

# Synthesis, Characterization and D. C. Conductivity Studies of Polypyrrole/Molybdenum Trioxide Composites<sup>1</sup>

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**Abstract**—In-situ polymerization of pyrrole (PPy) was carried out with molybdenum trioxide (MoO<sub>3</sub>) in the presence of oxidizing agent ammonium persulphate to synthesize polypyrrole/molybdenum trioxide composites (PPy/MoO<sub>3</sub>) by chemical oxidation method. The PPy/MoO<sub>3</sub> composites were synthesized with various compositions viz., 10, 20, 30, 40 and 50 wt % of MoO<sub>3</sub> in pyrrole. The powder X-ray diffraction (XRD) spectrograph, suggests that they exhibit semi-crystalline behavior. The Fourier Transform Infra-Red Spectroscopy (FTIR) reveals the stretching frequencies are shifted towards higher frequency side. The surface morphologies of these composites using Scanning Electron Microscopy (SEM), show that MoO<sub>3</sub> particles are embedded in PPy chain to form multiple phases. The D.C. conductivities were studied in the temperature range from 30–200°C. The values of the conductivity increase up to 40 wt % MoO<sub>3</sub> in PPy and decreases thereafter. This percent weight is the percolation threshold for these composites. The composites obey percolation theory. The dimensions of molybdenum trioxide particles in the matrix have a greater influence on the conductivity values.

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## INTRODUCTION

Conducting polymer composites with some suitable compositions of one or more insulating materials lead to desirable properties. These materials are especially important owing to their bridging role between the world of conducting polymers [1] and that of nanoparticles. For application of conducting polymers, knowing how these conducting polymer composites will affect the behavior in an electric field is a long-standing problem and is of great importance. The discovery of doping in conducting polymer [2–4] has led to further dramatic increase in the conductivities of such conjugated polymers to values as high as 10<sup>5</sup> S/cm.

Polypyrrole (PPy) is one of the most attractive polymers due to its special transport properties [5]. Molybdenum trioxide is most abundant of any molybdenum compound. It occurs as the rare mineral molybdite. The oxidation state [6] of molybdenum in this compound is +6.

The main applications of MoO<sub>3</sub> are as an adhesive between enamels and metals, as an additive to steel and corrosion-resistant alloys, as a co-catalyst, as a component in electrochemical devices and displays

[7]. Molybdenum trioxide has also been suggested as a potential anti-microbial agent, e.g., in polymers. In contact with water, it forms H<sup>+</sup> ions that can kill bacteria effectively [8].

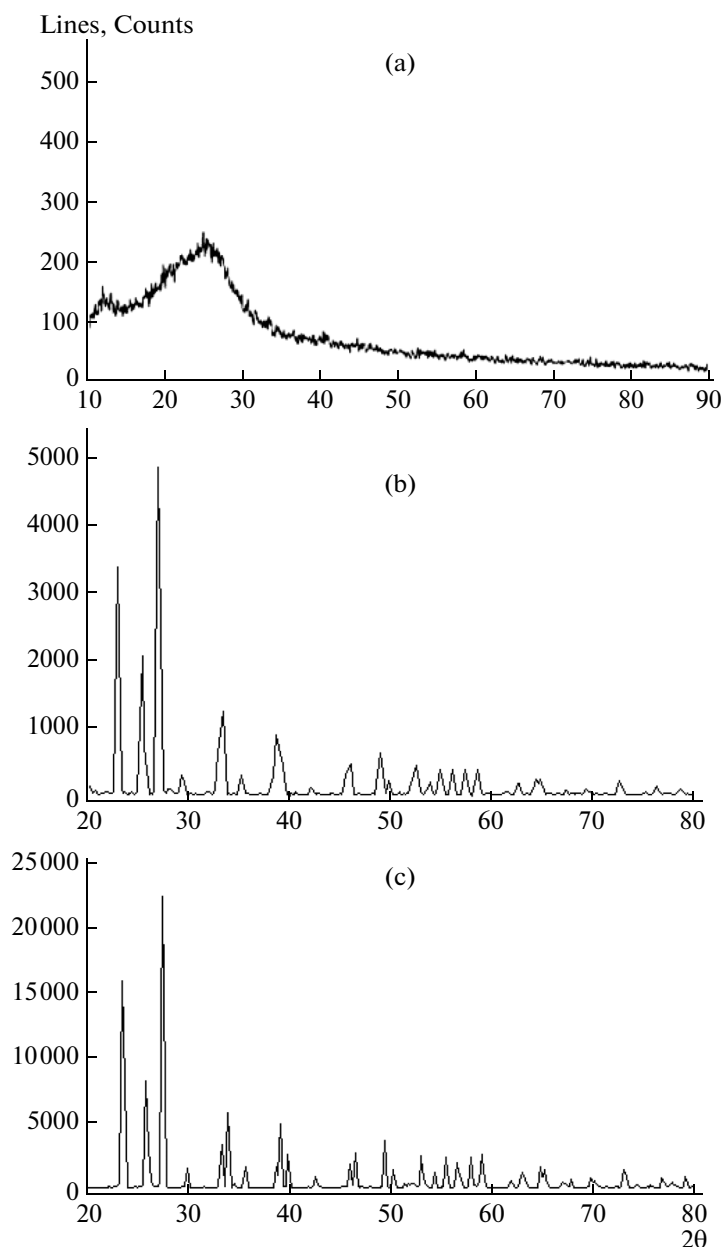
Authors have synthesized pure polypyrrole and its molybdenum trioxide composites by chemical polymerization method in the presence of oxidizing agent. The synthesized pure polypyrrole and its composites were analyzed by characterization techniques such as SEM, XRD and FTIR. The D. C. conductivities of the synthesized samples were studied. The authors report few aspects of above studies in this paper.

## EXPERIMENTAL

### Synthesis

The AR grade [SpectroChem Pvt. Ltd.] pyrrole [9] was purified by distillation under reduced pressure. 0.3 M pyrrole solution was contained in a beaker which was placed in an ice tray mounted on a magnetic stirrer. 0.06 M ammonium persulphate solution was continuously added drop-wise with the help of a burette to the above 0.3 M pyrrole solution. The reaction was allowed for 6 hours under continuous stirring by maintaining a temperature of 0 to 5°C. The precipitated polypyrrole was filtered and dried in hot air oven and subsequently in a muffle furnace at 100°C. The

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**Fig. 1.** X-ray diffraction pattern of (a) pure PPy, (b) PPy/MoO<sub>3</sub> (40 wt %) composite, and (c) MoO<sub>3</sub>.

yield of the polypyrrole was 3.2 g (to be taken as 100 wt %).

For 0.3 M pyrrole solution, 0.32 g (10 wt %) of MoO<sub>3</sub> was added and mixed thoroughly, further 0.06 M ammonium persulphate was continuously added drop-wise with the help of a burette to the above solution to get PPy/MoO<sub>3</sub>wt. 10% composite. Similarly, for 20, 30, 40 and 50 wt %, 0.64, 0.96, 1.28 and 1.6 g of MoO<sub>3</sub> [Sisco Research Lab Ltd] powder [11] is taken and the above procedure is followed to get PPy/MoO<sub>3</sub> composites. The yield of PPy/MoO<sub>3</sub> composites for 10 wt % is 3.84 g, 20 wt % is 4.81 g, 30 wt % is 5.33 g, 40 wt % is 5.72 g and 50 wt % is 4 g.

The pure PPy and PPy/MoO<sub>3</sub> powder was pressed in the form of pellets of 10 mm diameter using hydraulic press. The conducting silver paste was applied to the pellets of synthesized composites to act as electrodes. The D. C. conductivity of the synthesized composites was measured in the temperature range from 30 to 200°C.

#### Characterization

The X-ray diffraction patterns of PPy/MoO<sub>3</sub> composites were recorded on X-ray Diffractometer (Bruker AXS D8 Advance) [12–13, 16–17, 20] using

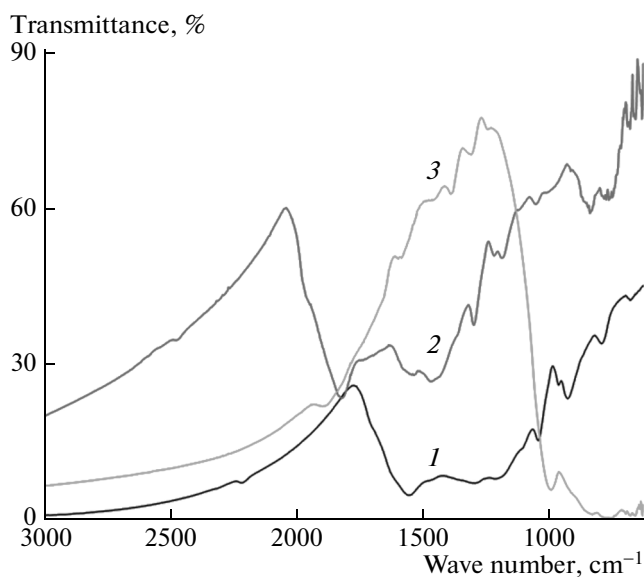


Fig. 2. FTIR spectra of (1) pure PPy, (2) PPy/MoO<sub>3</sub> (40 wt %) composite, and (3) MoO<sub>3</sub>.

CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the  $2\theta$  range  $20^\circ$ – $80^\circ$ . The FTIR [13–14, 16–17, 20] spectra of the PPy/MoO<sub>3</sub> composites were recorded on IR Affinity-1 (Shimadzu, Japan) spectrometer in KBr medium at room temperature. The SEM [14, 17–20] images of PPy/MoO<sub>3</sub> composites were recorded using Scanning Electron Microscope (Jeol 6390LV).

## RESULTS AND DISCUSSION

### XRD Analysis

Figure 1a represents X-ray diffraction pattern of pure PPy, which has a broad peak at about  $2\theta = 25^\circ$ , shows a characteristic peak of amorphous polypyrrole. In the XRD pattern of PPy/MoO<sub>3</sub> (40 wt %) composite, characteristic peaks are indexed by lattice parameter values. Main peaks are observed with  $2\theta$  at  $23.1^\circ$ ,  $25.4^\circ$ ,  $27.0^\circ$ ,  $29.4^\circ$ ,  $32.8^\circ$ ,  $39.4^\circ$ ,  $49.8^\circ$ ,  $52.5^\circ$ , and  $58.5^\circ$  with respect to inter-planar spacing  $d$  3.8, 3.5, 3.3, 3.0, 2.7, 2.2, 1.8, 1.7, and 1.5  $\text{\AA}$ , respectively. Careful analysis of X-ray diffraction of PPy/MoO<sub>3</sub> (40 wt %) composite suggests that it exhibits semi-crystalline behavior. Figure 1c represents XRD pattern of MoO<sub>3</sub> revealing the partial crystalline nature [11, 13, 20].

### FTIR Analysis

The FTIR spectra of pure PPy, PPy/MoO<sub>3</sub> (40%) composite and MoO<sub>3</sub> are shown in Fig. 2. The characteristic stretching frequencies are observed at 1545, 1294, 1182, 1045, 964, 912, 804 and 619  $\text{cm}^{-1}$  may be attributed due to the presence of C=N stretching, N–H bending deformation, C–N stretching and

C–H bending deformation frequencies. In comparison with pure PPy and MoO<sub>3</sub>, the stretching frequencies are shifted towards higher frequency side. This indicates that, there is homogeneous distribution of MoO<sub>3</sub> particles in the polymeric chain due to the Vander Walls interaction between polymeric chain and MoO<sub>3</sub> [13–14, 16–17, 20].

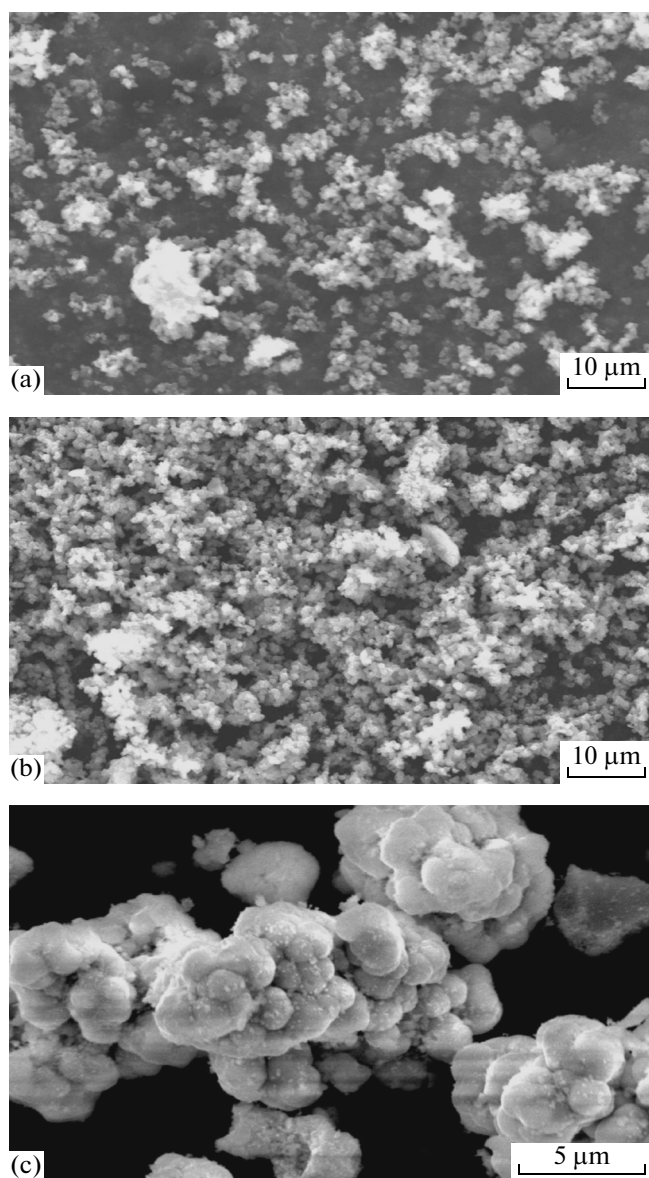
### SEM Analysis

Figures 3a, 3b, and 3c show SEM micrographs of pure PPy, PPy/MoO<sub>3</sub> (40 wt %) composite and pure MoO<sub>3</sub>. It is seen clearly from the SEM micrograph of polypyrrole that, it has clusters of spherical shaped particles. The polypyrrole particles with elongated chain pattern are observed. The chemically polymerized polypyrrole samples prepared with polypyrrole powder have a much larger specific surface than the electrochemically polymerized film. A granular morphology of the polypyrrole particle structures is measured from SEM photographs and is found to be about 1  $\mu\text{m}$  in diameter, which is consistent with other reports [11]. A very high magnification of the SEM images show the presence of hemi spherical nature of polymer as clusters in the composite. MoO<sub>3</sub> particles are embedded in PPy chain to form multiple phases, presumably because of weak inter-particle interactions [11, 20].

### D.C. Conductivity Studies

The variation of D.C. conductivities as a function of temperature for PPy/MoO<sub>3</sub> composites is shown in Fig. 4. It is observed that, the conductivity increases with temperature showing two phases of conductivity. It can also be seen that, the values of conductivities increases up to  $72.27 \times 10^{-6} \text{ S/cm}$  for 30 wt % of MoO<sub>3</sub> in polypyrrole. This may be due to the extended chain length of polypyrrole which facilitate the hopping of charge carriers when the content of MoO<sub>3</sub> is increased up to 30 wt %. Further the conductivity increases rapidly up to  $297.80 \times 10^{-6} \text{ S/cm}$  for 40 wt % composite. The increase in conductivity for 40 wt % may be due to the variation in the distribution of MoO<sub>3</sub> particles which may support more number of charge carriers to hop between favorable localized sites causing increase in conductivity.

The variation of D.C. conductivities as a function of the weight percentage of MoO<sub>3</sub> in PPy at different temperatures is shown in Fig. 5. In all the composites, the conductivity increases with respect to the temperature as compared to pure polypyrrole. The values of the conductivity increase up to 40 wt % MoO<sub>3</sub> in PPy and decreases thereafter. This percent weight is the percolation threshold for these composites. The composites obey percolation theory. Furthermore, a decrease in the conductivity can be observed after 40 wt % and can be attributed to the distribution of

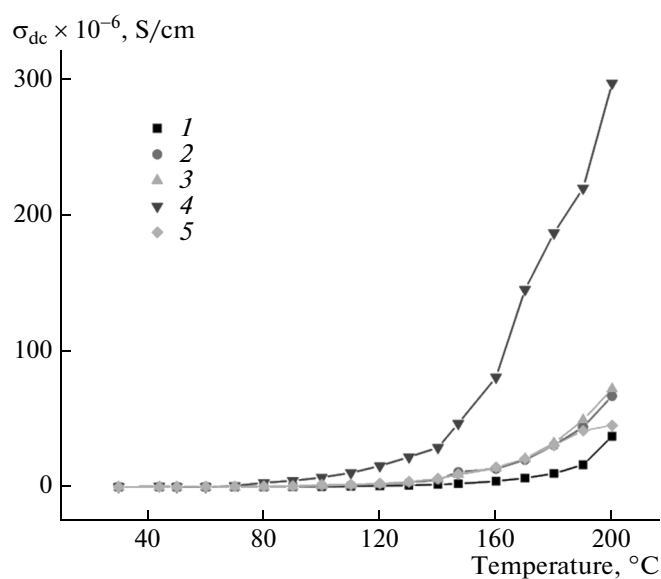


**Fig. 3.** SEM micrographs of (a) pure PPy, (b) PPy/MoO<sub>3</sub> (40 wt %) composite, and (c) MoO<sub>3</sub>.

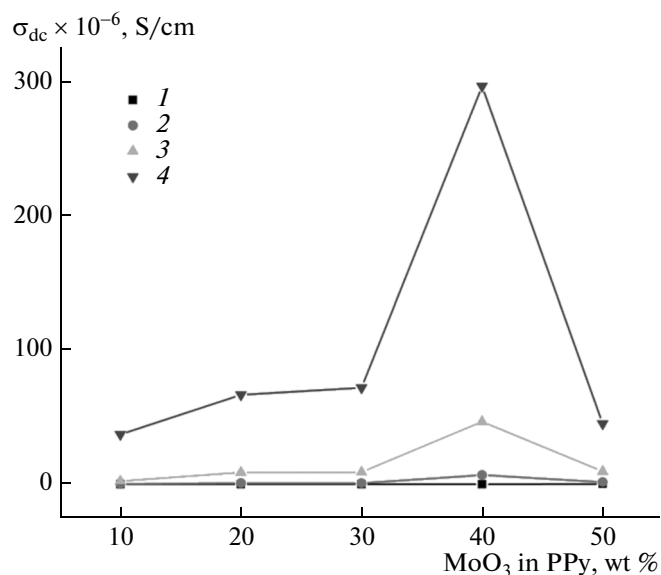
MoO<sub>3</sub> particles of larger grain sizes, which are partially blocking the hopping of charge carriers. Charge trapping in PPy and blends is a general universal feature of these materials [11, 18, 20–22].

## CONCLUSIONS

The polypyrrole/molybdenum trioxide composites were synthesized to tailor the transport properties. Detailed characterizations of the composites were carried out using SEM, XRD and FTIR techniques. The results of D.C. conductivities of polypyrrole/molybdenum trioxide composites show a strong dependence on the weight percent of molybdenum trioxide in



**Fig. 4.** Variation of D.C. conductivity as a function of temperature for PPy/MoO<sub>3</sub> composites: (1) 10, (2) 20, (3) 30, (4) 40, and (5) 50 wt %.



**Fig. 5.** Variation of D. C. conductivity as a function of wt % of PPy/MoO<sub>3</sub> composites at (1) 50, (2) 100, (3) 150, and (4) 200°C.

polypyrrole. Polypyrrole/molybdenum trioxide composites may find applications in sensors.

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## REFERENCES

1. *Handbook of Conducting Polymers, Third Edition, Conjugated Polymers*, Ed. by T. A. Skotheim and J. R. Reynolds, (CRC Press Inc, USA, 2006).
2. M. H. Harun, E. Saion, A. Kassim, N. Yahya, and E. Mahmud, *J. Acoust. Soc. Am.* **2**, 63 (2007).
3. G. Inzelt, *J. Solid State Electrochem.* **15**, 1711 (2011).
4. J. L. Bredas and G. B. Street, *Acc. Chem. Res.* **18**, 309 (1985).
5. "Molybdenum," in *CRC Handbook of Chemistry and Physics*, Ed. by R. D. Lide (Chemical Rubber Publishing Company, 1994), Vol. 4.
6. *Structural Inorganic Chemistry*, Ed. by A. F. Wells (Clarendon Press, Oxford, 1984).
7. F. F. Ferreira, T. G. S. Cruz, M. C. A. Fantini, M. H. Tabacniks, S. C. de Castro, J. Morais, A. de Siervo, and R. Landers, *Solid State Ionics* **357**, 136 (2000).
8. C. Zollfrank, K. Gutbrod, P. Wechsler, and J. P. Guggenbichler, *Mater. Sci. Eng., C* **32**, 47 (2012).
9. R. Ansari, *E-J. Chem.* **3**, 186 (2006).
10. V. K. Gade, D. J. Shirale, P. D. Gaikwad, K. P. Kakde, P. A. Savale, H. J. Kharat, B. H. Pawar, and M. D. Shirat, *Int. J. Electrochem. Sci.* **2** (3), 270 (2007).
11. M. V. Murugendrappa and M. V. N. Ambika Prasad, *J. App. Polym. Sci.* **103**, 2797 (2007).
12. Y. Kobayashi, S. Ishida, K. Ihara, Y. Yasuda, T. Morita, S. Yamada, *Colloid Polym. Sci.* **287**, 877 (2009).
13. C. Basavaraja, Y. Veeranagouda, K. Lee, T. K. Vishnuvardhan, R. Pierson, D. S. Huh, *J. Polym. Res.* **17**, 233 (2010).
14. A. Reung-U-Rai, A. Prom-Jun, W. Prissanaroon-Ouajai, and S. Ouajai, *J. Met., Mater. Miner.* **18** (2), 27 (2008).
15. A. B. Kaiser and S. A. Rogers, *Mol. Cryst. Liq. Cryst.* **415**, 115 (2004).
16. Q. Luo, X. Li, D. Wang, Y. Wang, *J. An, J. Mater. Sci.* **46**, 1646 (2011).
17. L. Ai and J. Jiang, *J. Mater. Sci.: Mater. Electron.* **21**, 410 (2010).
18. L. Gang, L. Xia, S. Xinghua, Y. Jian, and H. E. Jiasong, *Front. Chem. Eng. China* **2** (2), 118 (2007).
19. K. Jradi, B. Bideau, B. Chabot, and C. Daneault, *J. Mater. Sci.* **47**, 3752 (2012).
20. T. K. Vishnuvardhan, V. R. Kulkarni, C. Basavaraja, and S. C. Raghavendra, *Bull. Mater. Sci.* **29** (1), 77 (2006).
21. A. N. Papathanassiou, J. Grammatikakis, S. Sakkopoulos, E. Vitoratos, and E. Dalas, *J. Phys. Chem. Solids* **63**, 1771 (2002).
22. S. Sakkopoulos, E. Vitoratos, J. Grammatikakis, A. N. Papathanassiou, and E. Dalas, *J. Mater. Sci.* **37**, 2865 (2002).