

Study of Polyaniline – Polymethylmethacrylate Blend Films for Amine Sensor

D.B.DUPARE¹

¹*Department of Chemistry ShriDr R.G Rathod Arts and Science College Murtizapur
Di- Akola*

Abstract -Electrically conducting films are useful in many applications in the fields of sensors, and nanoelectronics. However, it is very difficult to obtain fibers of conducting polymers like polyaniline (PANI) and polypyrrole. Hence they are invariably mixed with other insulating polymers such as polymethylmethacrylate (PMMA) to obtain a conducting composite depending on the percolation of the conducting polymer. Here, we report the preparation of PANI-PMMA composite films by chemical deposition method polymer fibers are investigated at room temperature with different concentrations of PANI (0.05M, 0.1M, 0.2M, 0.5M,). It is observed that there is a significant enhancement in the conductivity of these fibers with the increase in the concentration of PANI. Here to study the D.C. conductivity, SEM, FTIR and Gas detecting properties of films.

Keywords- polyaniline, polymethylmethacrylate, blend amine sensor.

I. Introduction

Generally polymers are insulators by nature, but some of them show intrinsically good conductivity due to their conjugation. Polyaniline (PANI) is one of the most promising intrinsically conducting polymers due to its ease of polymerization and environmental stability(1-2). In last some decades polyaniline is promising material for industrial application.(3). The very large range of conductivities achieved with doping allows us to adopt it for different types applications(4). PMMA is one of the most popular polymeric materials used for the preparation of fibers and fabrics in textile industry due to its high strength, resistance to shrinkage and abrasion.(5) Most studies have focused on detecting CO₂, CO, SO₂, O₂, O₃, H₂, Ar, N₂, NH₃ and H₂O, because of their toxicity, their relation with atmospheric composition or the fact that they can be found at high levels in some environments(6). Our goal is not to promote the use of sensors based on nanostructured materials but to make these promising materials applied to gas sensing, with particular attention to the quality parameters of these sensors, and their weaknesses and strengths(7-8). Increasing demands for ever more sensitive sensors for global environmental monitoring, food inspection and medical diagnostics have led to an upsurge of interests in nanostructured materials (9).

The production of stable aqueous suspensions of water insoluble polymers remains a challenging and important problem to widen the scope of the application of these polymers. In continuation of our ongoing research in this direction we have developed conditions for the preparation of a stable aqueous

suspension of the polyaniline –polymethylmethacralayte composite via aqueous polymerization of MMA.

II. Experimental

MATERIALS AND METHODS: Aniline, ammonia per-oxodisulphate (APS), and ammonia solution were of analytical grade from Rankemranbaxy New Delhi (India). Aniline was distilled under reduced pressure in presence zinc dust prior to used. as produced from. All process was carried out double distilled conductivity water. Methyl methacrylate[Merck-Schuchardt (99 %), stabilized with 100 ppm hydroquinone] was washed with a small amount of sodium hydroxide solution (10), benzoyl peroxide, toluene were obtained from Quiligen chem.

Preparation of PMMA

In order to fully exploit the excellent optical properties and the mechanical strength of PMMA, we have worked with bulk polymerized PMMA. The monomer methylmethacrylate (MMA) is washed first with 20% sodium hydroxide solution to remove the inhibitors and then with distilled water. The initiator benzoyl peroxide is added to MMA and stirred for 2-3 hours at around 40°C till the solution becomes viscous to obtain Polymethylmethacrylates

Synthesis of PANI-PMMA composites

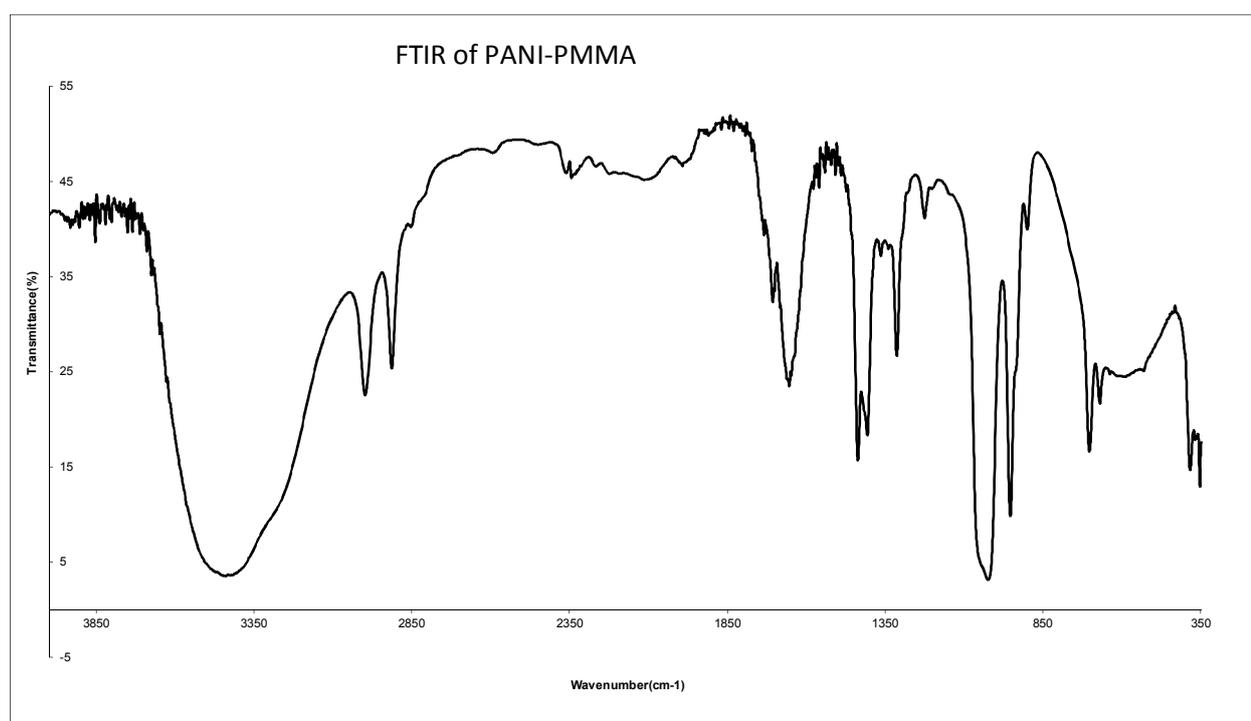
Freshly distilled aniline (AR grade) is mixed with 1.M hydrochloric acid. PMMA dissolved in toluene is added to it. Ammonium persulphate (APS) dissolved in water is added drop wise to the resulting mixture with continuous stirring. Aniline to APS weight ratio is fixed. The temperature is maintained at around -10⁰c and stirring is allowed to proceed for 4-5 hours with immersing the thin glass substrate. The precipitate obtained is filtered, washed several times and dried. Since the synthesis temperature is low at room temperature and the molarity of the oxidant high, the amount of unutilized reagents is very small. As given in table

Synthesis of PANI-PMMA Blend films	Monomer (Aniline)	Dopant HCL	Monomer of MMA	Oxidant APS
M1	0.05M	1 M	0.5g	1M
M2	0.1M	1 M	0.5g	1M
M3	0.225M	1 M	0.5g	1M
M4	0.50M	1 M	0.5g	1M
M5	0.75M	1 M	0.5g	1M
M6	1.00M	1 M	0.5g	1M

III. Results and Discussions

1) FTIR, SPECTRA-The FTIR- spectra of PANI-PMMA films recorded in the range of 400-4000 cm^{-1} as shown in fig-1 shows all the major peaks of HCl doped PANI as well as PMMA(10-11). This confirms the fact that PANI has been dispersed as an interpenetrating network in the PMMA matrix.

The sharp and intense peak observed at 1722 cm^{-1} is attributed to the $\text{C}=\text{O}$ stretching in PMMA. A broad peak observed at 3436 cm^{-1} N-H Stretching Vibration in PANI. The peak at 2945 cm^{-1} is due to the C-H stretching in PMMA. 1250-970 cm^{-1} is attributed to ester bonding in PMMA. Peak at 1387 cm^{-1} is a characteristic peak of intrinsic PANI indicates C-N stretching. The main peak for PANI observed at 1144 cm^{-1} and 840 cm^{-1} due to the vibration mode of B-NH=Q (benzene-NH-Quinone) or B-NH-B formed in doping reaction. PANI used in the preparation was protonated and a higher doping levels lead to higher conductivity. In general, by the addition conducting polymer PANI to the thermoplastic polymer such as PMMA would enhance the optical and mechanical properties of composite films.



2) Morphology of the blend films

Fig. 2 shows SEM photos of the surface of the coating film of polyaniline-polymethylmethacrylate. These figures show that small PANI particles are distributed homogeneously in the blend films., the PANI particles are completely covered with the matrix polymer. The dark region observed in Fig 2 is ascribed to conductive PANI phase, while the bright region with tubular shape is ascribed to non conducting PMMA phase. It is further observed that PANI content is markedly localized in the PMMA matrix, On the other hand, there are many pores on the surface in film. The PANI particles appear inside the pores. The formation of these pores for the coating of sensor was reproducible. These pores seem to contribute to the short response time and good reversibility of sensor. This is due to the fact that gas

diffusion occurs more easily in porous structures, and the reaction between gas molecules and dopant therefore occurs easily.

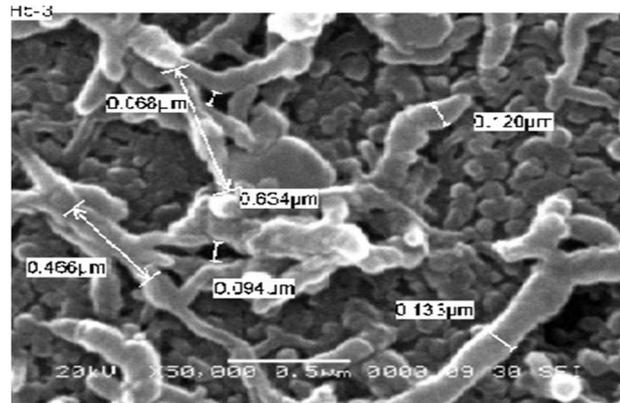
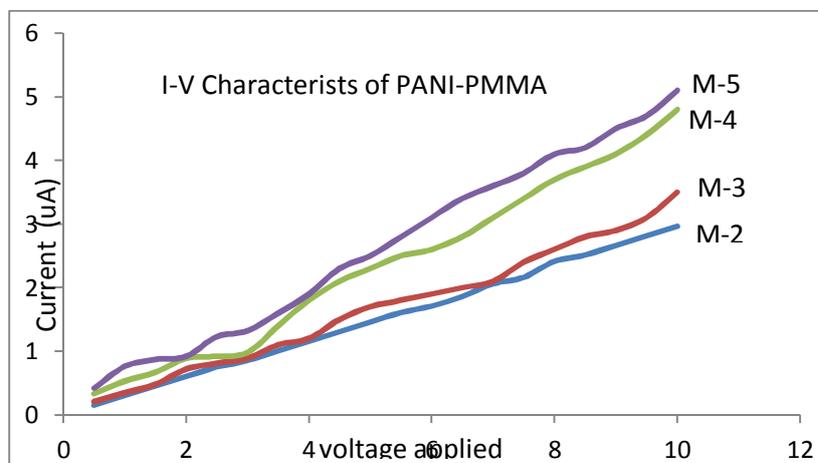


Fig. 2 SEM photos PANI-PMMA Composites films

3) I-V measurement synthesized PANI-PMMA

The I-V characterization measurement of the PANI-PMMA film was recorded by an indigenously developed computer controlled I-V measurement system using four-probe method at room temperature. The current-voltage (I-V) characteristics of the synthesized Blend PANI-PMMA thin films were studied to ensure an ohmic behavior of the films. A linear relationship of the I-V characteristics shown in Fig.3 reveals that the PANI-PMMA composite films have an ohmic behavior.



.Fig 3 I-V characteristics of PANI-PMMA Composites films.

4) Ammonia Gas Sensing Characteristics-

The sensing property to ammonia of the PANI-PMMA blend film sample was tested. PANI-PMMA Composites thin films were studied for ammonia a gas at room temperature (303k) by using indigenous developed computer controlled gas sensing system. The film was first exposed for five minutes to predefined concentration of ammonia gas, and then it was exposed to air to recover initial resistance for

five to seven minutes. The reversibility and repeatability of the sample were tested on 10 ppm, 20 ppm, 30 ppm and 40 ppm ammonia concentration, as shown in Fig. 4. The period of the test cycle is 3000 sec. The gas dispersion process and pump process take half of the period separately. Which illustrated that the PANI/PMMA film gas sensors can not only detect the existence of ultra-low concentration of ammonia, but also can estimate the values of concentration in a short reverse time of tens of ppm level.

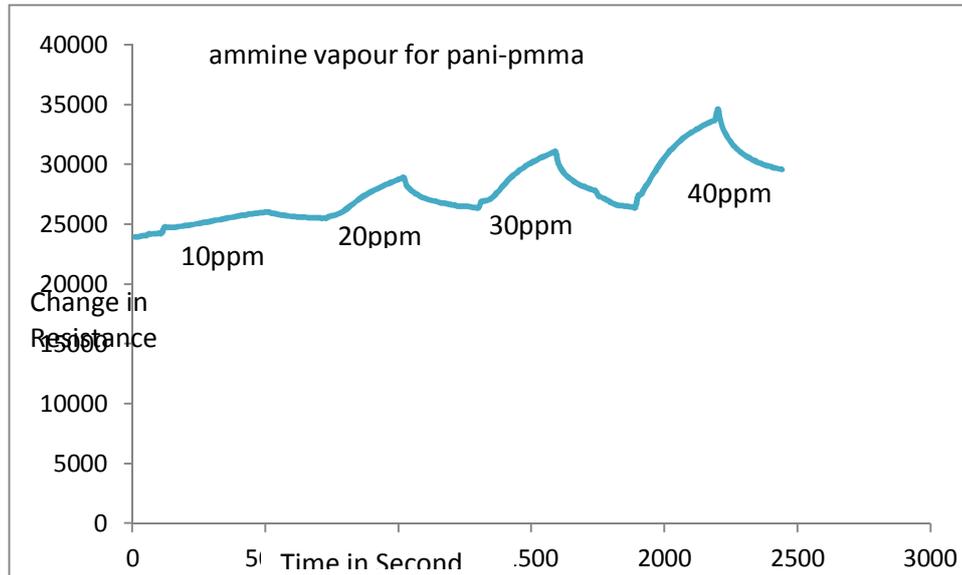


Fig -4 Gas sensing behaviors of PANI-PMMA Composites thin films.

IV. Conclusion

In PANI-PMMA films are Synthesized by an *in situ* chemical oxidative polymerization method on glass substrate on different concentration of aniline but good and comparative high conductive uniform, M-5 film are selected for gas sensing application.

PANI-PMMA, M-5 films have a larger surface area and thus higher gas sensitivity, which can be used to detect trace level of ammonia (10 ppm). Furthermore, are electrically and structurally stable even after more than 150 days. These results indicate that the nano-branched PANI PMMA films concentration determination of toxic gases like ammonia due their good environmental stability, high sensitivity and low costs.

REFERENCES

- 1) Veluru J. , Pavan Kumar V. S , Subha G.J., Vasantha Kumari. Natarajan T.S , Appukuttan S. N., and Ramakrishna S. "AC Conductivity Studies on PMMA-PANI (HCl) Nanocomposite Fibers Produced by Electrospinning" Journal of Engineered Fibers and Fabrics 54 (2011)V-6, pp54-59.
- 2) Devikala S. and K amraj P. "Development of Polymethylmethacrylate Based Composite for Gas Sensing Application" Journal of Chemistry (2011) 8, S165-S170.

- 3) Tzi-Yi Wu, Wen-Bin Li, Chung-Wen Kuo, Chiu-Fong Chou, Jian-Wei Liao, Ho-Rei Chen, Ching-Guey Tseng “ Study of Poly(Methyl Methacrylate)-Based Gel Electrolyte for Electrochromic Device” *Int. J. Electrochem. Sci.*, (2013) Vol. 8, pp 10720 – 10732.
- 4) Deshmukh S. H., Burghate D K, Akhare V P, Deogaonkar V S, Deshmukh P. T and Deshmukh M S. “Electrical conductivity of polyaniline doped PVC–PMMA polymer Blends” *Bull. Mater. Sci.*, (2007), V-30 pp. 51–56.
- 5) Mohd. K., Srivastava A., Clodoaldo I.L. Dearaujo, Vinicius C. Z. and Andre A. P. “Electrical conductivity study of polyaniline-polymethylmethacrylate composite fibers”, *World Journal of Applied Sciences and Research* (2012) V-2, pp 51-54.
- 6) Giselle Jimenez-Cadena, Jordi Riu and F. Xavier Rius “Gas sensors based on nanostructured Materials” *Analyst*, (2007), 132, pp1083–1099.
- 7) Tomar A. K., Suman Mahendia and Shyam Kumar “Structural characterization of PMMA blended with chemically synthesized PANi” *Advances in Applied Science Research*, 2011, 2 (3): 327-333.
- 8) Aksimentyeva O., Konopelnyk O., Opanych I., Tsizh B., Ukrainets A., Ulansky Y., Martyniuk G., “INTERACTION OF COMPONENTS AND CONDUCTIVITY IN POLYANILINE – POLYMETHYLMETHACRYLATE NANOCOMPOSITES” *Rev. Adv. Mater Sci.* (2010) 23 pp 185-188.
- 9) Araujo P. L. B., Santos R. F. S., Araujo E. S “Polyaniline nanofibers as a new gamma radiation stabilizer agent for PMMA” *eXPRESS Polymer Letters* (2007) Vol.1, No.6 pp385–390.
- 10) Fawzia. I. El-Dib, Wafaa M. Sayed, Sahar. M. Ahmed, Mohamed Elkodary “Synthesis of Polyaniline Nanostructures in Micellar Solutions” *Journal of Applied Polymer Science* (2011) pp 1-8.
- 11) Sujithk., Asha A.M., Anjali P., Sivakumar N., Subramanian K.R.V., Shantikumar V.N., Balkrishnan A. “Fabrication of highly porous conducting PANI-C composites fiber mats via electrospinning” *Material Letters* (2012) 67, pp 376-378.
- 12) Aseel A. Kareem, Harith I. Jaffer, Hussein K. Al-Lamy “Photoconductivity of An Inorganic /Organic Composites Containing Dye-Sensitized (Zinc Oxide) *Jour. for Pure & Appl. Sci.* (2013) Vol. 26 (1) pp 124-130.
- 13) Al-Osaimi J., Alhosiny N., Ali Badawi and Abdallah S. “The Effects of CNTs Types on The Structural and Electrical Properties of CNTs/PMMA Nanocomposite Films” *International Journal of Engineering & Technology* (2013) Vol:13 pp 77-79.
- 14) Arjun Maity and Mukul Biswas “Water-Dispersible Conducting Nanocomposites of Polymethylmethacrylate-SiO₂ Modified by Polyaniline and Polypyrrole” *J. Ind. Eng. Chem.* (2006) V-12 pp 626-634
- 15) Salma M. Hassan “Optical Properties of Prepared Polyaniline and Polymethylmethacrylate blends” *International Journal of Application or Innovation in Engineering & Management. International Journal of Application or Innovation in Engineering & Management* (2013) V-2 PP-232-234.

