Nanocomposite Copolymer of 1-(2-aminophenyl) Pyrrole and 2-3-dimethyl Aniline Synthesis and Characterization

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Nanocomposites of copolymer of 1-(2-aminophenyl) pyrrole and 2-3-dimethyl aniline is synthesized using chemical oxidative polymerization doped with HCl and Ammonium persulfate (APS) used as an oxidant. Nanocomposite copolymer obtained is characterized for physical and structural configurations by UV-Vis., FTIR spectrophotometer and XRD. TGA for thermal stability and 4-probe method is used to determine the electrical conductivity. Spectral study confirms the π-π^* transition in nanocomposite copolymer. The formation of copolymer and its structure is confirmed by FTIR. The amorphous nature of polymer nanocomposite is established by the XRD. The electrical conductivity of sample was comparable to the intrinsic conductive polymers used. SEM micrographs are used to estimate the size and surface morphology.

Key words: Nanocomposite, Copolymer, SEM, FTIR, XRD.

1. INTRODUCTION

Intrinsically conductive polymers (ICP) are the special class of organic polymers have electric conduction in the range from high metallic conductivity to semiconductive [1]. ICPs are highly advantageous over conventional electric conductors in terms of their processability, especially in dispersions [2]. Nanocomposites of one such conducting polymer, the Polyaniline, have attracted special attention due to its excellent redox recyclability [3]. The derivatives of Polyaniline is deliberated to be one of the most promising classes of organic conducting polymers [4] owning good environmental stability [5], ease of doping [6] etc. Polypyrrole, because of good environmental stability and ease of synthesis is another important and most studied conducting polymer [7,8]. It's an integral biocompatible polymer [9]. Polypyrrol and polyaniline, due to their exceptional properties are likely to be used in diverse applications such as biosensors [10,11], gas sensors [12], anti-electrostatic coating [13], solid electrolytic capacitors [14,15], light weight batteries and anticorrosive devices [16] etc. Inorganic nanoparticles of different nature and size can be combined with the conducting polymers, giving rise to a host of nanocomposites with interesting physical properties and important application potential [17]. This work reports the synthesis of nanocomposite of copolymer of 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA) by chemical oxidative polymerization and evaluation of synthesized nanocomposite for various physical properties like optical, thermal stability,

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surface morphology, electrical conductivity, crystallinity and solubility. Results hence obtain are compared and discussed based on previously reported literature.

2. MATERIALS AND METHODS

Analytical grade chemical 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA) was obtained from Acros Organics, USA, while ammonium persulphate (APS) and hydrochloric acid (HCl) were obtained from Qualigens, India. All the solutions were prepared in double distilled water. Among various prominent polymerization techniques, chemical oxidative method [19-21] is the most versatile and easy route-to-synthesize, even in scale up arrangement for obtaining the conducting polymers, hence been adopted to synthesize the nanocomposite of the copolymer of 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA). Chemical oxidative polymerization [22] is followed by oxidation of comonomer to cation radical and their coupling to form di-cation and repetition of this process generates a polymer.

2.1. Synthesis of nanocomposite of copolymer of 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA)

1.4831g (0.004687 moles) of 1-(2-aminophenyl) pyrrole and 0.5680g (0.004687moles) of 2, 3-dimethyl aniline were mixed with 1M 100 ml HCl with continuous stirring for 30 minutes in a reactor. The APS solution was prepared by using 0.009375 mole i.e., 2.139g, with 50ml of 1M HCl. Then APS solution is dropped (by stirring for 30 minutes) into a reactor which contain aniline and pyrrole solution at melting ice temperature. Further agitation was applied for 12 hours after dropping process and the solution was left undisturbed till brown coloured precipitate is formed in good yield. Thereafter the compound was filtered, washed and dried for further characterization [23]

2.2. Characterization

Absorption spectra is obtained using UV-Vis (Shimadzu 1900) double beam spectrometer to characterize the structures of intrinsically conducting polymers (ICPs) and to determine the conjugation in polymer backbone. The Fourier transform infrared spectrophotometer (Perkin Elmer) was used to determine the chemical structure of the nanocomposite. Surface morphology of the prepared nanocomposite was characterized by scanning electron microscopy (SEM.LEO 435 VP). The ordered structure and crystallinity of the composites were obtained by X-ray diffraction method (XRD). Thermal analysis was done by using Thermogravimetric analyzer. Electrical conductivity was measured by Four Probe method.

3. RESULTS AND DISCUSSIONS

3.1. UV-VIS Spectrum

UV-VIS absorption spectral analysis of the synthesized copolymer nanocomposite of 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA) is shown in Figure 1.

Absorption peaks are observed at around 309 nm and 615 nm. First peak around 309 nm is due to the π-π^* transition (band gap) and is directly related to the extent of conjugation. The other peak near 615 nm is due to molecular exciton associated with the quinine-diamine structure [24] i.e. transition between HOMO orbital of benzenoid rings and LUMO of the quinoid rings. UV-VIS spectra of a aniline and pyrrole cannot be obtained as a linear combination of the spectra of the constituent homopolymer [25]. The copolymer exhibits roughly uniform absorption throughout the whole visible region. While both polyaniline and polypyrrole show a pronounced absorption above 800 nm corresponding to the presence of localized polaron responsible for the electrical conduction, the absorption of a copolymer in the region is reduced. This is in accordance with the low conductivity observed for copolymer prepared at equimolar proportion of co-monomer.

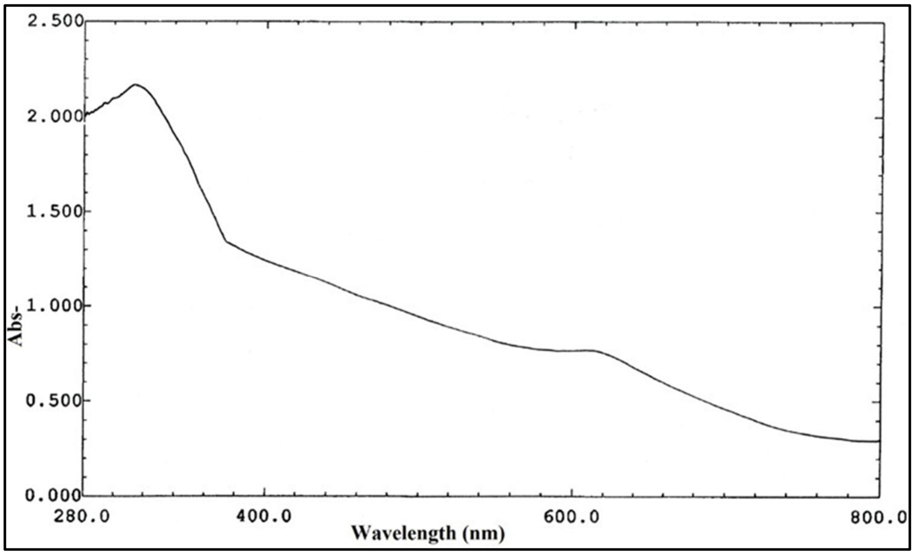


Fig. 1: UV-Vis absorption spectra of copolymer nanocomposite of 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA).

3.2. FTIR Spectrum

The FTIR spectra of doped form of 1-(2-Aminophenyl) pyrrole (APy), 2,3-Dimethyl aniline (DMA) and the nanocomposite of the two materials, in the range 400-4000 cm^{-1} is shown in Figure 2, Figure 3 and Figure 4 respectively. The main characteristic bands observed in the IR region have been recorded in Table 1. The spectrum for DMA shows peaks at 1640 cm^{-1} and 1490 cm^{-1} which are due to the stretching vibrations of quinoid and benzenoid structure respectively [26-28]. These peaks also appear in the spectrum of nanocomposite at 1560 cm^{-1} and 1458 cm^{-1}. C- N stretching vibration occurs at 1261 cm^{-1}, 1312 cm^{-1} and 1370 cm^{-1} in APy, DMA and nanocomposite respectively. All characteristics peaks of APy and DMA also exist in the spectrum of nanocomposite confirming the presence of aniline and pyrrole unit in it. The spectrum of nanocomposite reveals all characteristic peaks of homopolymers. It correlates to observed for nanocomposite copolymer of 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA)composite [29]. It is observed that the peaks shifted towards lower wave number and it confirms the presence of copolymer unit in composite material.

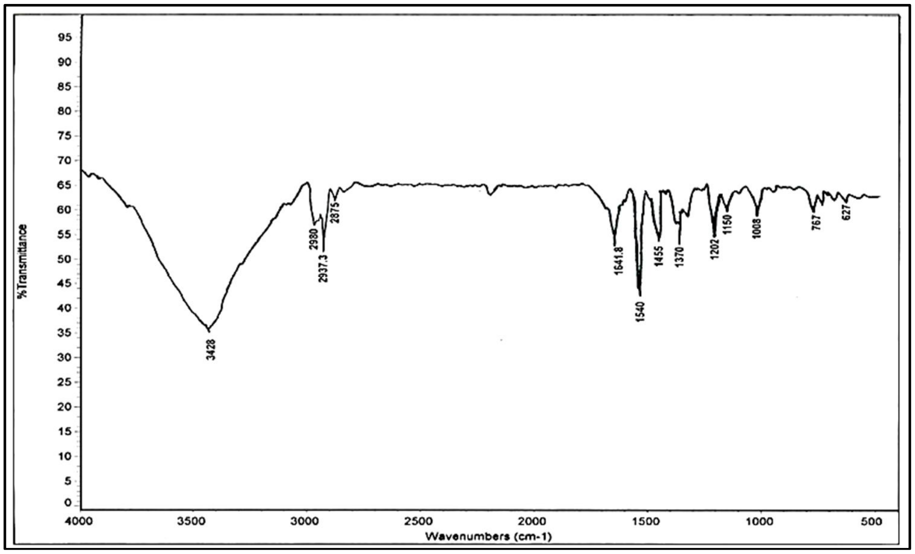


Fig. 2: FTIR of homopolymer of 1-(2-Aminophenyl) pyrrole (APy).

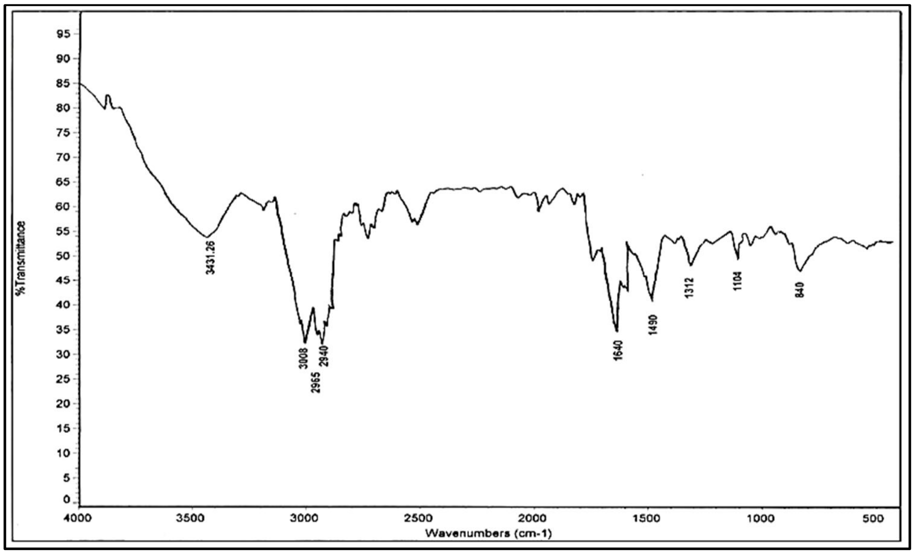


Fig. 3: FTIR of homopolymer of 2,3-Dimethyl aniline (DMA).

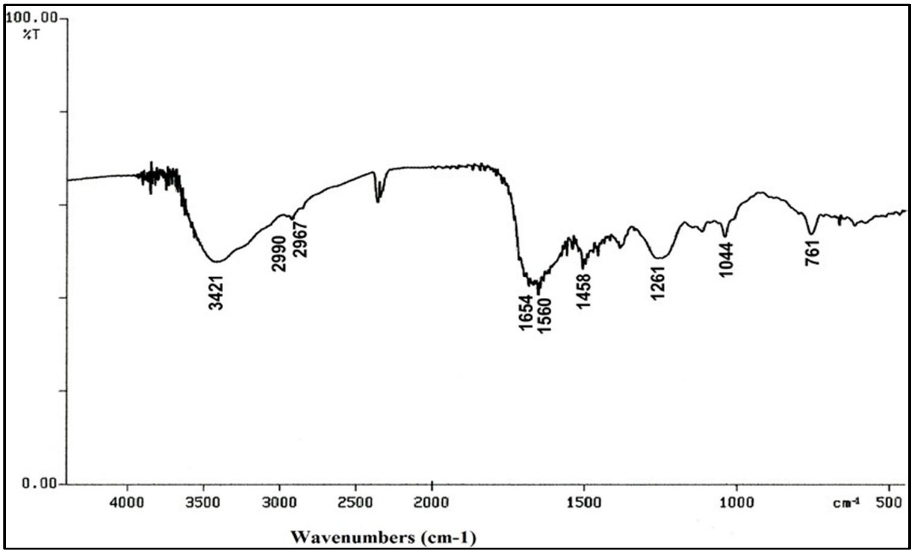


Fig. 4: FTIR of copolymer of 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA).

Table. 1: FTIR data of homopolymers and copolymer nanocomposite of 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA) (All units cm^{-1}).

	N – H stretch	**- CH_3 Stretch**	**C – N stretch**	**C – H in plane**	**C – H out of plane**
APy homopolymer	3428	2980, 2937, 2875	1370	1008	767
DMA homopolymer	3431	3008, 2965, 2940	1312	1104	840
Copolymer nanocomposite	3421	2990,2967	1261	1044	761

3.3. Thermal Analysis

Thermogravimetric analysis measurements were carried out from room temperature to 800° C at a heating rate of 10° per minute under nitrogenous atmosphere. The comparative TGA curves of homopolymers of ICP and the copolymer nanocomposite (CP - 10) of 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA) is given in Fig. 5. Thermogram of nanocomposite shows three distinct regions of weight loss. All results are tabulated in Table 2.

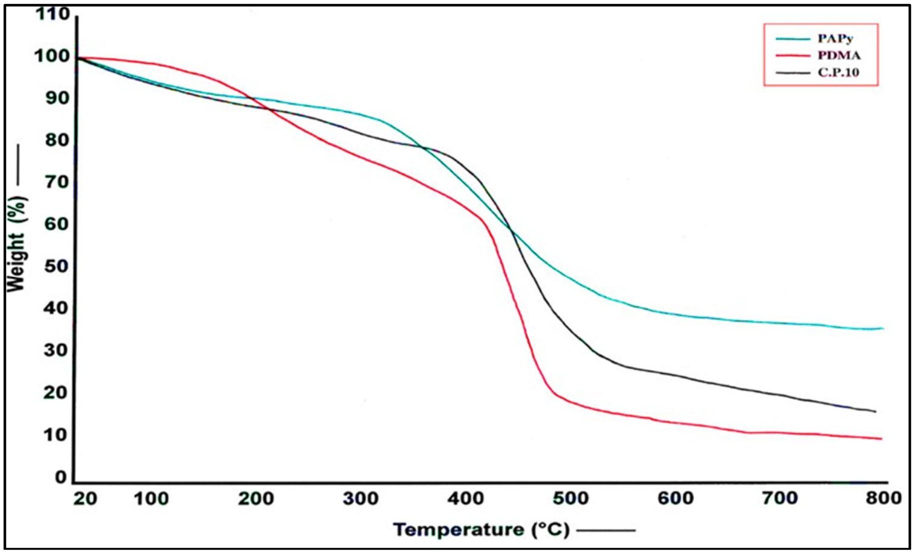


Fig. 5: TGA curves of APy, DMA and nanocomposite of copolymer of APy and DMA.

From this table and figure, it can be inferred that nanocomposite has shown good thermal stability. It shows three stages of decomposition. The TGA curves shows loss of water molecule from the polymer matrix in the first step of decomposition after 100^o C. Second weight loss occurs at around 270^0 – 280^0 C due the removal of the dopants. Final decomposition is due to polymer backbone decomposition, the highest percentage weight loss observed at decomposition temperature between 400^o C to 550^o C. The maximum weight loss occurs at 595°C, 487°C and 543°C for PAPy, PDMA and nanocomposite respectively. Prepared nanocomposite has shown good thermal stability upto 250°C but it is highest for PAPy which might be due presence of phenyl ring in PAPy and nanocomposite also.

Table 2: TGA weight loss in APy, DMA and nanocomposite of copolymer of APy and DMA.

	1st weight loss		**2nd weight loss**		**3rd weight loss**	
APy	7.5%	149°C	6.5%	310°C	45.5%	595°C
DMA	3%	130°C	15%	240°C	62%	487°C
Nanocomposite	11%	166°C	6%	287°C	55%	543°C

3.4. X-Ray Diffraction

XRD pattern shown in Fig.6 for the nanocomposite exhibits broad peak at $2\theta = 20^o$ to 30^o and these peaks are indicative of an amorphous behavior. The broad peak is characteristic of amorphous poly-pyrrole at $2\theta = 24^o$ [25] and it is due to the scattering from PPy chains at the interplanar spacing [26]. The copolymer of 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA) has shown broad characteristic peaks for their amorphous nature [27,28]. Thus, on the basis of earlier reported XRD graphs of poly-aniline, poly-pyrrole and copolymer of aniline and pyrrole we can predict the formation of nanocomposites of substituted aniline and pyrrole and broadness of peak in the range of 20^o to $30^o$is due to their amorphous nature.

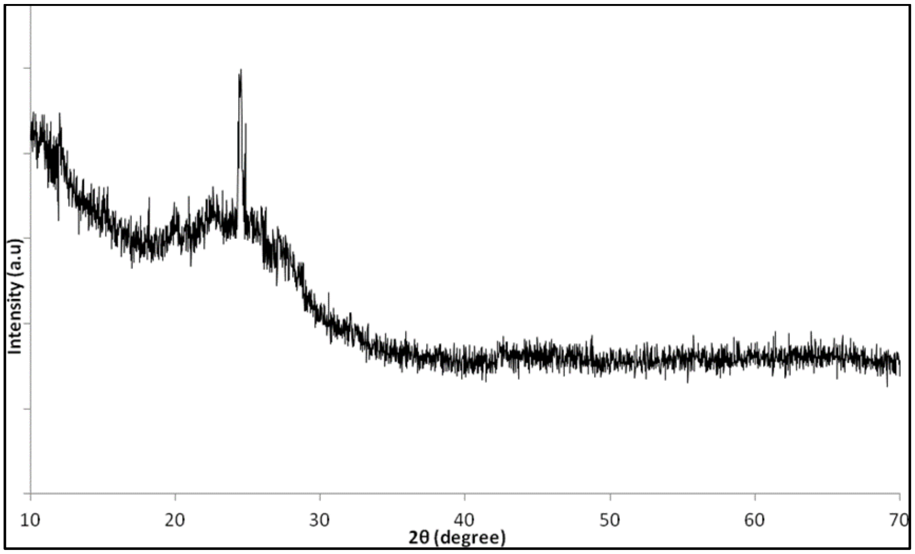
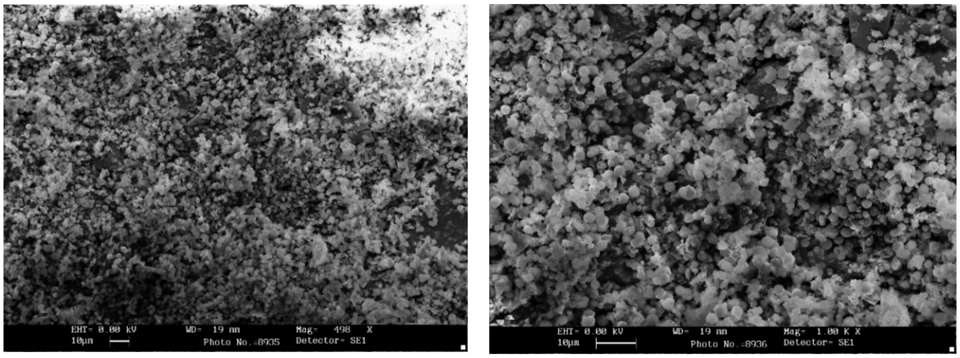


Fig. 6: XRD spectrum of nanocomposite of copolymer of APy and DMA.

3.5. Surface Morphology

Surface morphology of the nanocomposite was studied by scanning electron microscopy (SEM). Fig. 7a and 7b shows the SEM micrographs at 500X and 1000X magnifications. The micrograph shows a mixed morphology of small flakey particles and network of large fibers. At 1000X (7b), micrograph shows that small globular particles (thickness ~300 nm) are randomly distributed across the polymer network. The globular particle consist of large number of polymer chans thar are coiled to give spherical morphology. This may be due to presence of many alkyl groups [30] present in copolymer of APy and DMA.



7(a) **7(b)**

Fig. 7: SEM images of nanocomposite copolymer of APy and DMA at (a) 500X and (b) 1000X magnification.

3.6. Electrical Conductivity Measurement

Electrical conductivity of prepared nanocomposite was measured by Four Probe method using cross bridge arrangements [31]. It is observed that the conductivity decreases from 10^{-2} to 10^{-5} when aniline was polymerized with pyrrole. This is in agreement of prior results for polypyrrole-polyaniline composite [32]. The conductivity of prepared APy and DMA nanocomposite was 2.8×10^{-5} s/cm. The lowering of conductivity for copolymer than Polyaniline is expected to arise from the steric effect of the bulky substituent ($-OCH_3$, $-C_2H_5$ etc.) may provide torsional twist in the polymer backbone, reducing the coplanarity and average electron delocalization length. Such type of observation has been noted for substituted polyaniline and copolymers of aniline with substituted aniline. The results indicate that when polymerizing aniline with pyrrole. The conductivity decreases for polyaniline and improve for polypyrrole. This means copolymerization can increase the conductivity of polypyrrole. This is evidence that the copolymer formed is not just the combination of polypyrrole and polyaniline but completely new material with new properties.

The presence of longer alkyl chain forms globular particles and would reduce the conjugation length in copolymer backbone which in turn lower the concentration of charge carrier/conductivity.

3.7. Solubility Test

The pale brown nanocomposite of APy and DMA copolymer of substituted aniline and pyrrole was tested for solubility in preferred solvents for ICPs such as DMSO, NMP, H_2O_2, CCl_4, and H_2O. Solubility for the synthesized nanocomposite was found to be insoluble in H_2O_2, CCl_4, and H_2O solvents except for DMSO and NMP which showed sparingly solubility forming a light brown coloured solution similar to earlier reported nanocomposite copolymer [33,34]

4. CONCLUSIONS

The nanocomposite of copolymer 1-(2-Aminophenyl) pyrrole (APy) and 2,3-Dimethyl aniline (DMA) was successfully synthesized via chemical oxidative polymerization using APS as dopant. The nanocomposite of copolymer had a fibrous structure. Prepared nanocomposite has shown good thermal stability, electrical conductivity, and was almost insoluble in common solvent except for specific DSMO and NMP.

REFERENCES

[1] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang and A.J. Heeger; “Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, $(CH)_x$”, J. Chem. Soc., Chem. Commun., Vol. 16, pp. 578-580, 1977.

[2] Toribio Fernandez Otero; “Conducting Polymers”, Royal Society of Chemistry, Cambridge, 2016

[3] T. Liu, L. Finn, M. Yu, H. Wang, T. Zhai, X. Lu, Y. Tong and Y. Li; “Polyaniline and Polypyrrole Pseudocapacitor Electrodes with Excellent Cycling Stability”, Nano letters, Vol. 14(5), pp. 2522–2527, 2014. DOI: 10.1021/nl500255v

[4] N.V. Blinova, J. Stejskal, M. Trchová, J. Prokeš and M. Omastová; “Polyaniline and polypyrrole: A comparative study of the preparation”, European Polymer Journal, Vol. 43(6), pp. 2331-2341, 2007. DOI: 10.1016/j.eurpolymj.2007.03.045

[5] J.L. Camalet, J.C. Lacroix, S. Aeiyach, K. Chane-Ching and P.C. Lacaze; “Electrosynthesis of adherent polyaniline films on iron and mild steel in aqueous oxalic acid medium”, Synthetic Metals, Vol. 93(2), pp. 133-142, 1998.

[6] E.W. Paul, A.J. Ricco and M.S. Wrighton; “Resistance of polyaniline films as a function of electrochemical potential and the fabrication of polyaniline-based microelectronic devices”, J. Phys. Chem., Vol. 89(8), pp. 1441-1447, 1985.

[7] T.M. Wu and S.H. Lin; “Synthesis, characterization, and electrical properties of polypyrrole/multiwalled carbon nanotube composites”, J. Polym. Sci. A Polym. Chem., Vol. 44(21), pp. 6449-6457, 2006. DOI: 10.1002/pola.21724

[8] P.M. Carrasco, H.J. Grande, M. Cortazar, J.M. Alberdi, J. Areizaga and J.A. Pomposo; “Structure–conductivity relationships in chemical polypyrroles of low, medium and high conductivity”, Synthetic Metals, Vol. 156(5-6), pp. 420-425, 2006.

[9] A. Ramanavicius, A. Ramanaviciene and A. Malinauskas; “Electrochemical Sensors Based on Conducting Polymer-Polypyrrole”, Electrochimica Acta, Vol. 51(27), pp. 6025-6037, 2006. DOI: 10.1016/j.electacta.2005.11.052

[10] J.C. Vidal, E. Garcia and J.R. Castillo; "In situ preparation of a cholesterol biosensor: entrapment of cholesterol oxidase in an overoxidized polypyrrole film electrodeposited in a flow system: determination of total cholesterol in serum," Analytica Chimica Acta, Vol. 385(1-3), pp. 213-222, 1999.

[11] T.E. Campbell, A.J. Hodgson and G.G. Wallace; "Incorporation of Erythrocytes into Polypyrrole to Form the Basis of a Biosensor to Screen for Rhesus (D) Blood Groups and Rhesus (D) Antibodies", Electroanalysis, Vol. 11(4), pp. 215-222, 1999.

[12] D. Kincal, A. Kamer, A.D. Child and J.R. Reynolds; "Conductivity Switching in Polypyrrole-Coated Textile Fabrics as Gas Sensors", Synthetic Metals, Vol. 92(1), pp. 53-55, 1998. DOI: 10.1016/S0379-6779(98)80022-2

[13] C.J. Weng, Y.L. Chen, Y.S. Jhu, L. Yi-Li and J.M. Yeh; "Advanced antistatic/anticorrosion coatings prepared from polystyrene composites incorporating dodecylbenzenesulfonic acid-doped SiO_2@polyaniline core–shell microspheres", Polym. Int., Vol. 62(5), pp. 774-782, 2013. DOI: 10.1002/pi.4362

[14] Y. Taketani, K. Yoshida, H. Kamigawa, Y. Kishimoto, Y. Kojima and T. Takamatsu; "SOLID ELECTROLYTE CAPACITOR", US Patent No. 6,313,979 B1, Nov. 6, 2001.

[15] Y. Kojima, H. Kamikawa and T. Takamatsu; "Manufacture of solid electrolytic capacitor", Patent No. JPH118165A, Application number: JP16229997A, Jun. 19, 1997.

[16] M. Fahlman, S. Jasty, A.J. Epstein; "Corrosion protection of iron/steel by emeraldine base polyaniline: an X-ray photoelectron spectroscopy study", Synthetic Metals, Vol. 85(1-3), pp. 1323-1326, 1997. DOI: 10.1016/S0379-6779(97)80256-1

[17] R. Gangopadhyay and Amitabha De; "Conducting Polymer Nanocomposites: A Brief Overview", Chemistry of Materials, Vol. 12(3), pp. 608-622, 2000.

[18] R. Rathore and A. Chauhan; "Synthesis and Characterization of Copolymer Nanocomposite NMethyl Pyrrole (NMPy) and Aniline-2-Sulphonic Acid (ASA)", JPAST, Vol. 9(1), pp. 25-34, 2019.

[19] S.A. Chen and C.C. Tsai; "Structure/properties of conjugated conductive polymers. 2. 3-Ether-substituted polythiophenes and poly(4-methylthiophenes)", Macromolecules, Vol. 26(9), pp. 2234–2239, 1993. DOI: 10.1021/ma00061a015

[20] L. Huang, J. Hu, L. Lang, X. Wang, P. Zhang, X. Jing, X. Wang, X. Chen, P.I. Lelkes, A.G. MacDiarmid and Yen Wei; "Synthesis and characterization of electroactive and biodegradable ABA block copolymer of polylactide and aniline pentamer", Biomaterials, Vol. 28(10), pp. 1741-1751, 2007.

[21] N. Somanathan and G. Wegner; "Studies on poly(3-cyclohexylthiophene)", IJC-A Vol. 33A, pp. 572-579, 1994. http://nopr.niscair.res.in/handle/123456789/40915

[22] A. Ohtani and T. Shimidzu; "Effective Doping of Polymer Anion during Chemical Polymerization of Pyrrole Using $Fe(OH)_3$ Oxidant", Bull. Chem. Soc. Jpn., Vol. 62(1), pp. 234-238, 1989.

[23] A. Chauhan, R. Rathore and R. Singh; "Synthesis and Characterization of Lithium Perchlorate Doped PANI thin films", Int. J. Sci. Res. Sci., Engg. Tech., Vol. 4(4), pp. 1412-1417, 2018. http://ijsrset.com/IJSRSET184823

[24] J.E. de Albuquerque, L.H.C. Mattoso, R.M. Faria, J.G. Masters and A.G. MacDiarmid; "Study of the interconversion of polyaniline oxidation states by optical absorption spectroscopy", Synthetic Metals, Vol. 146(1), pp. 1-10, 2004.

[25] J. Stejkal, M. Trchova, I.A. Ananieva, J. Janca, J. Prokes, S. Fedorova and I. Sapurina; "Poly(aniline-*co*-pyrrole): powders, films, and colloids. Thermophoretic mobility of colloidal particles", Synthetic Metals, Vol. 146(1), pp. 29-36, 2004.

[26] R. Partch, S.G Gangolli, E. Matijević, W. Cal and S. Arajs; "Conducting polymer composites: I. Surface-induced polymerization of pyrrole on iron (III) and cerium (IV) oxide particles", Journal of Colloid and Interface Science, Vol. 144(1), pp. 27-35, 1991. DOI: 10.1016/0021-9797(91)90234-Y

[27] S. Mavundla, G.F. Malgas, D.E. Motaung and E.I. Iwuoha; "Physicochemical and morphological properties of poly(aniline-co-pyrrole)", J. Mater. Sci., Vol. 45, pp. 3325-3330, 2010. DOI: 10.1007/s10853-010-4351-5

[28] H.K. Chaudhari and D.S. Kelkar; "Investigation of Structure and Electrical Conductivity in Doped Polyaniline", Polymer International, Vol. 42(4), pp. 380-384, 1997. DOI: 10.1002/(SICI)1097-0126(199704)42:4<380::AID-PI727>3.0.CO;2-F

[29] R. Rathore, A. Chauhan and P.K. Yadav; "Study of Chemically Synthesized Nanocomposite Copolymer of N-methyl Pyrrole and 2,5-Dimethoxy Aniline", J. Pure Ap. Sci. & Tech., Vol. 9(2), pp. 30-40, 2019.

[30] M. Masikini, S.N. Malu, A. Tsegaye, C.O. Ikpo, N. Njomo, T.T. Waryo, P.G.L. Baker and E.I. Iwuoha; "In - situ Electrochemical Synthesis, Microscopic and Spectroscopic Characterisations of Electroactive poly(2,5dimethoxyaniline) – Multi-Walled Carbon Nanotubes Composite Films in Neutral Media", Int. J. Electrochem. Sci., Vol. 9, pp. 7003-7020, 2014

[31] A. Chauhan, R. Rathore and A. Kumar; "Structural and Electrical Properties of $LiClO_4$ Doped PANI Composite Films", Int. J. Res. Appd. Sci. Engg. Techn., Vol. 7(1), pp. 811-818, 2019. DOI: 10.22214

[32] R. Rathore, A. Chauhan and P.K. Yadav; "Study of Chemically Synthesized Nanocomposite Copolymer of 3,4-dimethyl Pyrrole and 2-ethyl Aniline", J. of Pure Apd. Sci. & Tech., Vol. 10(1), pp. 9-19, 2020.

[33] R. Rathore, S. Sharma, A.K. Manglik; "Nano composite of copolymer of N-methyl pyrrole and 2,3-di methyl Aniline: Synthesis and Characterization", J. of Chemistry in Asia, Vol. 6(1-4), pp. 35-44, 2015.

[34] R. Rathore, S. Sharma; "Synthesis and Characterization of Nanocomposite of Copolymer of 3,4-Dimethyl Pyrrole (DMPY) and 2,4-Dimethoxy Aniline (DMOA)", International Journal of Scientific Research, Vol. 7(1), pp. 17-19, 2018. DOI: 10.36106/ijsr