



STUDIES ON *p*TSA DOPED POLYANILINE AND ITS NANOCOMPOSITES TOWARD AMMONIA SENSING

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Abstract

A series of conducting polymer nanocomposites containing polyaniline and molybdenum disulphide were synthesized by *in-situ* oxidative polymerization of acidified aniline. These samples were characterized by FTIR (Fourier Transform Infrared Spectroscopy), UV-Vis (Ultraviolet-Visible Spectroscopy) and XRD (X-Ray Diffraction). Particle size was obtained by SEM (Scanning Electron Microscopy). Electrical conductivity was studied using four in line probe conductivity meter. These above studies suggest formation of polyaniline/molybdenum disulphide nanocomposites. The specific peaks for the individual components may be observed in the FTIR spectra which are also supported by the UV spectra of nanocomposites for their specific peaks. The SEM micrographs reveal that the size of particles these nanocomposites are in nanometer range. The nanocomposites so prepared were doped with *p*-TSA (*p*-toluene sulphonic acid). These *p*TSA doped samples exhibited electrically semiconducting nature, were evaluated for their sensing behavior towards ammonia and these nanocomposites exhibited good sensing response toward ammonia vapour.

Keywords: Polyaniline, MoS₂, Conducting Polymers, Nanocomposites.

1. INTRODUCTION

In the past few decades, conducting polymers (CPs) have gained attention of researchers and scientists because of their highly tunable conductivity, good stability, unique electrical and optical properties, easy and facile synthesis. Conducting polymers consist of non linear defects, eg. solitons, polarons or bipolarons. These entities are responsible for the conducting nature of the polymers. CPs have exhibited good sensing ability for several gases, such as volatile organic compounds (VOCs), H₂S, NH₃, SO₂ etc. In comparison to metal oxides, the sensing ability of CPs shows high sensitivity, short response time, operation at room temperature, and fine tuning of chemical and physical properties, using appropriate substituent. Sensors based on polymers have high sensitivity, due to large surface to volume ratio. Their fast response, low power consumption, light weight and easy handling have made them the substance of choice for fabricating sensors^[1].

Properties of CPs can further be modified by adding inorganic particles in the polymer matrix. By doing so, the semiconducting behavior of polymer exhibits the conducting properties of the metal also. Addition of inorganic nanoparticles in polymer matrix further increases the surface area of polymers for better absorption/adsorption of gases. The inorganic nanofillers also enhance the electrical and sensing properties of the nanocomposites. Sensors have been described that detect ammonia using the change in frequency of a resonator, coated with ammonia sensitive polymer^[1]. The reaction of the polymer with ammonia causes a change in the conductivity of the material, making it a suitable material for ammonia detection with method resistometric^[2] or amperometric^[3]. Response times of this type of sensors has been showed to be in the order of several minutes^[4]. The irreversible reaction with ammonia results in an increase of mass in the polymer film. Keeping this point in view, PANI/MoS₂ nanocomposites are synthesized. These nanocomposites are synthesized by polymerization of aniline in presence of exfoliated MoS₂ particles presence of suitable surfactant. A series of nanocomposites have been synthesized containing different amount of MoS₂ to a constant amount of PANI. In our paper we have discussed the sensing of NH₃ gas, by change in electrical properties (electrical conductivity) of the PANI/MoS₂ nanocomposite.

2. MATERIALS & METHOD:

2.1 Materials:

Aniline (merck, India), molybdenum disulphide (MoS_2) (CDH, India), potassium persulphate (CDH, India), cetyltrimethyl ammonium bromide (CTAB) (CDH, India), HCl (merck, India), ammonia (merck, India) were used as obtained. Double distilled water was used during the process.

2.2 Preparation of *p*-TSA doped PANI/ MoS_2 nanocomposites:

A series of *p*-TSA doped nanocomposites containing PANI and MoS_2 was synthesized by a simple technique. Herein, hydrochloric acid (HCl) doped PANI/ MoS_2 nanocomposites were synthesized and then doped with *p*-TSA. In a typical procedure as reported in our previous communication^[5] calculated amount of CTAB was dissolved in 1M HCl solution and MoS_2 was added in it which was sonicated for 30 min at 4-8 °C. After due time of sonication, aniline was added to the above solution, after few minutes, oxidant (potassium persulphate) was added slowly and the sonication was continued for another 1 hr at the temperature. After 1 hr, the sonication was stopped and the reaction mixture containing reactants and products was kept in refrigerator for overnight for the completion of reaction. The nanocomposites so obtained were filtered over a Buchner funnel, thoroughly washed with distilled water and ethanol. These nanocomposites were dedoped with aqueous ammonia solution (1M) and again washed thoroughly with distilled water till it gets ammonia free and dried in air oven at 60 °C for 48 hrs. The dried powder samples were then doped with *p*-TSA solution (0.1M), thoroughly washed with distilled water and dried in the above conditions. The dried *p*-TSA doped nanocomposites were used for studies discussed herein this communication.

Table 1: Detail of synthesis of *p*-TSA doped PANI/MoS₂ nanocomposites.

Sample Code	Amount of MoS ₂
ES	0 mole
A1	0.001 mole
A3	0.003 mole
A5	0.005 mole

Note: The amount of CTAB (0.01 mole), aniline (0.1 mole) and potassium persulphate (0.05 mole) in 1000 mL of 1M HCl solution.

3. Characterization:

The *p*-TSA doped nanocomposites containing PANI/MoS₂ so prepared were characterized by advance analytical techniques like Fourier transform infrared spectroscopy (FTIR) by Perkin-Elmer 1725 instrument. Scanning Electron Microscopy (SEM) by (JEOL, JSM 7600F). Electrical conductivity and sensing studies were done using a four-in-line probe d.c. electrical conductivity-meter (PID-200, Scientific Equipments, Roorkee, India).

4. Results and Discussion

4.1 UV-Visible Spectroscopy

Absorbance of selected samples was plotted using UV-Visible spectrometer. The wavelength range was 340-700nm. The two main peaks were obtained at 312nm and at 612nm. The characteristic peaks of pure PANI lies in the range of 280-335 nm and at 638 nm^[6]. MoS₂ nanosheets showed characteristic absorption peaks around 600 and 400 nm^[7,8,9]. An absorption maximum at 444.2 nm was observed for MoS₂/PANI composite, when irradiated with UV light, which is in agreement with the absorption phenomena shown by both MoS₂ and PANI, indicating the formation of inorganic-organic nanocomposite. The peak at 312nm may be attributed to π - π^* transition in PANI, it is also related to the extent of conjugation between the adjacent phenyl rings in the polymer chain. The bands around 440 are due to the polaronic transitions^[10]. The peak at 612nm is due to π -polaron transition between benzenoid and quinoid rings. This absorption

band at 612nm is attributed to the quinoid ring transition (charge transfer from HOMO of the benzenoid ring to LUMO of the quinoid ring)^[11]. This band is dependent on the overall oxidation state of the polymer.

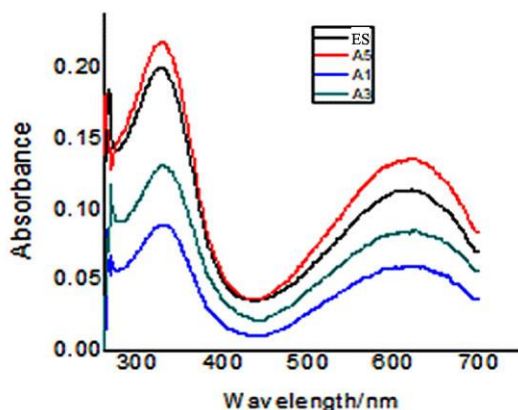


Figure 1. UV-Visible spectra of selected samples.

4.2. Fourier Transform Infrared Spectroscopy (FTIR) Study

The molecular structure MoS₂/PANI nanocomposite was identified using FTIR spectroscopy as shown in Figure 2. The nanocomposite shows a peak at 809 cm⁻¹ which may be assigned to the out of plane C–H in the benzene ring. The peaks at 1130 cm⁻¹ and 820 cm⁻¹ are attributed to the C–H in-plane bending vibration and C–H out-of-plane bending vibration of the benzene ring^[12-14]. The small hump (1118–1135 cm⁻¹) may be assigned to the in-plane C–H vibration. The peak at 1256 cm⁻¹ is attributed to C–N stretching. The peak at 1298 cm⁻¹ is assigned to C–N stretching mode of benzenoid unit. The peaks at 1540 and 1558 cm⁻¹ indicate C=C stretching in the quinone and benzene rings, respectively, the peaks at 1562 and 1498 cm⁻¹ corresponded to the C=C and C=N stretch of quinoid rings and benzenoid structure of PANI^[15]. PANI shows FT-IR characteristic transmission peaks. The peak at 3429 cm⁻¹ is attributed to the presence of C–H stretching vibration. The characteristic peak for Mo–S vibrations which occurs at 480 cm⁻¹, has undergone a shift towards higher wavenumber at 548 cm⁻¹ in case of PANI/MoS₂ nanocomposite. O–H stretching vibrations in MoS₂ were also observed at 1650 cm⁻¹^[16-17]. The major peaks pertained to PANI can be observed in the FTIR spectrum of PANI/MoS₂ samples. In addition, a new peak appeared at 913 cm⁻¹ in the FTIR spectrum of PANI/MoS₂ and PANI composite is due to the presence of MoS₂^[18]. The FTIR characterization results manifest the successful synthesis of as-prepared samples via in-situ chemical oxidative polymerization.

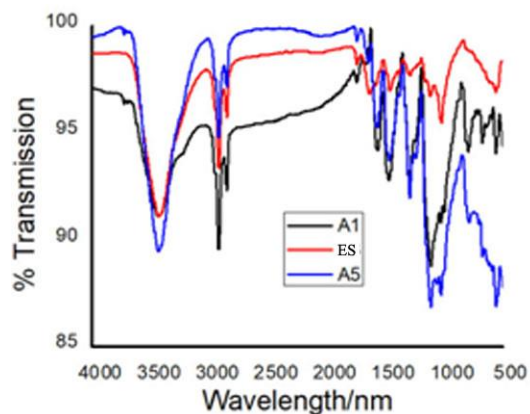


Figure 2. FTIR spectra of selected samples.

3.3. Scanning Electron Microscopy:

Morphology of PANI and PANI/MoS₂ (A5) nanocomposite were observed using electron microscope and are given in the Figure 3. It can be observed from the Figure 3a that as prepared PANI (HCl doped, emeraldine salt) possesses nano fibrillar structure and large amounts of these fibers are also stacked together at different regions thereby exhibiting flaky structure. The morphology of the bulk MoS₂ particles used is given in Figure 3b, the micrograph shows sheet like structure with dimension in the range of few hundred nanometers. It can also be seen in the Figure 3b that bulk MoS₂ particles are agglomerated and the layers of MoS₂ particles are not exfoliated. While on the other hand, in PANI/MoS₂ (A5) nanocomposite, the layers of MoS₂ have been exfoliated and PANI is present within the interlayer space as well as on the surface of MoS₂ (Figure 3c). It might be suggested that the *in-situ* polymerization process under oxidative conditions resulted in expansion-contraction forces which caused exfoliation of the MoS₂ particles. Figure 3 also suggests about the transformation of morphology from flat MoS₂, with increasing percentage of MoS₂. Moreover, porosity is increased by increasing percentage of MoS₂ due to formation of core-shell in PANI/MoS₂ (A5) nanocomposites and uniform distribution of MoS₂ particles and PANI could also be observed in the Figure 3.

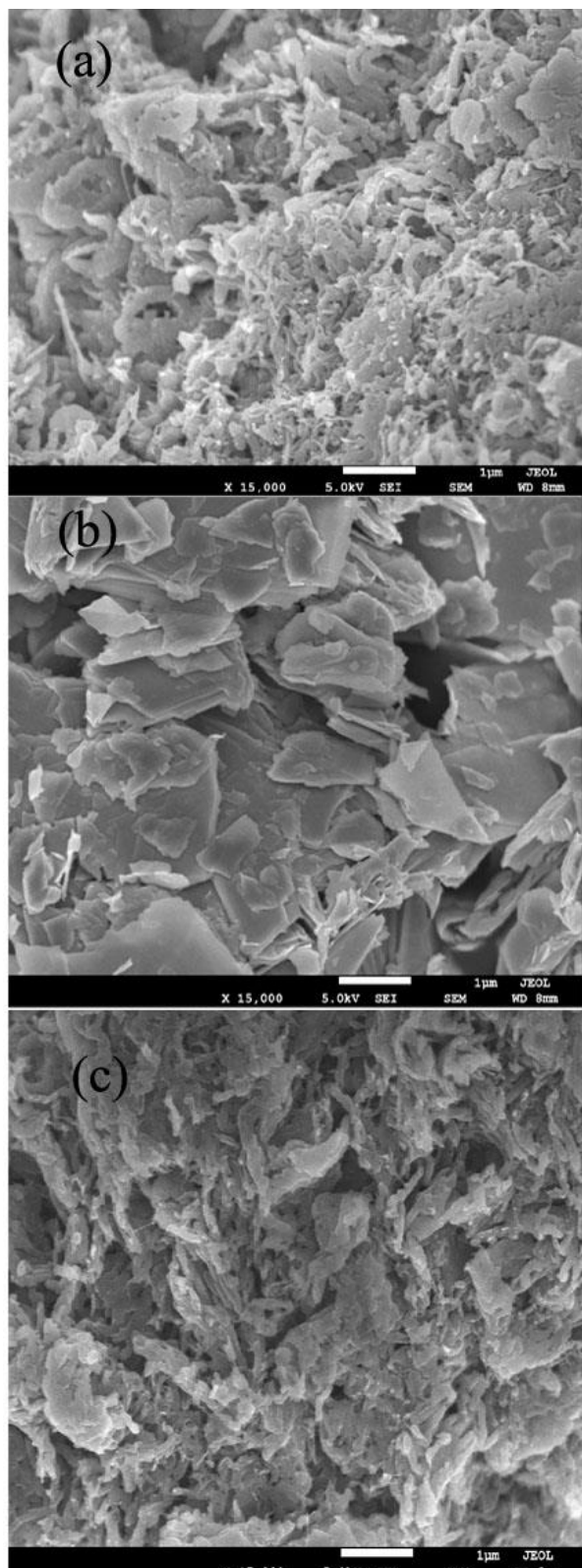


Figure 3. SEM micrographs of (a) HCl doped PANI (b) MoS₂ particles and (c) A5 nanocomposite.

4.4. Electrical Conductivity Study:

Four in line probe method was used to measure the DC electrical conductivity of PANI and PANI/MoS₂ nanocomposites and was found to be in the semiconducting range. The semiconducting nature of the

prepared samples may be seen from the Arrhenius plot (Figure 4) of the electrical conductivity data. Increase in the electrical conductivity was observed with the increase in the amount of MoS₂ in the nanocomposites [5]. Similar cases are also reported by Ansari et al. for various nanocomposites based on PANI and zinc oxide nanoparticles [19,20,21]. It was also observed that the electrical conductivity of PANI/MoS₂ got improved with the load of MoS₂ nanoparticles. Improvement in electrical conductivity of PANI/MoS₂ was due to formation of efficient network of PANI chains and also due to interaction of PANI with MoS₂, which increased the mobility of charge carriers in PANI/MoS₂ nanocomposites leading to increase in electrical conductivity. Ansari et. al., also reported similar increase in the conductivity of PANI after loading it with TiO₂ [22].

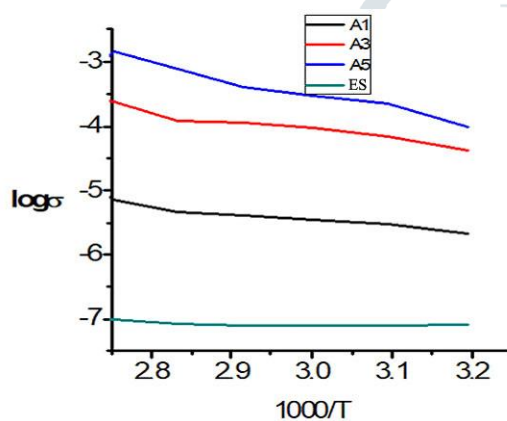


Figure 4. Arrhenius plot of D.C electrical conductivity of nanocomposites.

4.5. Ammonia Sensing Study:

Sensing of ammonia vapour by PANI and PANI/MoS₂ was based on change in electrical conductivity of the samples in presence of atmosphere of ammonia vapour (Figure 5). Though the PANI and PANI/MoS₂ nanocomposites exhibited sensitivity toward the ammonia vapour, the signals obtained from PANI/MoS₂ are more stable and better compared to pure PANI which may be attributed to the synergistic effect of PANI and MoS₂ in nanocomposites samples. Emeraldine salt form of PANI achieves protons from -N-H due to oxidative polymerization. When ammonia vapour interact with the surface of PANI and PANI/MoS₂ it reacts with -NH of PANI and PANI/MoS₂ which gets converted to NH₄⁺ and decreases the conductivity of PANI and PANI/MoS₂. Binding of NH₃ with PANI is reversible. When PANI and its nanocomposites are

exposed to air, NH_3 is released and PANI or PANI/MoS₂ regains its conductivity. PANI gets converted to emeraldine salt form with available $-\text{NH}$ groups, which are responsible for conductivity of PANI. MoS₂ enhances the sensitivity, by increasing the surface area for absorption/adsorption of the gas. The contact sites for NH_3 to be adsorbed/absorbed on PANI/MoS₂ surface are increased with increasing percentage of MoS₂. Moreover, PANI swells up after NH_3 gets absorbed on its surface. This reduces the conductivity of PANI, which is another reason for enhanced sensitivity of the PANI/MoS₂ for NH_3 . Thus the synergistic effect PANI and MoS₂ is clearly visible.

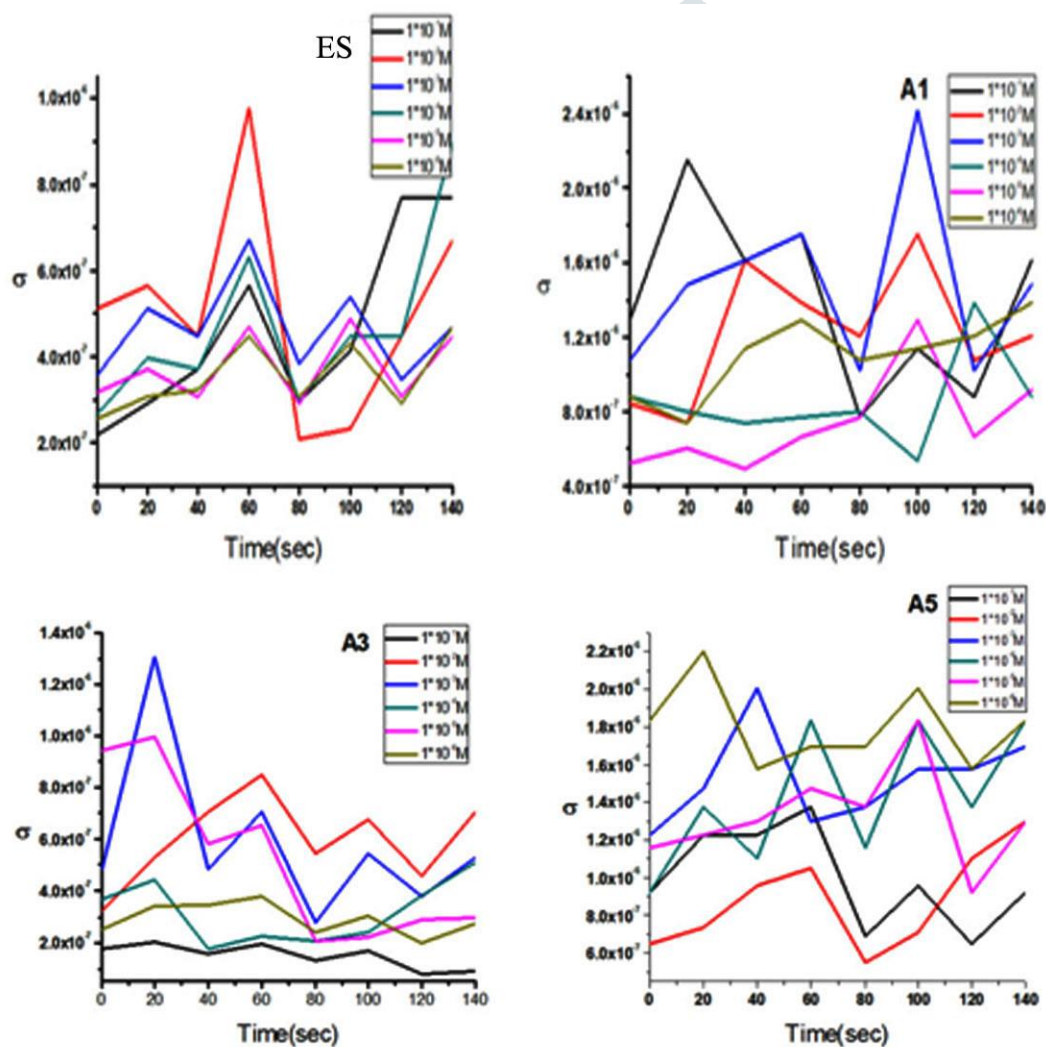


Figure 5. Sensing responses of different samples toward ammonia vapour at room temperature.

5. Conclusions:

We have successfully synthesized PANI/MoS₂ nanocomposites using economical bulk MoS₂ particles by simple route. The SEM micrographs confirm that the layers of the MoS₂ particles are exfoliated during the preparation of nanocomposites. Higher electrical conductivity and stability were observed for PANI/MoS₂ nanocomposites compared to PANI itself. The ammonia vapour sensing study showed that the PANI/MoS₂ nanocomposites are better at sensing the various VOCs in ambient conditions. FTIR data suggest about the existence of interaction between PANI and MoS₂ particles in the nanocomposites which is believed to cause higher electrical conductivity, better stability and ammonia vapour sensing ability of the PANI/MoS₂ nanocomposites.

REFERENCES

1. Q.Y. Cai, M.K. Jain, C.A. Grimes. *Sens. Actuators B* 77(3), (2001) 614-619.
2. M. Xue et al. *Adv. Mater.* 28 (2016) 8265-8270.
3. M. Rashid et al. *Sens. Actuators, B* 208 (2015) 7-13.
4. H. Kebiche et al. (Trans Tech Publications, Zurich, (2013).
5. R. Ahmed, M.O. Ansari, F. Ali, S.P. Ansari, *J. Polym. Mater.* 36 (2019) 243-251.
6. M. Wang, G.D. Li, H.Y. Xu, Y.T. Qian, J. Yang *ACS Appl. Mater. Interfaces* 5, (2013), 1003-1008.
7. L. Yuwen, L. Xu, B. Xue, Z. Luo, Q. Zhang, B. Bao, S. Su, L. Weng, W. Huang, L. Wang, *Nanoscale*, 6(11), (2014) 5762-5769.
8. P.T. Patil, R.S. Anwane, S.B. Kondawar, *Procedia Mater. Sci.* 10(2015), 195–204.
9. F. Hu, W. Li, J. Zhang, W. Meng, *J. Mater. Res. Technol.* 30(2014), 321–327.
10. P. Savitha, D.N. Sathyanarayana, *J. Polym. Sci. Polym. Chem.* (2004) in press.
11. K. Tzou, R.V. Gregory, *Synth. Met.* 53 (1993) 365.

12. X. Lu, Y. Hu, W. Li, Q. Guo, S. Chen, S. Chen, H. Hou, Y. Song *Electrochim. Acta*, 189 (2016), 158-165.
13. R. Oraon, A. De Adhikari, S.K. Tiwari, G.C. Nayak *RSC Adv.*, 5 (2015), 68334-68344.
14. M. Majumder, R.B. Choudhary, A.K. Thakur, I. Karbhal, *RSC Adv.*, 7 (2017), 20037-20048.
15. J. Li, W. Tang, H. Yang, Z. Dong, J. Huang, S. Li, J. Wang, J. Jin, J. Ma, *RSC Adv.* 4(4), (2014), 1988–1995.
16. Y. Gao, C. Chen, X. Tan, H. Xu, K. Zhu, *Colloid Interface Sci.* **476**, (2016), 62–70.
17. L. Hu,,Y. Ren, H. Yang, Q. Xu, *ACS Appl. Mater. Interfaces.* **6**(16), (2014,) 14644–14652.
18. L. Ren, G. Zhang, Z. Yan, L. Kang, H. Xu, F. Shi, Z. Lei, *Z. Mater. Interfaces*, 7 (2015), 28294-28302.
19. SP. Ansari, F. Mohammad, *IUP J. Chem.* 4, (2010), 7-18.
20. S. P. Ansari, F. Mohammad, *ISRN Material Science* (2012), ID 129869, 1-7.
21. S. P. Ansari, F. Mohammad, *SMC bulletin* 9, (2018), 13-19.
22. M.O. Ansari, F. Mohammad, *J. App. Polym. Sci.*, 124, (2012), 4433-4442.