International Journal of Current Science Research and Review
ISSN: 2581-8341
Volume 05 Issue 03 March 2022
DOI: 10.47191/ijcsrr/V5-i3-19, Impact Factor: 5.825
IJCSRR @ 2022
www.ijcsrr.org

Effect of Molar Ratio on Structure of PPy-PVA Composite Film

Miss. Niyanta V. Dave[1], Dattatray. M. Nerkar[2], Narendra R. Kishan[3]
[1] Shri Jagdishprasad Jhabarmal Tibrewala University, Rajasthan-333 001, India
[2,3] Sathaye College, Dixit Road, Vile Parle (East), Mumbai 400057, India

ABSTRACT: A chemical oxidation method is used to synthesize pyrrole with ferric chloride as oxidant to prepare polypyrrole. Multiple chemical oxidations were carried out using various molar ratios. A stock solution of PolyVinyl Alcohol was produced to form composites of polymers. The PPy-PVA composites were achieved with the help of solution casting method to obtained free standing films. These composites films were characterized using SEM, FTIR and XRD techniques. The result of SEM, FTIR, and XRD reveals that the surface morphology varies as per the molar ratio. Along with the surface morphology molar ratio the conductivity of composite films was studied in the temperature range 303 K-343 K using two probe conductivity method. It has been observed that molar ratio also plays an important role in the conductivity of composite films.

KEYWORDS: Composites, Chemical Oxidation, FTIR, Stock Solution, SEM, XRD.

INTRODUCTION

Many inventions were done in the field of polymers using different polymers such as polyaniline, polythyophine, polypyrrole etc. from past few decades [1, 2]. The interesting part of these inventions was how to prepare good conducting polymers with high flexibility and reliability over the metals. Among the mentioned polymers polypyrrole attract more attention because of its preparation technique, high stability, high conductivity and normal mechanical properties. It also has many commercial applications [3- 12]. To improve the properties of polypyrrole, PPy composites with available polymers play a major role. The blends of polymers improve mechanical and electrical properties according to their mixture. Many such insulating polymers are available but polyvinyl alcohol [13] is one of the best insulating polymers due to its water solubility and availability.

In this article we studied the free standing PPy and PVA composite films which are flexible in nature and prepared with the chemical oxidation of polymerization of pyrrole and solution casting technique. The 4% PVA is mixed with the pyrrole of different volume to weight proportion and molar ratio. These black color films were prepared with different molar ratio to understand effect of molar ratio on the mechanical properties of the composite films [14].

MATERIALS AND EXPERIMENTAL METHOD

Pyrrole was obtained from Spectrochem Pvt. Ltd, further it was double distilled at 131^{0}C and kept in fridge before synthesis. Polyvinyl alcohol (PVA) was obtained from S. D. Fine Chem. Ltd., Mumbai. The powder contained a degree of hydrolysis of 86-89 % and M.W. was 85000–124000.

Using chemical oxidation polymerization technique of pyrrole (PPy) Polypyrrole-polyvinylalcohol (PPy-PVA) composites was formed. In general, a PVA powder was dissolved in distilled water by taking 4% w/v ratio and prepared a PVA stock solution. In this stock solution, double distilled pyrrole was added with different v/w ratio of polyvinyl alcohol. Here ferric chloride was used in different proportion as oxidizing agent in the polymerization of pyrrole. The reaction of polymerization of pyrrole takes place on the PVA-transition-metal salt film. This reaction was proposed by Benseddik et al [15-16] as follows,

$$nC_4H_5N(PVA)_n + 2.25n\,FeCl_3 \rightarrow [C_4H_3N^{0.25+}Cl^{0.25-}]_n + 2n\,HCl + 2.25nFeCl_2(H_2O)$$

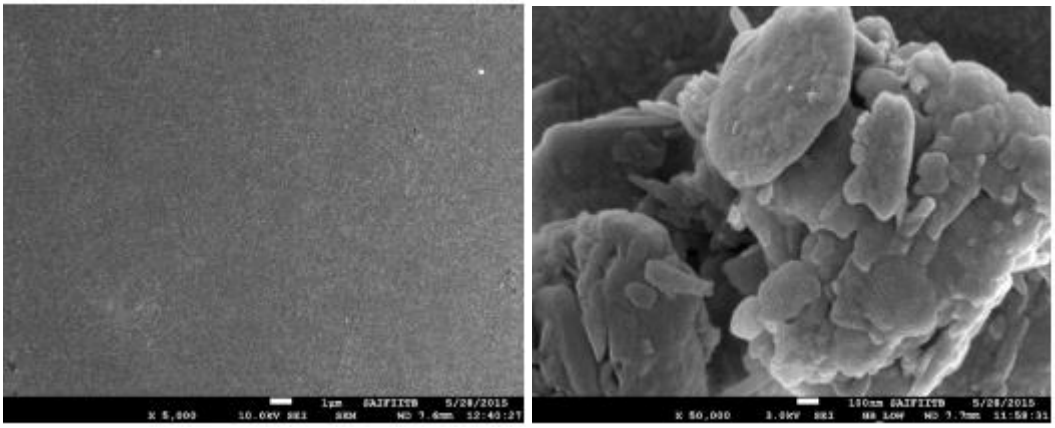
RESULT AND DISCUSSION

SEM Results:-

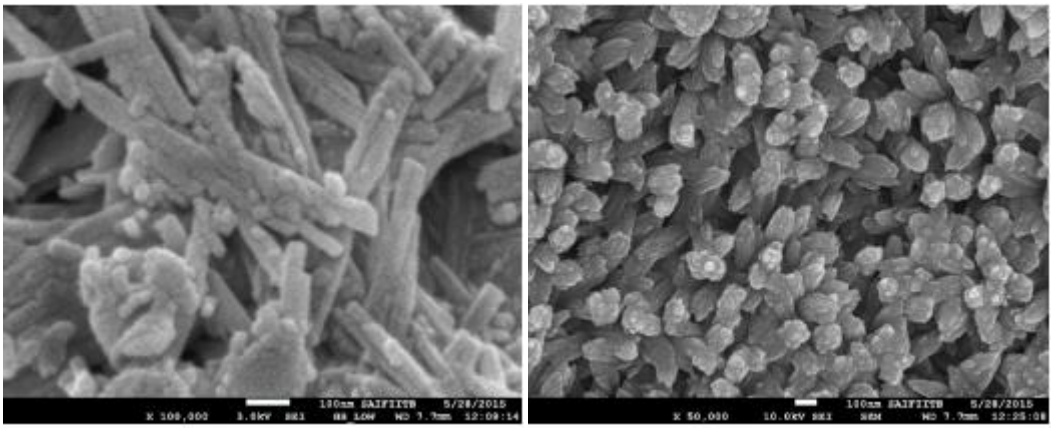
The SEM micrographs for PPy PVA composite films of different molar ratio are shown in the following fig.1 (a) to (g). These micrographs give an understanding of variations in the morphology of composite films according to their molar ratio.

International Journal of Current Science Research and Review
ISSN: 2581-8341
Volume 05 Issue 03 March 2022
DOI: 10.47191/ijcsrr/V5-i3-19, Impact Factor: 5.825
IJCSRR @ 2022
www.ijcsrr.org

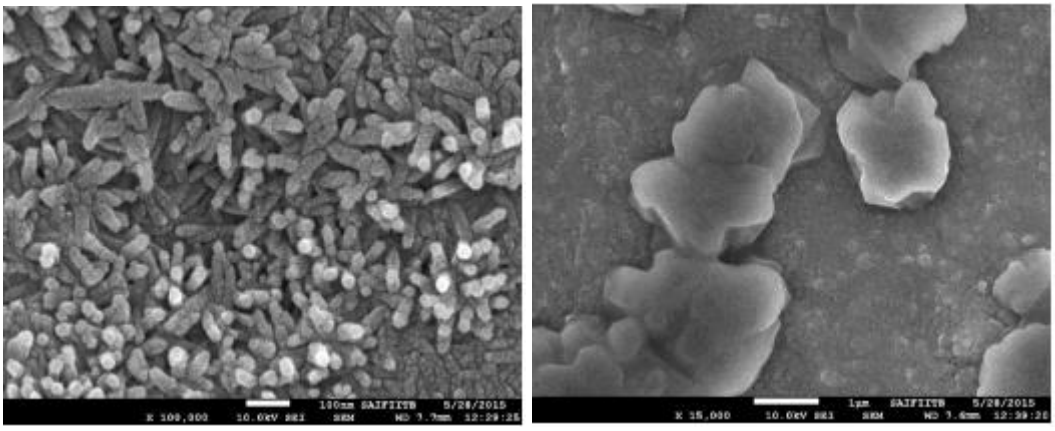
From the observations of SEM figures it is clear that pure PVA film has uniform surface with small globule or flake like structure as doping is added to pure PVA in different proportion then the surface uniformity vanishes gradually as seen in the figure. As molar ratio of doping increases surfaces were seen with some irregular polymer crystal shapes and rod like nanocrystal structure with diverse length and width. The mean length of these nanocrystals is ranging from 110 nm to 340 nm and average width is ranging from 10 nm to 35 nm for molar ratio 0.4 to 0.6. The flaky like structure were observed with little irregularity for 0.8 MR. Globules with flaky structure are observed as molar ratio increases from 0.8 to 1. For larger molar ratio crystal structure and size were observed as irregular in nature. The maximum crystal size is about 15 µm and minimum crystal size is about 0.7 µm.



(a) (b)

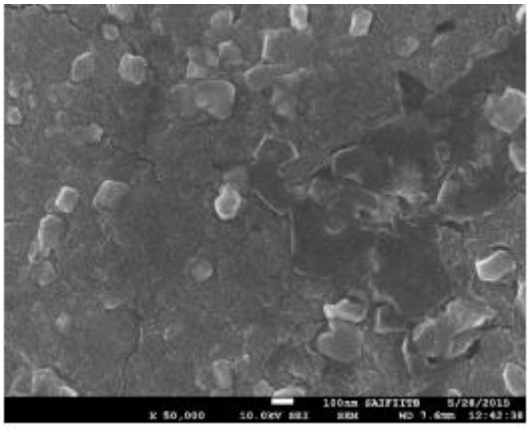


(c) (d)



(e) (f)

International Journal of Current Science Research and Review
ISSN: 2581-8341
Volume 05 Issue 03 March 2022
DOI: 10.47191/ijcsrr/V5-i3-19, Impact Factor: 5.825
IJCSRR @ 2022
www.ijcsrr.org



(g)

Fig. 1 SEM of PPy-PVA with different Molar Ratio
(a) Control PVA (b) 0.1 MR (c) 0.2 MR (d) 0.4 MR (e) 0.6 MR (f) 0.8 MR (g) 1.0 MR

FTIR Results:-

The FTIR spectrum of pure PVA film and composite films of PPy and PVA were shown in the figure 2. It is observed that as molar ratio increases the shift in the wave number were observed. This change in wave number indicates different level of crystalline nature of PVA is present in PPy PVA composite films and Fe-O stretching bands. It confirms the chemical interaction between PPy and PVA in composite films of different molar ratio.

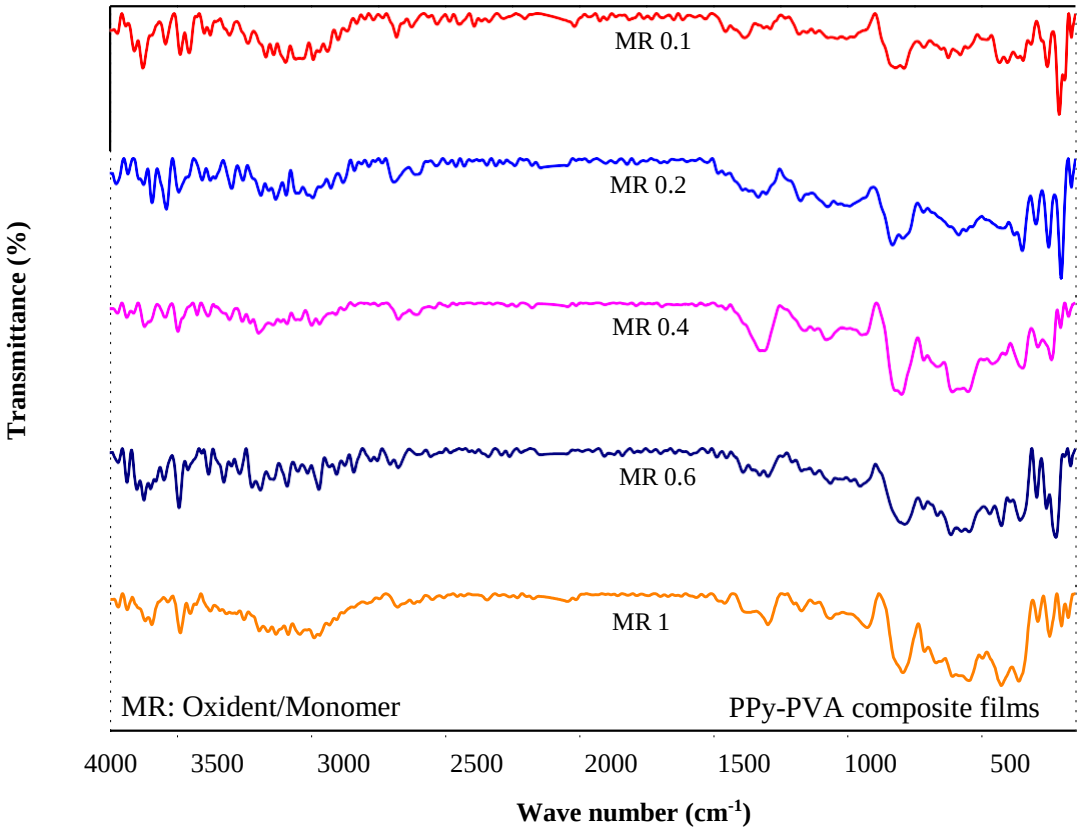


Fig. 2 FTIR spectra of PPy-PVA composite films of different Molar Ratio

International Journal of Current Science Research and Review
ISSN: 2581-8341
Volume 05 Issue 03 March 2022
DOI: 10.47191/ijcsrr/V5-i3-19, Impact Factor: 5.825
IJCSRR @ 2022
www.ijcsrr.org

XRD Results:-

To verify the structural growth along with the surface morphology of the PPy-PVA composite one of the reliable technique is X-ray Diffraction spectra. The XRD pattern in fig. 3 reveals that the pure PPy has amorphous nature whereas pure PVA has semi crystalline nature but the composite of PPy-PVA films shows amorphous nature depending on the molar ratio. As the concentration of monomer to oxidant ratio gradually goes on increasing the crystalline structure slowly changes to less crystalline structure which confirms the infusion of the PPy in the PVA matrix. Few more peaks are observed in the XRD pattern to shows the new crystalline structure formed in the composite films.

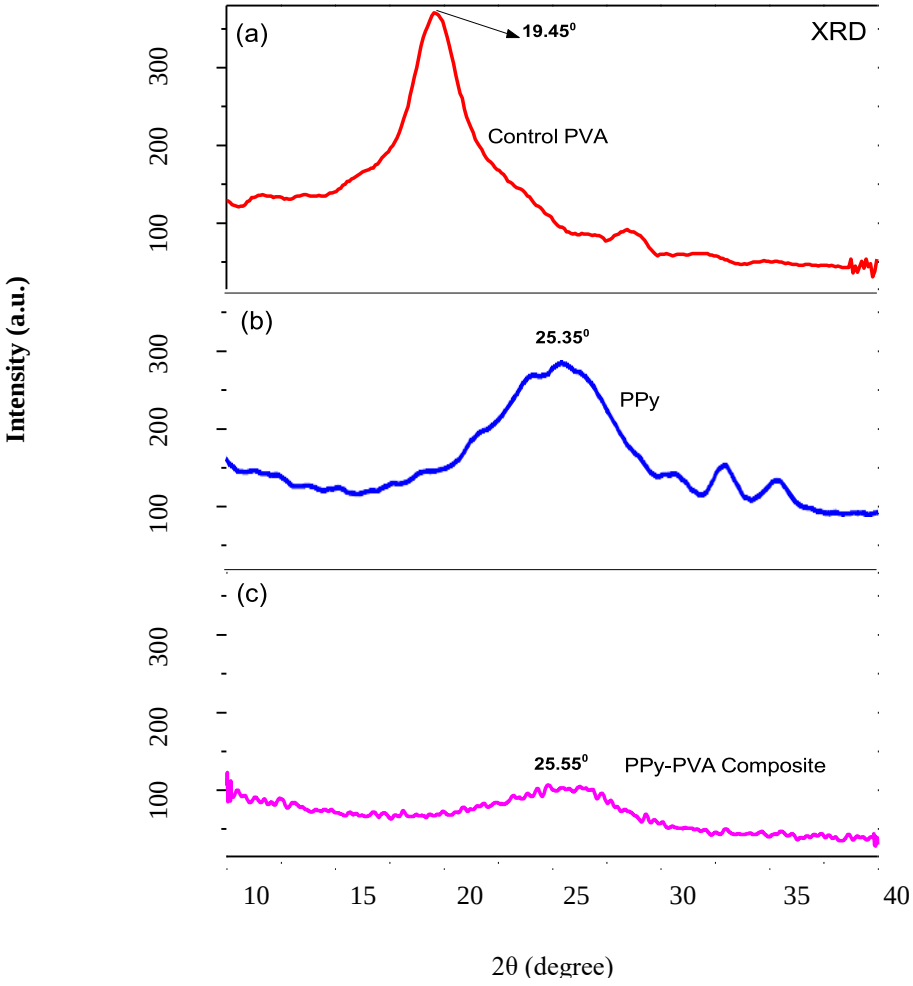


Fig. 3 XRD pattern for (a) control PVA film, (b) PPy, (c) PPy-PVA composite films

Conductivity Results:-

The figure 4(a) shows the conductivity for different molar ratio of PPy-PVA composite films at various temperatures. It is clear from the following figure that conductivity increases as molar ratio increases, the formation of polarons and bipolarons during the formation of composites due to dopant molecule.

International Journal of Current Science Research and Review
ISSN: 2581-8341
Volume 05 Issue 03 March 2022
DOI: 10.47191/ijcsrr/V5-i3-19, Impact Factor: 5.825
IJCSRR @ 2022
www.ijcsrr.org

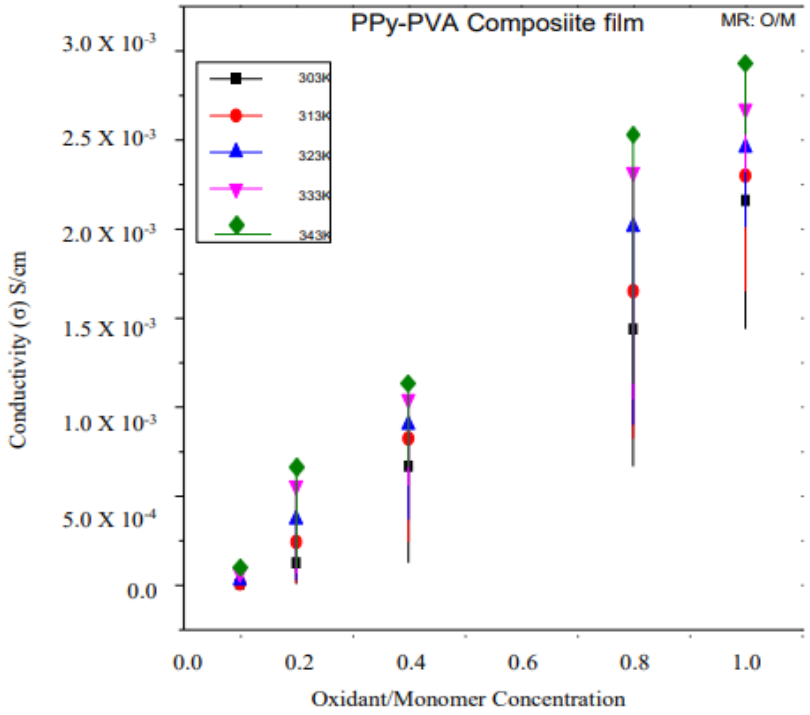


Fig. 4 (a) Plot of conductivity as function of MR

The figure 4(b) shows conductivity as a function of temperature ranging from 303K-343K. From the following fig 4(b) it is clear that conductivity increases as temperature increases, this increase is different for different molar ratio. It is same as the behavior of semiconductor, doping in semiconductor increases the conductivity by adding additional energy bands in the energy gap.

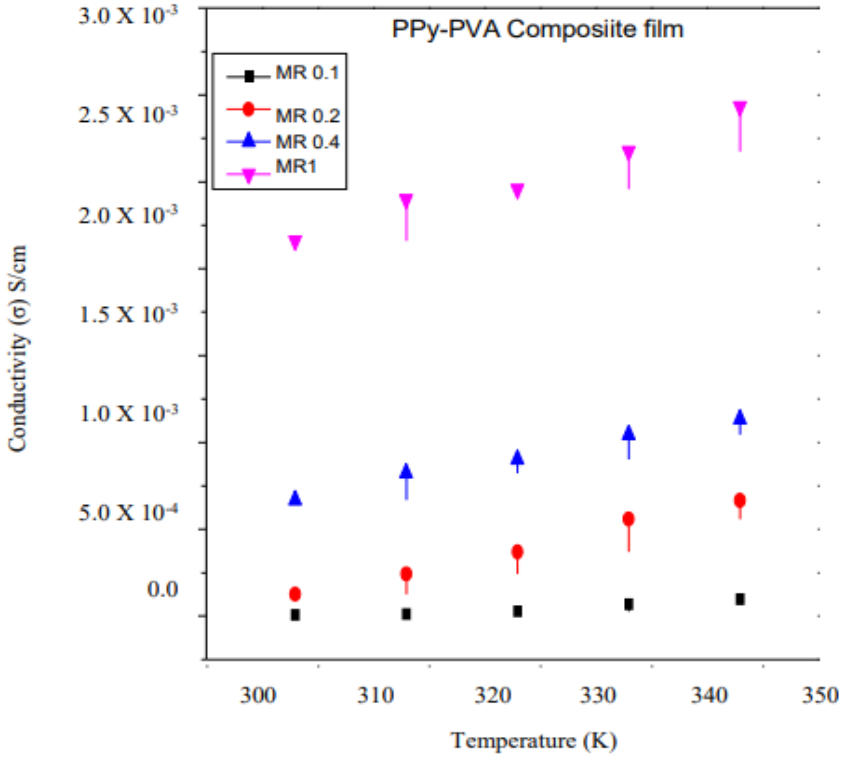


Fig. 4 (b) Plot of conductivity against temperature

International Journal of Current Science Research and Review
ISSN: 2581-8341
Volume 05 Issue 03 March 2022
DOI: 10.47191/ijcsrr/V5-i3-19, Impact Factor: 5.825
IJCSRR @ 2022
www.ijcsrr.org

CONCLUSION

Polypyrrole (PPy) was successfully synthesized by chemical oxidation of pyrrole using Ferric Chloride (FeCl3) as dopant/oxidant also 4% PVA stock solution was prepared and the formation of composite films by solution casting technique. The black colored films were obtained after drying the solution on petri dish. The SEM, FTIR and XRD results show the mechanical and morphological property varies as per the different molar ratio. The conductivity of PPy-PVA composite increases as oxidant to monomer ratio increases at increasing temperature confirms the semiconducting behavior.

REFERENCES

1. D. Kumar and R. C. Sharma; Advances in Conductive Polymers, Eur. Polym. J., 1998, 34(8), 1053–1060.
2. R Ansari; Polypyrrole Conducting Electroactive Polymers: Synthesis and Stability Studies, E-Journal of Chemistry, 2006, 3(13), 86–201.
3. P G Su, Y T Peng; Fabrication of a room-temperature H2S gas sensor based on PPy/WO3 nanocomposite films by in-situ photo polymerization, Sensors and Actuators B, 2014, 193, 637–643.
4. A Joshi, S A Gangal, S K Gupta; Ammonia sensing properties of polypyrrole thin films at room temperature , Sensors and Actuators B, 2011, 156, 938–942.
5. S T Navale, A T Mane, M.A. Chougule, R.D Sakhare, S.R. Nalage, V B Patil; Highly selective and sensitive room temperature NO2 gas sensor based on polypyrrole thin films, Sensors and Actuators B, 2014, 189, 94–99.
6. P V Wright, T C P Wong, B Chambers, A P Anderson; Electrical characteristics of polypyrrole composites at microwave frequencies, Advanced Materials for Optics and Electronics, 1994, 4(4), 253–263.
7. H Eisazadeh; Removal of mercury from water using polypyrrole and its composites, Chin. J. Polymer Sci., 2007, 25(4), 393–397.
8. E Armelin, R Pla, F Liesa, X Ramis, J I Iribarren; Corrosion protection with polyaniline and polypyrrole as anticorrosive additives for epoxy paint, Corrosion Science, 2008, 50(3), 721–728.
9. J Wang C O Too, D Zhou, G G Wallace; Novel electrode substrates for rechargeable lithium/polypyrrole batteries, Journal of Power Sources, 2005, 140(1), 162–167.
10. S Hara, T Zama, W Takashima, K Kaneto; Free-standing polypyrrole actuators with response rate of 10.8% s−1 , Synthetic Metals, 2005, 149 (2), 199–201.
11. R K Sharma, A C Rastogi, S B Desu; Manganese oxide embedded polypyrrole nanocomposites for electrochemical super capacitor, Electrochimica Acta, 2008, 53(26), 7690–7695.
12. D Zhou, C O Too, G G Wallace, A M Hodges, A W H Mau; Protein transport and separation using polypyrrole coated, platinised polyvinylidene fluoride membranes, Reactive & Functional Poly., 2000, 45(3), 217–226.
13. J Bhadra, D Sarkar; Polypyrrole nanocomposite made by polypyrrole dispersion in poly (vinyl alcohol) matrix, Indian J. Phys. 2010, 84 (10), 1321–1325.
14. T S Gaaz, A B Sulong, M N Akhtar , A A H Kadhum, A B Mohamad, A A AlAmiery; Properties and Applications of Polyvinyl Alcohol, Halloysite Nanotubes and Their Nanocomposites, Molecules, 2015, 20, 22833–22847.
15. E Benseddik, M Makhlouki, J C Bernede, S Lefrant, A Profic; XPS studies of environmental stability of polypyrrole-poly (vinyl alcohol) composites, Synthetic Metals, 1995, 72, 237–242.
16. M H Harun, E Saion, A Kassim, M Y Hussain, I S Mustafa, M A Ali Omer; Temperature Dependence of AC Electrical Conductivity of PVA-PPy-FeCl3 Composite Polymer Films, Malaysian Polymer Journal, 2008, 3(2), 24–31.

Cite this Article: *Miss. Niyanta V. Dave, Dattatray. M. Nerkar, Narendra R. Kishan (2022). Effect of Molar Ratio on Structure of PPy-PVA Composite Film. International Journal of Current Science Research and Review, 5(3), 748-753*