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Experimental Studies on Current, Susceptance, Impedance and Electrical Modulus of Polypyrrole/Molybdenum Trioxide Composites

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Abstract

Polypyrrole/molybdenum trioxide composites (PPy/MoO₃) were synthesized by chemical oxidation method, which involved the polymerization of pyrrole (PPy) with molybdenum trioxide (MoO₃). This process involved ammonium persulphate which acted as an oxidizing agent. Diverse compositions of MoO₃ such as 10, 20, 30, 40 and 50 wt. % in pyrrole were used to synthesize PPy/MoO₃ composites. Scanning Electron Microscopy (SEM) image of the above composites has revealed the presence of multiple phases comprising of MoO₃ particles embedded in PPy chain. The observed increase in current could be due to hopping of a large number of charge carriers between favorable localized sites and is attributed to change in the distribution pattern of MoO₃ particles. The present study also involved the measurement of susceptance, impedance and electrical modulus, and has disclosed the major influence of dimensions of MoO₃ particles present in the matrix on all the properties. The

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composites discussed in the present study may throw some light on their applications in various areas namely humidity sensor, micro power generator, dielectrics and as semiconductors.

Keywords: Molybdenum Trioxide; Composites; Modulus; Impedance.

1. Introduction

Conducting polymer composites are found to be very significant and interesting ones as they link conducting polymers and nanoparticles. Several desirable and pioneering properties of conducting polymer composites can be extracted by using their appropriate composition with one or more insulating materials [1]. The study of the behavior of conducting polymers in an electric field has aroused interest among the researchers, as it is a long standing problem and very important in terms of the possible applications. Also, a very high conductivity of the order of 10^5 S cm^{-1} has been achieved in the case of such conjugated polymers after the discovery of doping in conducting polymer [2-4].

Polypyrrole (PPy) has shown special transport properties and hence is regarded as one of the most attractive polymers[5]. Molybdenum trioxide used in the present investigation is available as a rare mineral molybdite and is the most abundant among all molybdenum compounds, with the oxidation state [6] of molybdenum being +6.

MoO_3 finds numerous applications such as an adhesive between metals and enamels, as a component in electrochemical devices and displays, and as a co-catalyst [7]. MoO_3 has been reported to be a potential anti-microbial agent and has also been found to form H^+ ions when in contact with water. The H^+ ions thus created can kill bacteria efficiently [8].

In view of the wide range applications of polypyrrole/molybdenum trioxide composites (PPy/ MoO_3) in different areas such as humidity sensor, dielectrics, micro power generator, and as semiconductors, we have synthesized them by employing chemical oxidation method. The synthesis involved the variation of wt. % of MoO_3 in pyrrole. Scanning Electron Microscopy (SEM) was used to

document the surface morphologies of the composites synthesized. The investigation on DC conductivity, thermo electric power, AC conductivity, dielectric properties and humidity sensor properties were carried out on the synthesized composites and the results were reported elsewhere [9-10]. However, in the present case, some properties of composites such as susceptance, impedance and electrical modulus are reported.

2. Experimental Methodology

2.1 Synthesis

2.1.1 Synthesis of Polypyrrole

0.06 M ammonium persulphate [11] (oxidative agent) was prepared using 13.69 g of ammonium persulphate weighed (up to second decimal) with a digital balance and transferred to a conical flask (Borosil: 250 ml). 100 ml of distilled water was measured by using a measuring jar (Borosil: 100 ml) and transferred to the same conical flask. The conical flask was shaken well several times to obtain the required 0.06 M ammonium persulphate solution. The above solution was filled in a burette attached to a laboratory stand for use in further processes.

0.3 M pyrrole [12] monomer i.e. 10.4 ml was measured using a burette and transferred into a beaker (Borosil: 1000 ml). 500 ml of distilled water was measured using a measuring jar and transferred into the same beaker. The beaker was shaken well to obtain a properly mixed pyrrole monomer solution. The beaker was kept on a plastic tray and ice-flakes (obtained by a continuous automatic ice-maker) were placed around the beaker. The temperature was maintained between 0° and 5° C. Then the tray was placed on a magnetic stirrer and a magnetic bead was dropped into the beaker, which helped the solution to rotate either in the clockwise or the anticlockwise direction, by means of a selection switch. The selected RPM (rotation per minute) of the magnetic bead ranged from 1500 to 2200.

Ammonium persulphate solution was added to pyrrole solution drop wise to initiate the chemical reaction i.e. polymerization. The polymerization thus started gradually turned the pyrrole solution

black. This process was continued for 5 hours until a precipitate was formed.

A filter paper was appropriately cut to snugly fit into the Buckner funnel. The polypyrrole precipitate solution was slowly poured into the Buckner funnel, which was kept in a side neck conical flask. Water was absorbed from the precipitate by using a vacuum pump. The precipitate thus obtained was transferred to a petri dish and kept in a hot air oven which was maintained at a maximum temperature of 100° C. The precipitate was dried for approximately 8 to 10 hours and later ground using an agate mortar. The ground powder was poured into a crucible and kept in the muffle furnace to complete the drying process. The dehumidification of the black polypyrrole precipitate was continued for about 4 to 6 hours in the muffle furnace at a maximum temperature of 100° C. The completely dried black polypyrrole powder was then removed from the muffle furnace and ground into a finer powder. The weight of the black polypyrrole powder thus obtained was 3.17 g. It was labeled as sample 1 of the polypyrrole.

Similarly, the above procedure was employed to get the black polypyrrole powder which was labeled as sample 2 which weighed 3.23 g. Average weight of both samples of the pure polypyrrole powders was taken as the weight of the synthesized polypyrrole sample which was 3.20 g. This was done for experimental optimization of the polypyrrole.

2.1.2 Synthesis of Polypyrrole/Molybdenum Trioxide Composites

To obtain PPy/MoO₃ (10 wt. %) composite, a 0.3 M pyrrole solution was taken and 0.32 g (10 wt. %) of molybdenum trioxide [13] was added to it and mixed thoroughly. This was followed by a continuous and drop-wise addition of 0.06 M ammonium persulphate to the mixture of 0.3 M pyrrole and 0.32 g molybdenum trioxide using a burette. In order to prepare PPy/MoO₃ composites of other wt. % (20, 30, 40 and 50), MoO₃ powder of weights 0.64, 0.96, 1.28 and 1.6 g (Sisco Research Lab Ltd.) was added to the pyrrole solution of wt. % 20, 30, 40 and 50 respectively and the above mentioned procedure was repeated. The final yields of the PPy/MoO₃ (10, 20, 30, 40 and 50 wt. %)

composites thus obtained were 3.84, 4.81, 5.33, 5.72 and 4.00 g respectively.

2.2 Characterization

A Scanning Electron Microscope (Jeol 6390LV) was employed to record the SEM images of PPy/MoO₃ composites. The 6500B series of Precision Impedance Analyzers (Wayne Kerr-U.K. Electronics Pvt. Ltd., India) provided impedance measurements of the components, in the 20 Hz to 1MHz.

3. Results and Discussion

3.1 SEM Analysis

The SEM analysis of the composites studied is carried out and the SEM photos of pure PPy, PPy/MoO₃ composites of different wt. % and MoO₃ are shown in Figures 1(a), 1(b-e) and 1(f) respectively. The SEM photo of polypyrrole has revealed the presence of clusters of nearly spherical shaped particles and the chain pattern of polypyrrole particles here and there. The polypyrrole samples prepared with polypyrrole powder by means of chemical polymerization are found to have a much larger specific surface when compared with electrochemically polymerized film. The granular morphology of the structure of polypyrrole particles is found to be about 1 μm in diameter as obtained from SEM photographs. This observation is consistent with the literature values[9-10, 14]. The SEM images, show the presence of almost spherical nature of polymer as clusters in PPy/MoO₃ composites. The MoO₃ particles are found to be embedded in PPy chain, owing to weak inter-particle interactions and the cauliflower shaped particles of MoO₃[9-10, 14] are depicted in Figure 1.f.

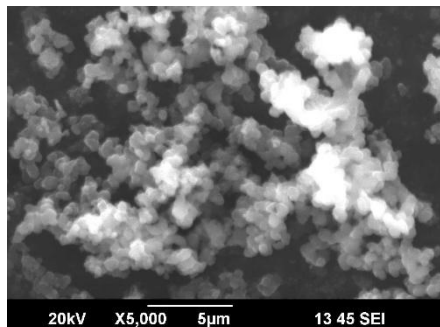


Figure 1(a) SEM photo of pure PPy

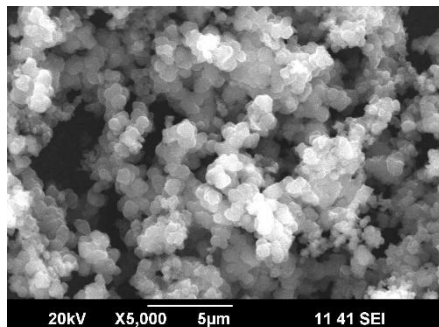


Figure 1(b) SEM photo of PPy/MoO₃ (10%)

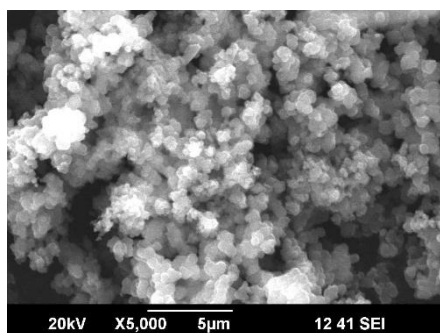


Figure 1(c) SEM photo of PPy/MoO₃ (20%)

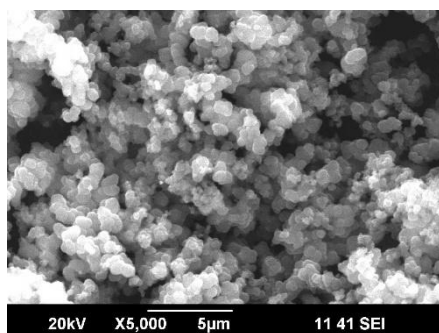


Figure 1(d) SEM photo of PPy/MoO₃ (30%)

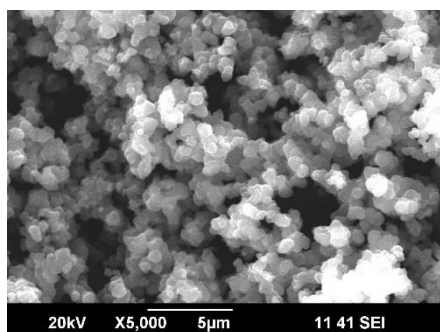


Figure 1(e) SEM photo of PPy/MoO₃ (40%)

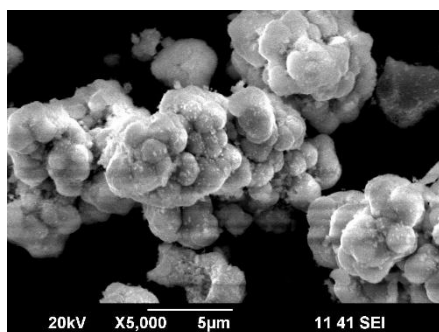


Figure 1(f) SEM photo of MoO₃

3.2 XRD Analysis

The X-ray diffraction pattern of pure PPy with a broad peak at $2\theta = 25^\circ$ and a characteristic peak of amorphous polypyrrole is shown in Figure 2(a). The lattice parameter values are used to index the

characteristic peaks in the XRD pattern of PPy/MoO₃ (40 wt. %) composite[Figure 2(b)]. However, the major peaks are observed with 2θ at 23.1°, 25.4°, 27.0°, 29.4°, 32.8°, 39.4°, 49.8°, 52.5° and 58.5° with respect to inter-planar spacing (d) 3.8 Å, 3.5 Å, 3.3 Å, 3.0 Å, 2.7 Å, 2.2 Å, 1.8 Å, 1.7 Å and 1.5 Å respectively. A cautious examination of X-ray diffraction of PPy/MoO₃ (40 wt. %) composite indicates their semi-crystalline nature. The XRD pattern of MoO₃ indicates their partial crystalline nature as shown in Figure 2(c)[9-10].

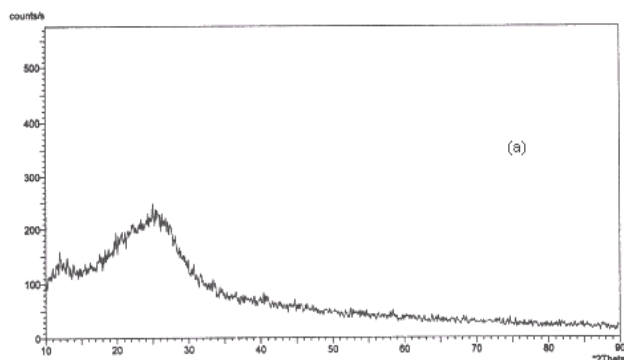


Figure 2(a) X-ray diffraction pattern of pure PPy

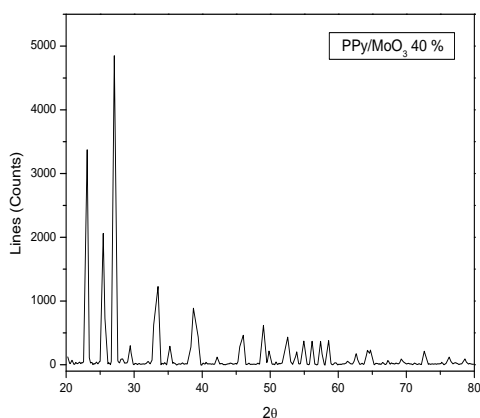
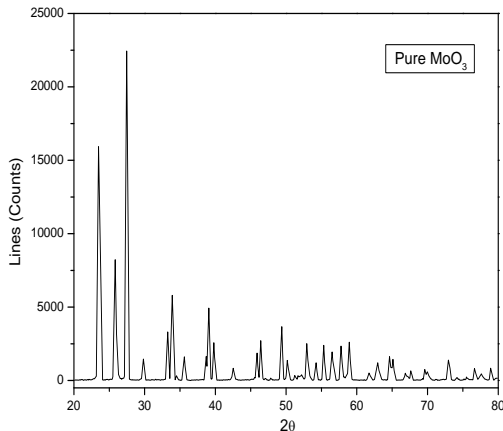


Figure 2(b) X-ray diffraction pattern of PPy/MoO₃ (40%) composite

Figure 2(c) X-ray diffraction pattern of MoO₃

3.3 Current and conductivity Studies

The plot of current versus temperature, at constant voltage (2 V) is shown in Figure 3(a). From the figure, it is observed that the current remains almost a constant till a temperature of 120°C and with the further increase in temperature beyond 120°C, the current increases exponentially till 200°C. The variation in current for PPy/MoO₃ composites may be attributed to the way the MoO₃ particles are distributed and this type of MoO₃ particle distribution may support the hopping of charge carriers between favorable localized sites in a larger number. This indicates that there is a larger influence of dimensions of molybdenum trioxide particles present in the matrix on the value of current. Figure 3(b) depicts the variation in current with weight percent of MoO₃ in PPy at various temperatures. It is also observed that 20 weight percent of MoO₃ in PPy has the highest current among all the composites. This is an indication that the percolation theory for composites is satisfied [15-16].

The current versus voltage plot is as shown in Figure 3(c). From the figure it is clear that as voltage increases current also increases showing the metallic behavior for the PPy/MoO₃ composites. The I-V characteristic of PPy/MoO₃ composites becomes strongly temperature dependent at higher temperatures and the linearity of the I-V characteristics is found to increase with the increase in

temperature. The variation in current for PPy/MoO₃ composites may be attributed to the way the MoO₃ particles are distributed and this type of MoO₃ particle distribution may support the hopping of charge carriers between favorable localized sites in a larger number. The current versus weight percent of MoO₃ in PPy at different voltages is shown in Figure 3(d). The percolation theory is satisfied here also [15-16].

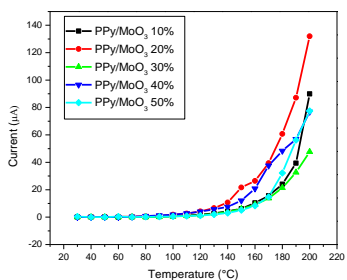


Figure 3(a) Current vs Temperature Weight Percent of MoO₃

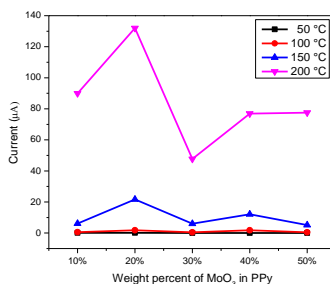


Figure 3(b) Current versus weight percent of MoO₃ at Constant Voltage in PPy at various Temperatures

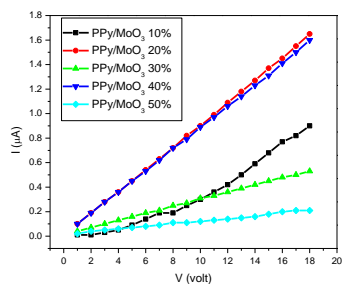


Figure 3(c) Current versus Voltage at Room Temperature

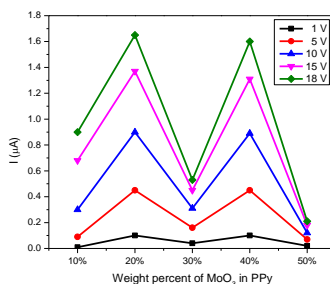


Figure 3(d) Current versus Weight Percent of MoO₃ in PPy at different voltage

Figure 3(e) shows the variation in D.C. conductivity with temperature for PPy/MoO₃ composites and the conductivity is found to increase exponentially with the increase in temperature in the higher temperature region. Also, the value of conductivity is found to increase to $298 \times 10^{-6} \text{ S/cm}$ for 40 weight percent of MoO₃ in polypyrrole and decrease subsequently. This could be because of the extended chain length of polypyrrole, which assisted the charge carriers to hop once the content of MoO₃ was increased to 40

weight percent. The increase in the conductivity of PPy/MoO₃ (40 %) composite is because of the variation in the distribution of MoO₃ particles, which in turn could be due to hopping a large number of charge carriers between favorable localized sites. However, the decrease in conductivity noticed for the PPy/MoO₃ (50 %) may be due to the trapping of charge carriers in the polymer chain. PPy and its blends are known for charge trapping in them and this property is a universal feature of these materials. The conductivity values of PPy/MoO₃ (10, 20, 30 & 40 %) composites at 200° C are found to be 37×10^{-6} S/cm, 67×10^{-6} S/cm, 72×10^{-6} S/cm and 46×10^{-6} S/cm respectively.

The variation in D.C. conductivity with different weight percentage of MoO₃ in PPy at different temperatures is shown in Figure 3(f). It is interesting to know that the values of conductivity increase in the case of 40 wt % MoO₃ in PPy. This particular point acts as percolation threshold indicating that the composites follow percolation theory. However, after 40 weight percent, the conductivity is found to decrease and this trend is supposed to be due to the distribution of bigger grain sized MoO₃ particles. These particles block the hopping of charge carriers.

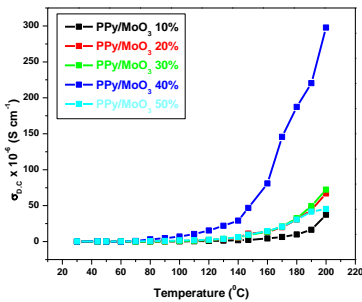


Figure 3(e) PPy/MoO₃ composites: D.C. conductivity versus temperature

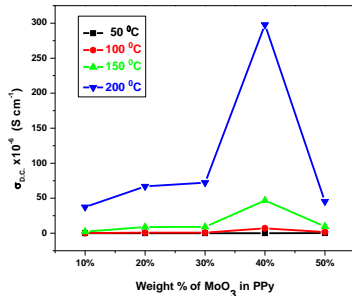
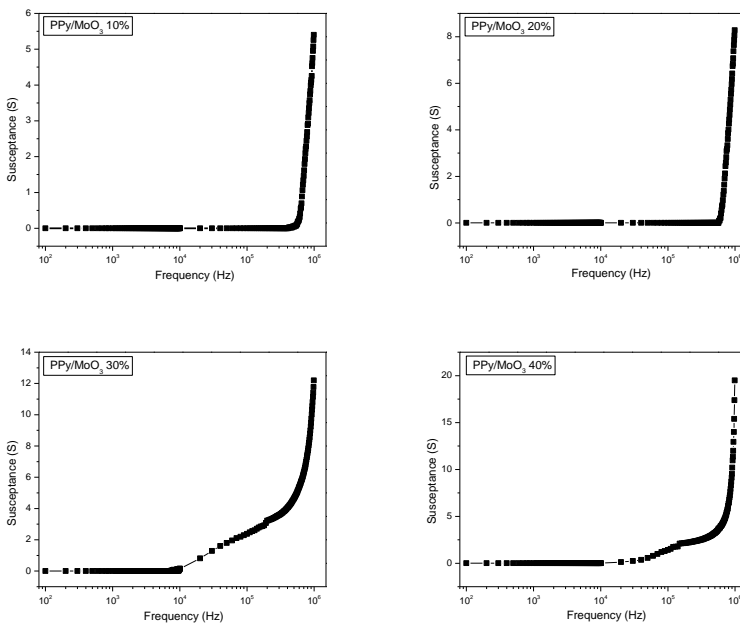


Figure 3(f) D.C. Conductivity versus weight percent of MoO₃ in PPy at different temperatures

3.4 Susceptance Study

The variation in susceptance with frequency of PPy/MoO₃ composites is as shown in Figure 4. The susceptance is found to be constant at low frequency range revealing the fact that lesser number of mobile charges is available for hopping from one site to another site. The susceptance is found to increase at high frequency range revealing that, very large numbers of mobile charges are available and support the charge carriers to hop from one site to another site due less conjugation length. The PPy/MoO₃ (40 %) composite has high susceptance (19.49 S) compared to rest of the composites. It is confirmed in Figure 3 in which the susceptance is plotted against different weight percent of MoO₃ added to PPy.



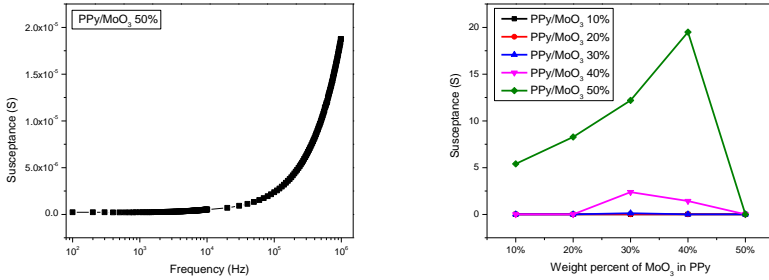


Figure 4 Susceptance versus Frequency and Susceptance versus weight percent of MoO₃ in PPy of PPy/MoO₃ Composites

3.5 Impedance Study

The impedance versus frequency plot of PPy/MoO₃ composites is as shown in Figure 5(a). From the figure, it is confirmed that, the PPy/MoO₃ (50 %) composite has highest impedance. It is also confirmed from Figure 5(b).

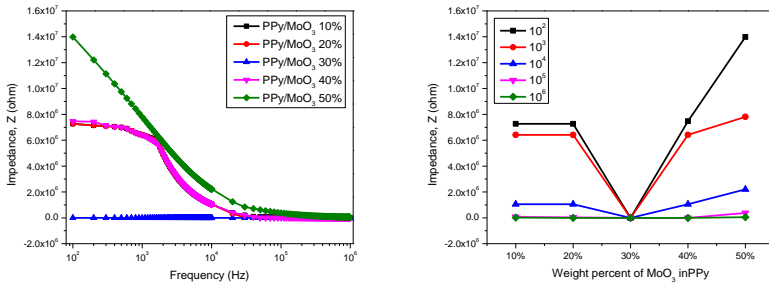


Figure 5(a) Impedance versus Frequency of PPy/MoO₃ Composites

Figure 5(b) Impedance versus Weight Percent of MoO₃ in PPy of PPy/MoO₃ Composites

3.6 Electrical Modulus Study

The plots of Electrical modulus (Real and Imaginary) versus frequency of PPy of the PPy/MoO₃ composites are shown in Figure 6(a) and Figure 6(b) respectively. The electrical modulus thus determined is found to be very high at lower frequency range, but becomes constant at higher frequency range. The orientation of mobile charges is quite easy at lower frequency range due to the field effect and less conjugation length. It will be reversed at higher frequency range due to large conjugation length. The PPy/MoO₃

(30 %) composite has high electrical modulus (Real and Imaginary) which is also confirmed in Figure 6(a) and Figure 6(b) respectively when electrical modulus (Real and Imaginary) is plotted against weight percent of MoO₃ in PPy of PPy/MoO₃ composites.

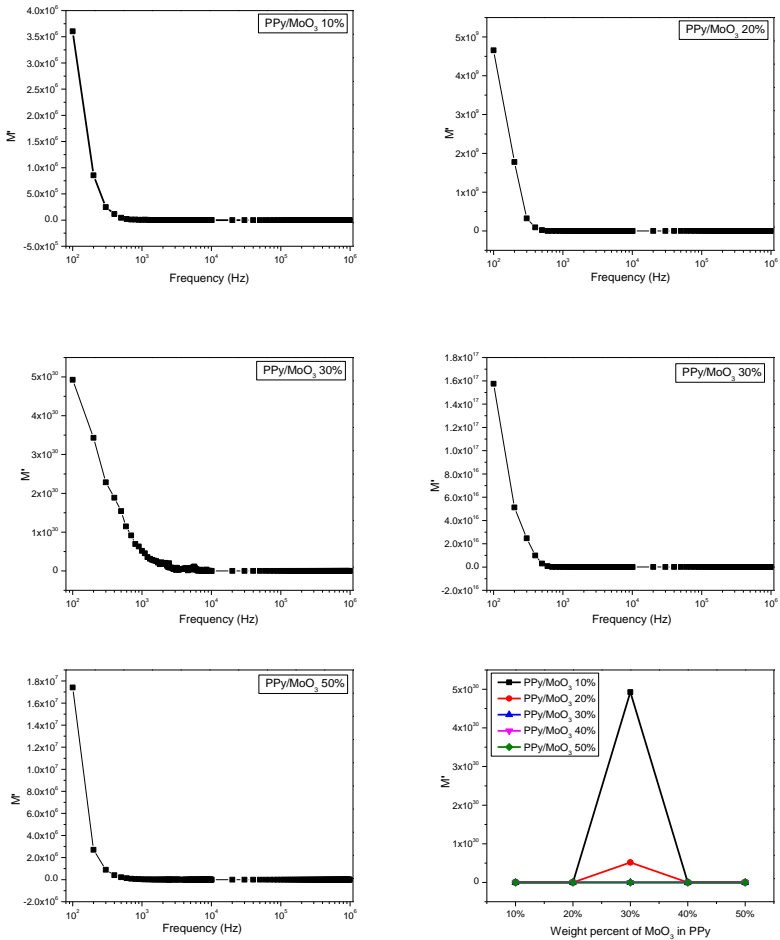


Figure 6(a) Electrical Modulus (Real) versus Frequency and Electrical Modulus (Real) versus Weight Percent of MoO₃ in PPy of PPy/MoO₃ Composites

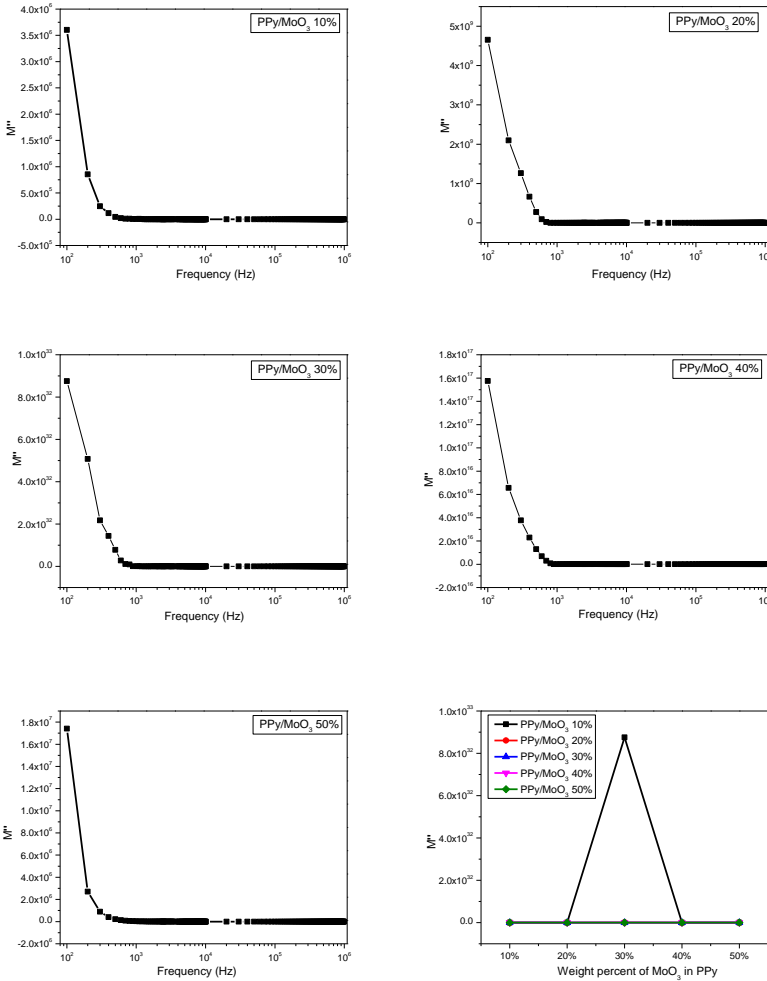


Figure 6(b) Electrical Modulus (Imaginary) versus Frequency and Electrical Modulus (Imaginary) versus Weight Percent of MoO₃ in PPy of PPy/MoO₃ Composites

4. Summary

The polypyrrole/molybdenum trioxide composites were synthesized in order to modify their transport properties. SEM technique was used to obtain the detailed characterization of the composites. The physical properties of polypyrrole/molybdenum trioxide composites studied in the present investigation show their dependence on the weight percent of molybdenum trioxide in polypyrrole to a greater extent. This behavior of

polypyrrole/molybdenum trioxide composites is on the lines of percolation theory. The composites may find applications in humidity sensor, micro power generator, dielectrics and as semiconductors.

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