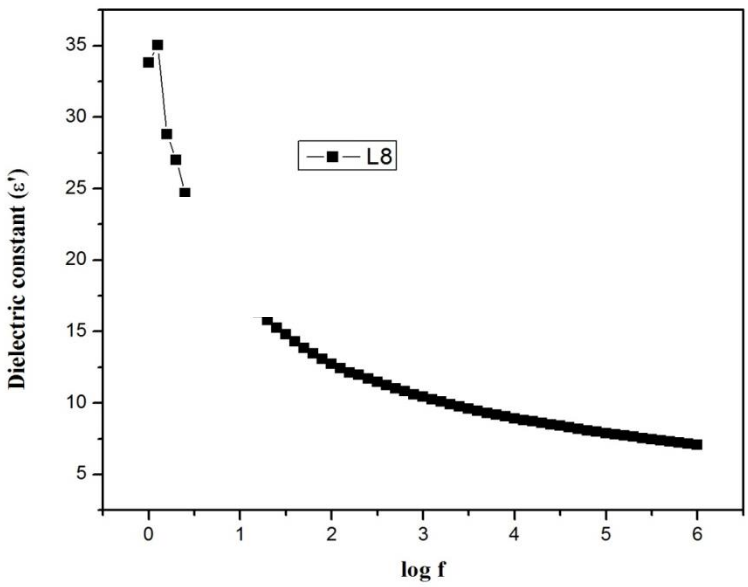

Figure 7: Dielectric constant versus frequency plot of poly (OCA-co-OMA)/ Na-bentonite

It is evident (Fig 7) that the values of dielectric constant is high in the low frequency region due to the contribution of charge accumulation at electrode–electrolyte interface. As the frequency increases the dielectric constant decreases and at higher frequencies the dielectric constant is independent of frequency, because at higher frequencies the charge carriers are unable to orient themselves in the field direction.[24]

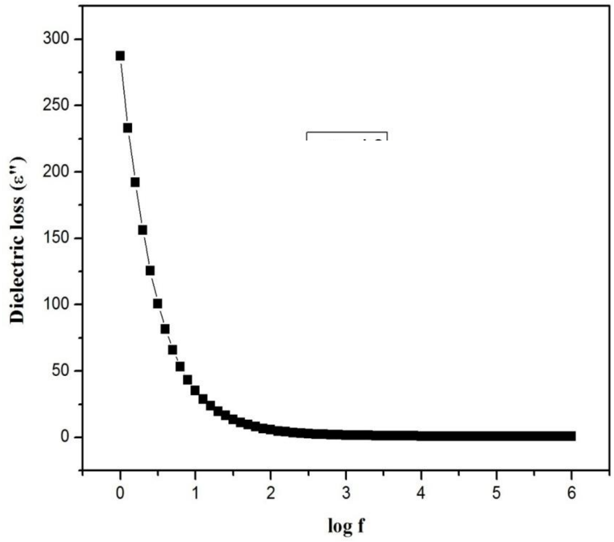

Figure 8: Dielectric loss versus frequency plot of poly (OCA-co-OMA)/ Na-bentonite

The dielectric loss factor used to measure the strength and frequency of relaxation, depends on the characteristic properties of dipolar relaxation. It is observed that the dielectric loss (Fig 8) decreases gradually as a frequency increases due to the migration of ions in the material.[25]

Modulus Spectroscopy:

The real and imaginary part of complex permittivity (Fig 9(a) and Fig 9(b) are used to interpret the bulk dielectric behavior in case of the polymer electrolytes as a function of the frequency. In the Cole-Cole plot, the high value of both real and imaginary part of complex permittivity at the low-frequency window is due to electrode polarization (EP) event. The modulus formalism is used to separate the bulk relaxation phenomena from the ionic relaxation [26].

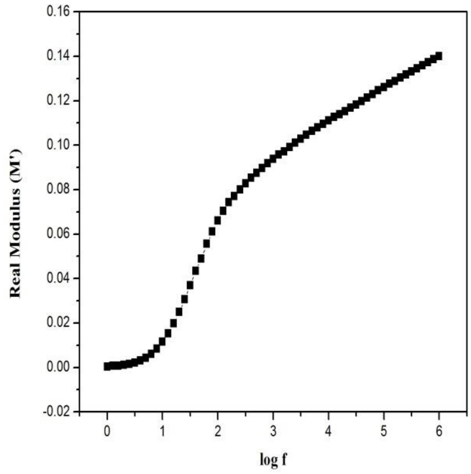

Figure 9(a)

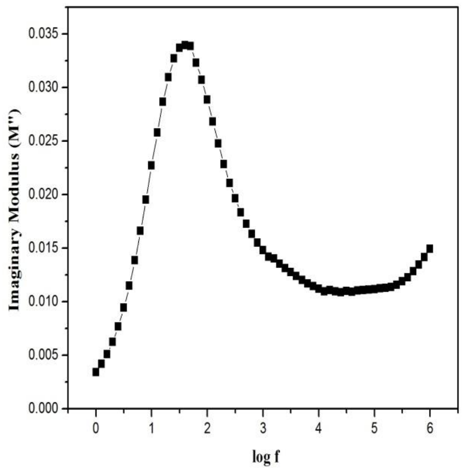

Figure 9(b)

Real and Imaginary part of complex permittivity of poly (OCA-co-OMA)/ Na-bentonite

Dielectric loss tangent

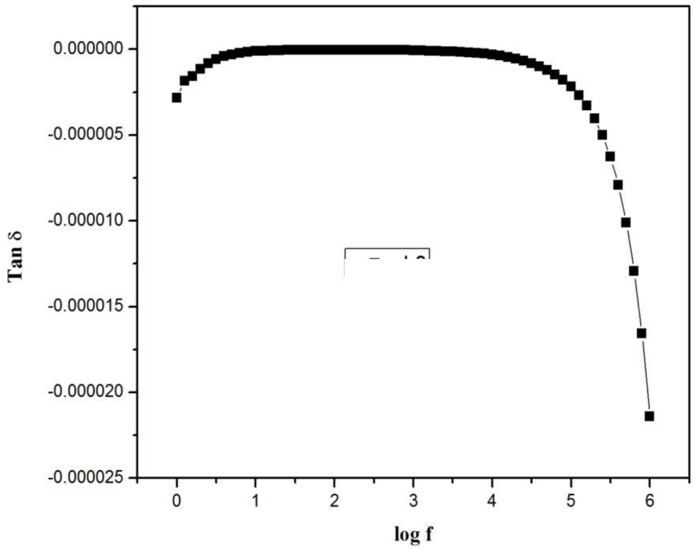

Figure 10: Dielectric loss tangent plot of poly (OCA-co-OMA)/ Na-bentonite

The loss tangent (tan δ) is the ratio of imaginary part of permittivity to the real part of permittivity or ratio of energy loss to energy stored. Initially, it is observed that loss tangent remains constant up to 4.5 Hz (Fig 10) and then decreases at higher frequencies due to dipole polarization.

DISCUSSION:

The IR spectrum shows the stretching frequencies due to –NH, -Cl, $-OCH_3$, quinonoid and benzenoid rings of the copolymer. An additional spectral band seen at 1046 cm^{-1} due to Si-O-Si linkage confirms that there is interaction between poly (2-chloroaniline-co-2-methoxy aniline) chains and the clay chains. The UV-Visible spectrum exhibits the π-π* transition of benzenoid rings and n-π* transition of quinonoid rings that take place in the copolymer nano composite. The XRD of poly(OMA-co-OCA) show peaks around 2θ=24.99° and 53.630° corresponding to the crystalline nature of the emeraldine salt structure of the copolymer which has been reported in our earlier work.[27]The introduction of nano sized clay mineral reflects a reduction in the crystallinity as evident from the XRD pattern of the copolymer composite. Two exothermic peaks in the DSC curve can be observed at 100°C and 364 °C with the enthalpy value of 181 J/g.

The poly(2-chloroaniline)-co-(2-methoxyaniline)/Na-bentonite nano composite shows electrical conductivity of 2.355×10^{-6} Scm^{-1} which is lesser than the conductivity of the copolymer 2.57×10^{-5} Scm^{-1} reported in our earlier work.[27] The dielectric constant and dielectric loss studies indicate the capacitance behavior of the composite.

CONCLUSION:

The poly(2-chloroaniline-co-2-methoxyaniline)/Na-bentonite nano composite was synthesized by *in situ* chemical oxidative polymerization method using ammonium persulphate as oxidizing agent, sodium lauryl sulphate as surfactant and HCl as dopant. The interaction between the copolymer and the clay mineral was confirmed by FTIR. The poly(2-chloroaniline-co-2-methoxyaniline)/Na-bentonite nano composite shows an electrical conductivity of 2.305x 10^{-6} S/cm at room temperature and has capacitance behavior.

REFERENCES

[1] Garcia-Alvanez J.L**.,** A review study of (bio)sensor systems based on conducting polymers Curr. Org. Chem. 12 (14): 1199–1219, (2008)

[2] Yamamoto T., Fukumoto H., Koizumi T., Organometallic Polycondensation for Conjugated Polymers. J. Inorg. Organomet. Polym. Mater. 19 (1): 3–11, (2009)

[3] Luis Garcia-Alvarez J., Synthesis of Conducting Organic Polymeric Materials Mediated by Metals How the Organic Chemists Make Some of the Most Advanced Polymeric Materials. Curr. Org. Chem, 12 (4): 1199–1219, (2008)

[4] Chen C.H., Larue J.C., Nelson R.D., Kulinsky L., M.J. Madou M.J., Electrical conductivity of polymer blends of poly (3,4-ethylene dioxy thiophene) Poly (styrene

sulfonate): N-methyl-2- pyrrolidinone and polyvinyl alcohol. J. Appl. Polym. Sci, 125 (4): 3134–3141, (2012)

[5] Olad A., Ilghami F., Nosrati R., Surfactant-assisted synthesis of polyaniline nanofibres without shaking and stirring: Effect of conditions on morphology and conductivity. Chem. Pap, 66 (8): 757–764, (2012)

[6] Pawar S.G., Chougule M.A., S. Sen S., V.B. Patil V.B., Effect of Camphor Sulfonic Acid Doping on Structural, Morphological, Optical and Electrical Transport Properties on Polyaniline- ZnO Nanocomposites. J. Appl. Polym. Sci, 125 (2): 1418–1424, (2012)

[7] Zan H.W; Li C.H., Yu C.K., Meng H.F., Sensitive gas sensor embedded in a vertical polymer space-charge-limited transistor. Appl. Phys. Lett, 101(2): 023303, (2012)

[8] Pirsa S., Alizadeh N., A selective DMSO gas sensor based on nano structured conducting Poly pyrrole doped with sulphonate ion. Sens. Actuators B Chem, 168: 303–309, (2012)

[9] Jang J., Conducting polymer nano materials and Applications.Adv. Polym. Sci, 199: 189-260, (2006)

[10] Su N., Li H.B., Yuan S.J., Yi S.P.,Yin E.Q., Synthesis and characterization of polypyrrole doped with anionic spherical polyelectrolyte brushes. Express Polym. Lett, 6(9): 697–705, (2012)

[11] Ates M., Karazehir T., Uludag N., Electrolyte effects of poly(3-methylthiohene) via PET/ITO and synthesis of 5-(3,6-di(thiophene-2-yl)-9H-carbazole-9-yl) pentanitrile on electrochemical impedance spectroscopy.J. Appl.Polym.Sci.125(4):3302–3312,(2012)

[12] Simitzis J., Soulis S., Triantou D., Electrochemical synthesis and characterization of conducting copolymers of biphenyl with pyrrole. J.Appl. Polym. Sci. 125 (3): 1928– 1941, (2012).

[13] Tabard-Cossa V., Godin M., Grutter P., Burgess I., Lennox R.B., Redox- induced, surface stress of polypyrrole-based actuators. J. Phys. Chem. B, 109(37): 17531–17537, (2005).

[14] Anil Ohlan., Kuldeep Singh., Bakhshi A.K., Dhawan S.K., Synthesis of conducting ferromagnetic nanocomposite with improved microwave absorption properties. Mater.Chem. Phys, 119: 201–207, (2010)

[15] Dhawan S.K., Kuldeep Singh A.K., Anil Ohlan Bakhshi., Conducting polymer embedded with nanoferrite and Titanium dioxide nanoparticles for microwave for microwave absorption. Synth.Metals, 159: 2259–2262, (2009)

[16] Fang Xu, Yang Bai, Kai Jiang, Li-jiang Qiao, Characterization of a Y-type hexagonalferrite-based frequency tunable microwave absorber. Int.J.Miner. Metall. Mater.19(5) (2012) 453.

[17] Pande S., Swaruparani H., Bedre M. D., Bhat, R., Deshpande and A. Venkataraman Synthesis, Characterization and Studies of PANI-MMT Nanocomposites. Nanoscience and Nanotechnology, 2(4): 90-98, (2012)

[18] Porselvi Linganathan, Jhancy Mary Samuel, Synthesis, characterization and electrical conductivity of poly (2- chloroaniline)/MMT and poly (2-chloroaniline)/Na-Bentonite nano composites in the presence of surfactants. Int. J. Sci. Technol. Res.3(2) 69-75 (2014).

[19] Lee D., Char K., Lee S.W *et al*. Structural changes of polyaniline/ montmorillonite nano composites and their effects on physical properties. J Mater Chem, 13: 2942–2947, (2003).

[20] Ritu Saharan, Amarjeet Kaur and Sandeep K, Dhawan, Synthesis and Characterization of poly (o-methoxy aniline) and its copolymer for electrochromic device energy applications. Indian J. Pure Appl. Phy, 53, 316-319: (2015)

[21] Kuestan A., Ibrahim, Synthesis and Characterization of polyaniline and poly (aniline-co-o-nitroaniline) using vibrational spectroscopy. Arab. J.Chem. 10, S2668-S2674 (2015)

[22] Oh M., Kim S., Effect of dodecyl benzene sulfonic acid on the preparation of polyaniline/activated carbon composites by in situ emulsion polymerization, Electrochim. Acta, 59 :196-201, (2012)

[23] Liu A., Huu Bac L., Kim J., Liu L., Preparation and characterization of Polyaniline-Copper composites by electrical explosion of wire. J.Nanosci. Nanotechnol. 12: 6031- 6035 (2012)

[24] Habibi M.H., Karimi B., Effect of the annealing on crystalline phase of copper oxide nano particle by copper acetate precursor and sol-gel Method. Thermal Analysis and Calorimetry,115 (1): 419-423, (2014)

[25] Tang Z., Qi L., and Gao G., Polymer electrolytes based on copolymer of poly (ethylene or poly (ethylene glycol) di methacrylate and imidazolium ionic liquid. Solid State Ion 180, 226 (2009).

[26] Çetinkaya H.G., Alialy S., Altındal Ş., Kaya A and Uslu İ; Investigation of negative dielectric constant in Au/1 % graphene (GP) doped-Ca1.9Pr0.1Co4Ox/n-Si structures at forward biases using impedance spectroscopy analysis. J. Mater. Sci. Mater. El, 26(5): 3186–3195, (2015)

[27] Lakshmi P., and Jhancy Mary S., Chemical synthesis, spectral characterization and electrical conductivity behavior of poly(2-methoxyaniline-co-2-chloroaniline) and its CuO nanocomposite and polypropylene glycol blend, Journal of Polymer and Composites, 6(3); 1-14,2018.