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Studies on Synthesis and Characterization of Copper Oxide Doped Polyaniline [CuO/PANI]

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ABSTRACT: Polyaniline & metal oxide doped polyaniline (CuO/PANI) composites prepared via chemical oxidative polymerization method incorporating with wt% (5%, 15%, 25%, 35% & 45%) of copper oxide ammonium persulphate is utilized as oxidant. The structural and morphological aspects of the composites were characterized by XRD & SEM methods respectively. The impedance analyzer was used to measure the electrical properties (AC & DC) & dielectric properties. The AC conductivity, Dielectric constant of all composites was determined with varying frequency at ambient temperature and DC conductivity was analyzed with respect to varying temperature.

KEYWORDS: Copper Oxide/Polyaniline Composite; X-ray Diffraction; Electrical Conductivity and Dielectric Permittivity.

I. INTRODUCTION

Conducting polymer composites are the future materials for emerging technologies as they possess the blending of unique characteristics of their constituents. These characteristics become more interesting when one of the components is in the nano range. Owing to the concurrent outcome of the polymer and the nano filler, the resulting materials are expected to display desirable properties with enhanced performance [1]. Polyaniline (PANI) was discovered over 150 years ago, it has lately conquered the recognition of the scientific group owing to its greater electrical conductivity when treated with protonic acids & became the most popular examined conducting polymer due to its discovery about three decades ago. It was initially synthesized in the year 1834 and has been the theme of moderate research henceforth [2].

However, the conducting properties of PANI were recognized and various research articles regarding this conducting polymer developed rapidly since 1980s. Amongst various conducting polymers, PANI has a peculiar depiction because of its distinctive properties like inexpensive, ease of preparation by chemical or electrochemical methods & greater environmental stability. The distinctive benefits of PANI include the capability to adjust its electrical properties easily by proton doping. These characteristics made PANI an interesting replacement material in various sectors of uses like electrodes, charge transfer and active layers, electrochromic displays, EM shielding as well as a growth template for neurons [3-4].

The characteristics of this kind of conducting polymers can be improved by adding the inorganic molecules. Nano scale particles are interesting because of their fascinating characteristics emerging from nano scale & substantial surface area. By inserting the nano scale fillers they may enhance electrical & sensing characteristics of the polymers [5]. Now-a-days, nano-sized metal particles have got more recognition owing to its distinctive optical, electrical & magnetic characteristics, which depends on the particle size and shape.

Copper oxide, a versatile semiconducting material, has been drawing the recognition owing to the materialistic exigency for optoelectronic gadgets controlling at blue & ultraviolet regions [6]. CuO is a monoclinic n-type semiconducting material with narrow band gap energy i.e, of order 1.5–1.8 eV, & it has substantial excitation binding energy (60 meV) at ambient temperature [7-8].

CuO has drawn much attention recently, owing to, its extravagant characteristics & extensive uses from heterogeneous catalysts, gas sensors, field-emission emitters to high temperature superconductors & solar cells. [9-10]. Since it has good mechanical versatility and environmental stability, and its resistivity could be managed with acid/base (doping/undoping), it has major applications in various sectors, such as lightweight battery electrode, EM shielding device, anticorrosion coatings, solar cells, photo detectors and sensors [11-14].

II. METHODOLOGY

Chemicals used to prepare polyaniline are aniline, hydrochloric acid (HCl), ammonium persulphate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ of analytical grade and synthesized by employing chemical oxidative polymerization method and utilizing as single unit of polymer in the presence of HCl as catalyst and ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant.

- Preparation of 0.2M of ammonium persulphate in first volumetric flask.
- Preparation of 1N of hydrochloric acid (HCl) in second volumetric flask.
- Preparation of 0.2M of aniline in third volumetric flask.

A. Preparation of Polyaniline:

The prepared solution of 0.2M of aniline in volumetric flask is dissolved in a beaker along with prepared solution of 1N of hydrochloric acid and this mixer is stirred for one hour by magnetic stirrer at room temperature. After one hour of constant stirring, the prepared solution of 0.2M of ammonium persulphate was added drop wise in the solution of aniline hydrochloric acid using pipette. This mixer is stirred for 10 hours for the completion of reaction, and then it left for 24 hours to settle down. Later the prepared solution is purified using vacuum pump & Buchner funnel. This precipitate was filtered, cleaned with deionised water, with acetone so as to eliminate the oligomers and excess ammonium persulphate, & with 1 N HCl solution to remove the Cl^- ions and unreacted aniline. At the end of the process, the precipitate was kept for drying in the hot air oven for 24 h at room temperature to achieve a constant mass.

B. Preparation of polyaniline and CuO/PANI composite:

The prepared solution of 0.2M of aniline in volumetric flask is dissolved in a beaker along with prepared solution of 1N of hydrochloric acid and this mixture is stirred for one hour by magnetic stirrer at room temperature. After one hour of constant stirring, the prepared solution of 0.2M of ammonium persulphate was added drop by drop in the mixture of aniline hydrochloric acid using pipette. Copper oxide was added in the mass fraction (5%, 15%, 25%, 35% & 45%) to above mixture with continuous stirring so as to keep the CuO uniformly suspended in the above mixture. This mixture is stirred for 10 hours for the completion of reaction, & then it is left for 24 hours to settle down. Later the prepared solution is purified by utilizing the vacuum pump & Buchner funnel. This precipitate was filtered, cleaned with deionised water, with acetone so as to eliminate the oligomers and excess ammonium persulphate, and with 1 N HCl solution to remove the Cl^- ions and unreacted aniline. At the end of the process, the precipitate was kept for drying in the hot air oven for 24 h at room temperature to achieve constant mass.

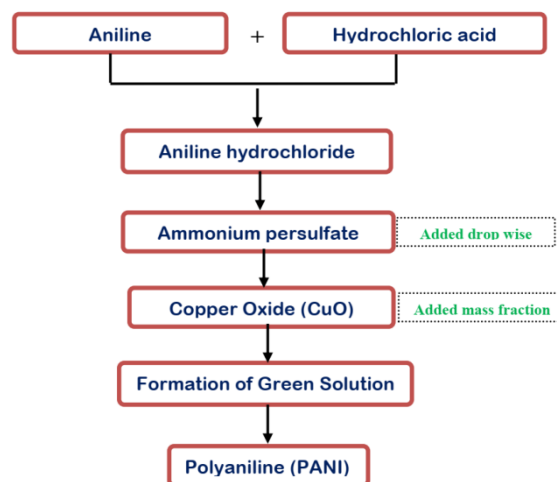


Figure-1: Flow chart of preparation of composite

III. EXPERIMENTAL RESULTS

A. STRUCTURAL REVIEW:

The structural analysis of sample was studied by X-ray diffraction technique. Figure-2 (a-f) reveals the XRD pattern of the Pure PANI & CuO/PANI for different additive weight percentage (5%, 15%, 25%, 35% & 45%) respectively. Generally polyaniline exists in amorphous form. From the pattern it reveals that, wide peak of pure polyaniline

represents the amorphous form of sample. The sample shows crystalline in nature when it is doped with CuO. Figure-1(a) reveals the prominent peak of pure polyaniline is in the range of 25° - 27° , which is characteristics peak of polyaniline. Figure-2(b-f) shows sharp peak of maximum intensity at 2θ values. The characteristic peaks located at $2\theta = 32.52^{\circ}, 35.69^{\circ}, 38.76^{\circ}, 48.01^{\circ}, 54.48^{\circ}, 61.97^{\circ}, 64.35^{\circ}$ are (110) (002) (111) (202) (020) (202) (113) (002) plane orientation of CuO particles. The average crystalline size of the PANI are estimated to be approximately 20-30 nm are estimated by using Debye -Scherrer formula,

$$(D=K\lambda/(\beta \cos\theta))$$

Where D indicates average crystalline size, λ is wavelength of X-ray, K is crystallite shape factor a good approximation is 0.9, β is FWHM of X-ray diffraction peak and 2θ is Bragg's angle (deg.).

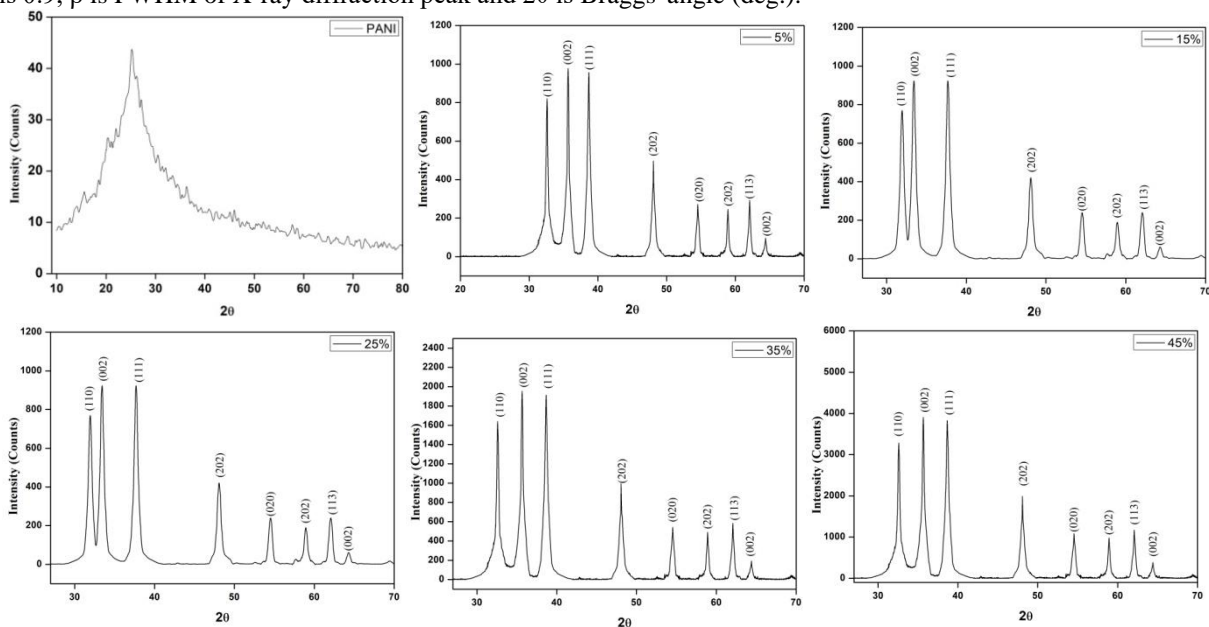


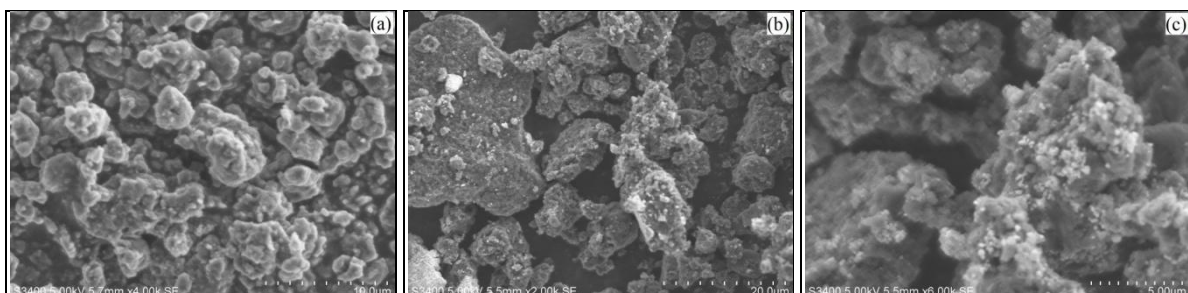
Fig-2: XRD image of Polyaniline & CuO/PANI composites

B. MORPHOLOGICAL STUDY:

Figure-3(a-f) illustrates the surface morphology of pure polyaniline and CuO/PANI (5%, 15%, 25%, 35% & 45%) respectively. The SEM image of PANI shows uniform morphology with semi-crystalline like structure. The SEM image of CuO/PANI reveals that the dopant metal oxide particles are dispersed in PANI which also justifies the successful composite formation and mainly composed of irregularly arranged granular, nonporous, aggregated surface morphologies with diverse sizes. Also, observed that, percentage of composites doesn't affect the morphological image considerably. The standard grain size was calculated as 30-40nm. The standard grain size was calculated by the linear intercept method. A number of lines were drawn on a photograph & number of intercepts between the test line & grain boundaries were counted. The standard grain size was calculated by utilizing

$$D = \frac{1.56 \times C}{M \times N}$$

Where, D- Average grain size,
N- Number of intercepts &
M- Magnification of photograph.



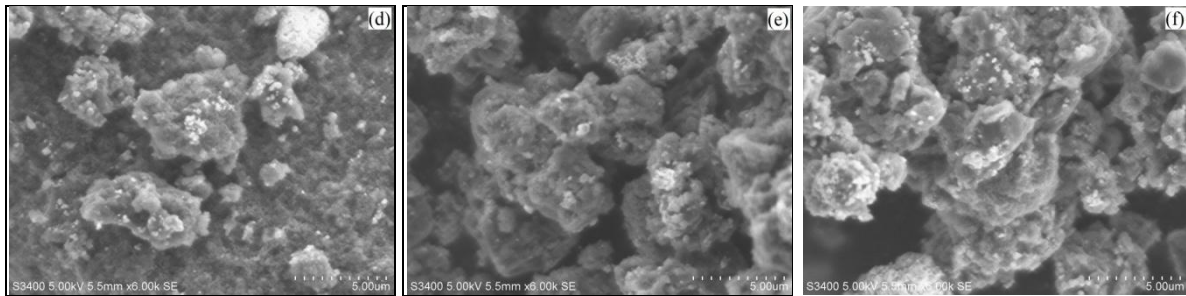


Figure-3: SEM image of PANI and CuO/PANI composites

C. AC conductivity:

The conductivity which depends on frequency for irregular materials like polymers is basically owing to interfacial polarization at contacts & grain boundaries of material [15]. Figure- 4 reveals the dependence of frequency of σ_{AC} conductivity with respect to the frequency for pure polyaniline & CuO/PANI composites with varying wt%. Conductivity of all the determined samples is noticed at room temperature. In all cases it observed that, the σ_{AC} conductivity increases as frequency increased from 1 KHz to 1 MHz. It is reported previously that, polyaniline has electrical conductivity in the order of 10^{-10} & 10^3 S/cm depending on the dopant of acid & filler materials [16]. From plots it is also noticed that, the conductivity of all composites are greater than the pure polyaniline. This observed high conductivity of composites may be owing to the dispersal of copper oxide in polyaniline matrix. The variation of the conductivity of polyaniline and its composites at 1 KHz and 1 MHz are shown in table-I. Previously reported that, the ac conductivity of pure polyaniline was found to be approximately 3×10^{-7} S/m at 1 KHz and there is an increment up to 6.5×10^{-6} S/m at 1 MHz [17]. Compared to previously reported, the conductivity was found to be higher for polyaniline at both the frequency 1 KHz and 1 MHz may be due to the variation aniline, oxidant and HCL in synthesis process. The conductivity of the polyaniline found to be $3.75.91 \times 10^{-8}$ S/m and 2.50×10^{-3} S/m which increases as doping increased then reaches to the value 3.68×10^{-7} S/m & 1.55×10^{-2} S/m at 1KHz & 1 MHz frequency respectively.

Sample	Conductivity (σ_{ac}) S/m At 1 KHz	Conductivity (σ_{ac}) S/m At 1 MHz
Pure PANI	5.91×10^{-8}	2.50×10^{-3}
PANI/CuO (5%)	7.10×10^{-8}	7.06×10^{-3}
PANI/ CuO (15%)	9.23×10^{-8}	7.92×10^{-3}
PANI/ CuO (25%)	1.29×10^{-7}	8.99×10^{-3}
PANI/ CuO (35%)	1.94×10^{-7}	9.99×10^{-3}
PANI/ CuO (45%)	3.68×10^{-7}	1.55×10^{-2}

Table-I: Variation of ac conductivity with respect to the composition at 1 KHz and 1 MHz frequency.

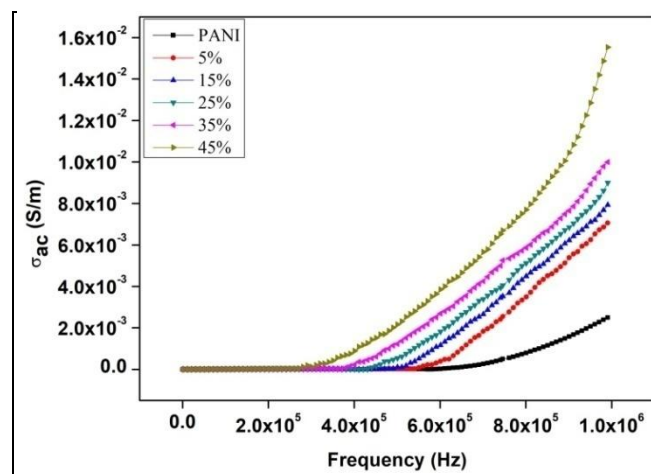


Figure-4: AC conductivity of Polyaniline & CuO/PANI composites



D. DC Conductivity:

Fig-5 reveals the variation of DC conductivity with respect to the varying temperature. It can be made that, the rate of DC conductivity of all the samples increases proportionally with respect to temperature. The DC electrical conductivity sustains same temperature up to 90°C & then it goes on increases drastically, owing to the unmitigated length of polyaniline chain, the hopping of the particles which carry the charge occurs among the favorable local sites due to the initial increase in the rate of conductivity, further it can be seen that the conductivity enhances with increment of weight percentage of CuO in PANI and is due to the variation in allocation of CuO content in PANI.

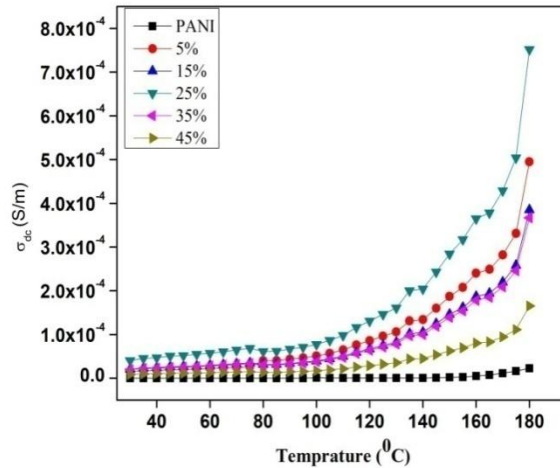


Figure-5: DC conductivity of PANI and CuO/PANI composites

E. Dielectric constant (ε’):

The dielectric properties of materials, like permittivity, are generally deliberated with respect to varying frequency & are referred to as impedance spectroscopy. The permittivity rate reveals the impact of an external field on electric dipole moment component. The evaluation of the dielectric property is significant mechanism to know the material behavior especially at greater frequencies since it can produce the electrical or magnetic properties of the materials, which is a crucial framework necessary to execute material in various uses.

Figure-6 reveals the deviation of dielectric constant ε’ with respect to frequency for varying weight percentage of polyaniline /CuO composites. Dielectric constant of polyaniline and polyaniline composites decreases as frequency increases over the measured frequency domain of 1 KHz to 1 MHz, which is a typical property of disordered conducting polymer. It is noticed that, in all the cases, the dielectric constant is relatively greater at lesser frequency (1 KHz) and further it decreases with increment in frequency. This kind of behavior is usually due to Debye like relaxation phenomenon which is occurring in this kind of materials. Previously studied that, the dielectric constant of polyaniline found to be approximately 122.38 at frequency 1 KHz and which decreases to approximately 85.68 at 500 KHz [18].

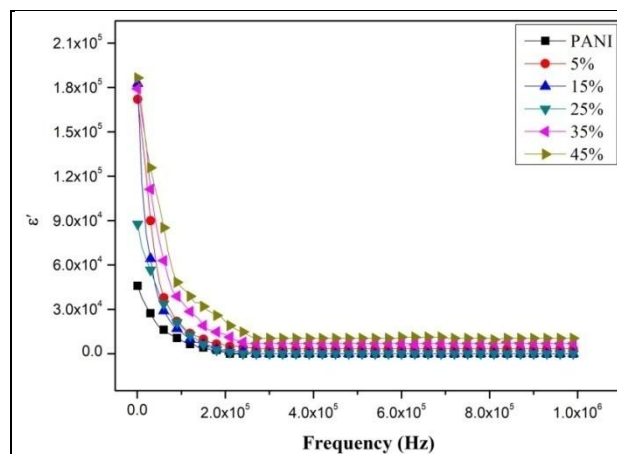


Figure-6: Dielectric constant of PANI and CuO/PANI composites



IV. CONCLUSION

Polyaniline and CuO/PANI were successfully synthesized by the chemical oxidative Polymerization method. The result of XRD and SEM shows formation of the composites and indicates the interaction between PANI and CuO. The average crystalline size of the PANI is estimated to be approximately 20-30 nm by XRD technique. The SEM image of PANI shows uniform morphology with semi-crystalline like structure. The SEM image of CuO/PANI reveals that the dopant metal oxide particles are dispersed in PANI which also justifies the successful composite formation and mainly composed of irregularly arranged granular, nonporous, aggregated surface morphologies with diverse sizes.

From AC conductivity it can be observed that, conductivity of all composites is greater than the pure polyaniline. The maximum conductivity is achieved 1.55×10^{-2} S/m for composites 50% at 1MHz frequency. The temperature dependence DC electrical conductivity of pure PANI & CuO/PANI composites was carried out from 30°C temperature to 200°C and increases with increase in the temperature indicates semiconductor behavior of PANI sample. It is noticed that, real dielectric constant (ϵ') of polyaniline & its composites reveals decrement with respect to the frequency.

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REFERENCES

- [1]. Mohd Omaish Ansari and Faiz Mohammad; Thermal stability of HCl-doped polyaniline and TiO₂ nanoparticles based nanocomposites. Journal of Applied Polymer Science (2011). DOI 10.1002/app.35444.
- [2]. H Letheby J. Chem. Soc., 1862, 15, 161.
- [3]. P Anilkumar, M Jayakannan, Langmuir, 2006, 22, 5952.
- [4]. G Cui, JS Lee, SJ Kim, H Nam, GS Cha, HD Kim, Analyst, 1998, 123, 1855.
- [5]. Mohd Omaish Ansari and Faiz Mohammad; Thermal stability, electrical conductivity and ammonia sensing studies on p-toluenesulfonic acid doped polyaniline: titanium dioxide (pTSA/Pani:TiO₂) nanocomposites, Sensors and Actuators B 157 (2011) 122- 129.
- [6]. Y.F. Lim, J.J. Choi, T. Hanrath, Facile synthesis of colloidal CuO nanocrystals for light-harvesting applications. J Nanomater 2012, 6 (2012).
- [7]. B. Balamurugan, B.R. Mehta, Optical and structural properties of nanocrystalline copper oxide thin films prepared by activated reactive evaporation. Thin Solid Films 396, 90–96 (2001).
- [8]. J. Ghijsen, L.H. Tjeng, J.V. Elp, H. Eskes, J. Westerink, G.A. Sawatzky, M.T. Czyzyk, Electronic structure of Cu₂O and CuO. Phys Rev B 38, 11322 (1998).
- [9]. B.T. Raut, M.A. Chougule, R.C. Pawar, C.S. Lee, V.B. Patil, Polyaniline-CdS nanocomposites: effect of camphor sulfonic acid doping on structural, microstructural, optical and electrical properties, J. Mater Sci Mater Electron 23(12), 2104–2109 (2012).
- [10]. L. Zhang, W. Lu, Y. Feng, J. Ni, Y. Lu, X. Shang, Facile Synthesis of Leaf-like Cu(OH)₂ and its conversion into CuO with nanopores. Acta Phys Chim Sin 24, 2257–2262 (2008).
- [11]. J. Huang, R.B. Kaner, A general chemical route to polyaniline nanofibers. J Am Chem Soc 126, 851 (2004).
- [12]. X. Zhang, W.J. Goux, S.K. Manohar, Synthesis of polyaniline nanofibers by nanofiber seeding. J Am Chem Soc 126, 4502 (2004).
- [13]. M. Matsuguchi, J. Io, G. Sugiyama, Y. Sakai, Effect of NH₃ gas on the electrical conductivity of polyaniline blend films. Synth Met 15, 128 (2002).
- [14]. A. Riul Jr, A.M. Gallardo Soto, S.V. Mello, S. Bone, D.M. Taylor, L.H.C. Mattoso, An electronic tongue using polypyrrole and polyaniline. Synth Met 132, 109 (2003).
- [15]. R. Patil, A.S. Roy, K.R. Anilkumar, K.M. Jadhav, S. Ekhelikar, Composites: Part B, 43 (2012) 3406.
- [16]. Y. Long, Z. Chen, N. Wang, J. Li, M. Wan, “Electrical transport in Polyaniline –CSA/Polyaniline – DBSA polyblends”, Physica B: Condensed Matter, 344 (2004), pp. 82-87.
- [17]. Sangshetty Kalyane, “ Synthesis, Characterization and ac conductivity Study of Polyaniline/ MgSnO₃ Composites”, International Journal of Materials Science ISSN 0973-4589 Volume 12, Number 2 (2017), pp. 175-180.
- [18]. Saxena Dinesh, Dwivedi Vivek and Mishra Pankaj Kumar, Dielectric Study of Polyaniline in Frequency Range 100Hz to 500 KHz at Temperature 200C and 300C, Research Journal of Chemical Sciences, Vol. 3(2), 16-19, February (2013), ISSN 2231-606X.



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