

# AC Conductivity Studies on PMMA-PANI (HCl) Nanocomposite Fibers Produced by Electrospinning

Veluru Jagadeesh Babu<sup>1</sup>, V. S. Pavan Kumar<sup>2</sup>, G.J.Subha<sup>3</sup>, Vasantha Kumari<sup>4</sup>  
T.S.Natarajan<sup>2</sup>, Appukuttan Sreekumaran Nair<sup>1</sup>, and Seeram Ramakrishna<sup>1</sup>

<sup>1</sup>Healthcare and Energy Materials Laboratory, NUSNNI, National University of Singapore, SINGAPORE

<sup>2</sup>Department of Physics, Indian Institute of Technology Madras, Chennai INDIA

<sup>3</sup>Department of Rubber and Plastics Technology, Chennai INDIA

<sup>4</sup>Department of Polymer Technology, Crescent Engineering College, Chennai INDIA

Correspondence to:

Veluru Jagadeesh Babu email: [nnivjb@nus.edu.sg](mailto:nnivjb@nus.edu.sg)

## ABSTRACT

Electrospinning is one of the techniques to produce non-woven fiber mats using polymers. The diameters of the fiber produced by this technique are in the range of 10  $\mu\text{m}$  to 10 nm. Electrically conducting ultra fine fibers 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 through electrospinning. 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 fibers by electrospinning. The scanning electron micrographs and the frequency dependent complex conductivity ( $\sigma^*(\omega)$ ) of these polymer fibers are investigated at room temperature with different concentrations of PANI (5%, 10%, 15%, 20% w/w). It is observed that there is a significant enhancement in the ac conductivity of these fibers with the increase in the concentration of PANI.

**Key Words:** Electrospinning, Nanocomposite fibers, Complex conductivity.

## 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 [1-4]. PANI provides the best material for industrial applications and it has been studied extensively over the last decade with improvements in processing and intrinsic electrical properties. The

PANI powder can be doped with aqueous protonic acids such as hydrochloric acid (HCl), camphor sulphonic acid (CSA), etc., to prepare conducting emeraldine salts [5]. The very large range of conductivities achieved with doping allows us to adopt it for different types applications [6]. The conducting polymers can be prepared in bulk (pellets), thin films and fibers. Fibers, especially in the micron and nanometer diameter ranges, have large surface area to volume ratio. Hence they are extensively used in sensor applications. There are many techniques available for producing fibers like dry spinning, template synthesis, drawing, etc., [7-9]. We used here electrospinning to form fibers of polymethylmethacrylate- HCl doped PANI (PMMA-PANI (HCl) composites.

Electrostatic generation of ultra-fine fibers (“electrospinning”) has been known since 1930s. This technique has recently gained prominence due to its simplicity and potential for applications in a variety of fields like filter membranes [10,11], scaffolds in tissue engineering [10], clean energy and healthcare [12]. In this non-mechanical electrostatic technique of electrospinning, a high electric field is applied between a polymer fluid contained in a syringe with a capillary tip and a counter electrode in the form of a metallic collecting screen [13]. When the voltage reaches a critical value, the forces due to the electric field overcomes the surface tension of the formed drop at the tip of the capillary and it is deformed into an inverted cone [14] (Taylor cone). On further increasing the field an electrically charged jet emanates which undergoes a series of electrically induced bending instabilities [15] during its passage to the collection screen. These subject the jet to a

hyper-stretching [16] and this is accompanied by rapid evaporation of the solvent molecules. The fibers are collected on the surface of the collecting screen in the form of a non-woven mesh with a range of diameters. This process can be optimised to control the fiber diameter by varying the charge density and concentration of the polymer solution in solvent, while the duration of electrospinning controls the thickness of fiber deposition [17]. The details of the apparatus used for electrospinning has been discussed elsewhere [18]. The complex Impedance Spectroscopy is a nondestructive method for the study of microstructure and electrical properties of materials. The impedance measurements on a material give us details corresponding to both resistive (real part) and reactive (imaginary part) components.

### Sample Preparation

Ammonium per sulphate (0.1 mole aqueous solutions in protonic acid) was added drop wise (to prevent warming of the mixture) to a stirring solution of 0.1mole aniline dissolved in 1 mole of aqueous solution of protonic acid precooled to 4°C. Then stirring is continued for 2-4 hours to ensure completion of the reaction. When HCl is used as protonic acid, the coloration of solution occurs almost after 1 minute at 27°C. The sequence of coloration is light blue → blue green → coppery tint → green precipitate. The precipitated salt is filtered and washed repeatedly with acidic water (distilled) [19] until the filtrate is cleaned well and finally with methyl alcohol. The green emeraldine salt thus obtained is dried under vacuum. The yield of the doped PANI product, PANI (HCl) is found to be nearly 95%. The polymerization method has been extended to bench scale to prepare a minimum quantity of 100-150g per batch. This HCl doped PANI (PANI (HCl)) is used for the preparation of different composites with (PMMA) composite with the solvent N-methylpyrrolidine (NMP). The concentration of PANI (HCl) was varied as 5 %, 10%, 15% and 20% (w/w) in PMMA.

### Measurements

In the electrospinning apparatus, the distance between the needle and the collecting drum was 10 cm. The speed of rotation of the collecting drum was 2000 rpm and the applied electric field was 7 kV/cm using a high voltage supply (Zeonics, Bangalore, India, 0-50kV). The images of composite fibers of PANI (HCl)-PMMA with NMP were recorded using SEM apparatus JEOL JSM 840A. Impedance Analyzer (HP 4192A) was used to measure the

complex impedance spectra of the fibers in the frequency range from 100 kHz to 13 MHz.

## RESULTS AND DISCUSSION

### Fiber Morphology

The typical SEM images for two different concentrations of PANI in PMMA, namely, 5% and 10% (w/w) were shown in *Figures 1(a)* and *1(c)*, respectively. We observed that the fibers are very long and almost aligned. There is a distribution in the diameters of the fibers with an average diameter of 290 nm and 788 nm for the two concentrations respectively *Figures 1(b)* & *1(d)* obtained from the SEM pictures using the software *UTHSCSA Image Tool 3.00*.

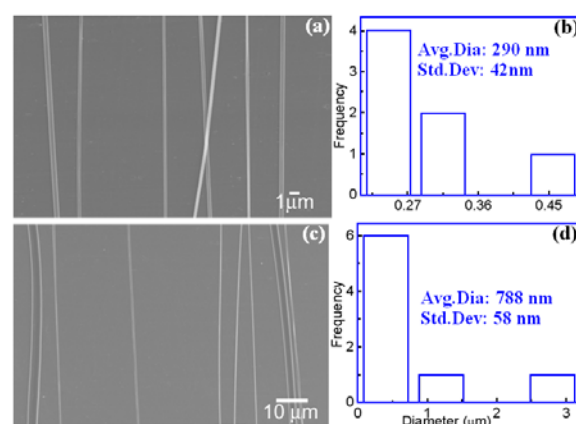


FIGURE 1. SEM Image and distribution of diameters of the fibers corresponding to concentrations 5% [1(a)&1(b)] and 10% [1(c)&1(d)] respectively.

However, the individual fibers had a uniform diameter throughout their length. The alignment was achieved by optimizing the rotation speed of the collecting drum and the flow rate of the solution. The fibers were also deposited on a glass substrate with an inter-digital electrode pattern with a separation of 200 μm made using standard photolithography technique for measuring the complex impedance.

### FTIR Spectral Analysis

The FTIR spectrum of PANI (HCl)-PMMA composite fibers in different doping levels is shown in *Figure 2*. It indicates all the major peaks of HCl doped PANI as well as PMMA. This confirms the fact that PANI has been dispersed as an interpenetrating network in the PMMA matrix. The sharp and intense peak observed at 1722cm<sup>-1</sup> is attributed to the -C=O stretching in PMMA. The peak at 2945cm<sup>-1</sup> is due to the C-H stretching in PMMA. 1250-970cm<sup>-1</sup> is attributed to esterbonding.

Precisely the peak at  $1250\text{ cm}^{-1}$  is due to C-O stretching vibration and the band at  $970\text{ cm}^{-1}$  is due to C-H bending in PMMA. Peak at  $1387\text{ cm}^{-1}$  is a characteristic peak of intrinsic PANI indicates C-N stretching.

The main peak for PANI observed at  $1144\text{ cm}^{-1}$  and  $840\text{ cm}^{-1}$  due to the vibration mode of B-NH=Q (benzene-NH-Quinone) or B-NH-B formed in doping reaction. Therefore, the IR results signified that the HCl would have hydrolyzed the host matrix as the intensity of the band at  $1722\text{ cm}^{-1}$  is decreased slightly as the doping increases. Also a band  $\sim 1550\text{ cm}^{-1}$  also indicates the extent of hydrolysis, which is not highly significant at this stage. PANI used in the preparation was protonated and a higher doping levels lead to higher conductivity. We may also infer that the cleavage is not observed very explicitly in the FTIR spectra indicates that the mechanical properties may have not been influenced much upon doping. 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. J.B Yadav et.al [20] studied the mechanical properties of deprotonized PANI and PMMA composite thin films and realized the improved mechanical properties.

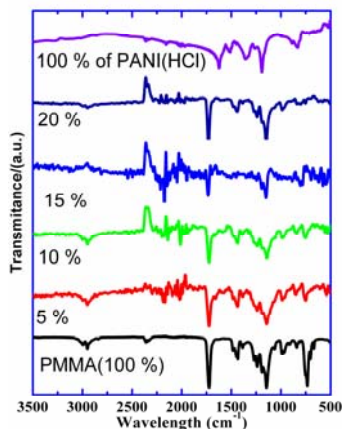


FIGURE 2. FT-IR spectra of PMMA-PANI (HCl) composite fibers.

### Electrical Properties

The real and imaginary parts of the complex impedance spectra for the PANI (HCl)-PMMA composite fibers for different concentrations have been plotted in the same complex plane (Nyquist

diagram) in *Figure 3*. The plot for 5% sample forms a semicircle, with a radius of  $\sim 2.58 \times 10^6\ \Omega$ . On the other hand the other concentrations of the composites show a semicircle along with a linear region at lower frequencies in these cases we apparently have two impedance processes: one at higher frequencies (low impedance regime) and the other at low frequencies (high impedance regime).

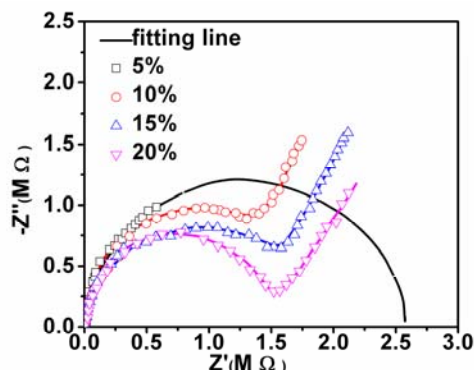


FIGURE 3. The complex impedance plots for 5%(□), 10%(○), 15%(△) and 20%(▽) w/w of PANI(HCl) in PMMA.

TABLE I. The parameters obtained from the complex impedance plots.

Sample % (w/w)	$Z'$ intercept ( $M\Omega$ )	$\sigma$ (S/m)	Angle ( $\alpha^\circ$ )	$\omega^*$ Hz (max.Fre.)	$\tau$ (Sec) ( $\times 10^{-5}$ )
5	2.581	1.673	5.14	10268	9.73
10	0.657	6.243	10.07	46785	2.13
15	0.637	6.442	2.40	72650	1.37
20	0.569	7.198	6.17	126750	0.78

The data was fitted using Z-View software (continuous line in the *Figure 3*) and the intercepts on the  $Z'$  axis (dc resistance) and the equivalent network are obtained from the fitting. For increasing concentrations of PANI (HCl) in PMMA (5% to 20%) the resistances show a corresponding decrease. Comparing to the pure PMMA the conductivity of PMMA-PANI (HCl) composite shows more than 12 orders of magnitude increase are shown in *Figure 3*. Even as low as 5% loading of conducting PANI the percolation threshold has been reached in this case. The dc conductivities calculated from the intercepts of the fitted semicircle on the  $Z'$  axis, are shown in *Table I*.

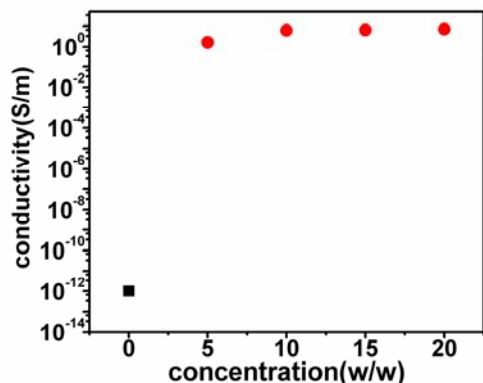


FIGURE 4. The variation of Conductivity of the PANI (HCl)-PMMA composite fibers with concentration. The conductivity data of pure PMMA (\*) is obtained from Ref. [21] for comparison.

The angular frequency ( $\omega^*$ ) corresponding to the maximum of the imaginary component ( $Z''_{\max}$ ) in the semicircle in *Figure 3*, yields a time constant  $\tau = 1/\omega^*$ . The average  $\tau$  is  $5.2 \times 10^{-5}$  s and this indicates fast charge-discharge characteristics. An equivalent circuit for impedance plots has been shown in *Figure 5*. In the equivalent circuit the constant phase elements represent an empirical relationship, which is introduced for the description of the frequency dependence caused by the surface roughness or by the non-uniformly distributed properties of the irregular electrode surface [22]. Its impedance is described as  $Z_{\text{CPE}}(j\omega) = A^{-1}(j\omega)^{-n}$ , where  $A$  is a proportionality factor and  $n$  is the exponent of Constant Phase Element (CPE), which characterizes the phase shift and  $\omega$  is the angular frequency ( $\omega = 2\pi f$ ). The CPE is a generalized element, since it can model Resistance ( $R$ ), Capacitance ( $C$ ), Inductor ( $L$ ), Warburg ( $W$ ), as well as distortion in these elements, which have following a definite type of frequency dependence.

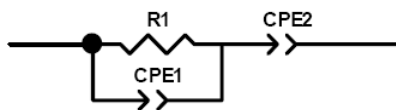


FIGURE 5. The equivalent circuit for the ac response of PANI (HCl)-PMMA fibers.  $R_1$  is the resistance of the sample; CPE1 and CPE2 denote the two constant phase elements.

TABLE II. The system parameters were deduced by fitting the Nyquist plots to the equivalent circuits in *Figure 3*.

Sample % (w/w)	$R_1$ (M $\Omega$ )	CPE <sub>1</sub> ( $10^{-12}$ )	CPE <sub>2</sub> ( $10^{-12}$ )	$n_1$	$n_2$
5	1.057	37.76	66.85	0.97	0.80
10	0.637	36.45	17094	0.92	0.55
15	0.522	51.56	24180	0.94	0.84
20	0.482	12.26	37592	0.92	0.64

The equivalent circuit parameters are obtained using nonlinear curve fitting and their values are shown in the *Table II*. The exponents  $n_1$  and  $n_2$  obtained from the definition  $Z_{\text{CPE1}} = [A^{-1}(j\omega)^{-n_1}]$  and  $Z_{\text{CPE2}} = [A^{-1}(j\omega)^{-n_2}]$  with exponents lying in the range 0.5 to 1. The  $n_1$  corresponds to the electrode and  $n_2$  to the capacitive nature of the system.

By knowing the value of bulk resistance  $R$  and the dimensions of the sample, the ac conductivity has been calculated. This frequency dependent conductivity  $\sigma_{\text{ac}}$  for PANI (HCl) in PMMA has been plotted against concentration in *Figure 5*.

It is observed from the *Figure 6* is that, at low frequencies the conductivity ( $\sigma$ ) remains a constant and beyond about 100 kHz it increases linearly with frequency. This later portion of the graph can be fitted to a power law in frequency with an exponent in the range 0.6 to 1, which is characteristic of many-disordered systems [23].

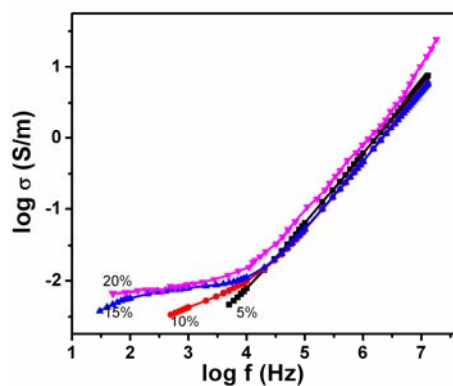


FIGURE 6. AC conductivity for the PANI (HCl)-PMMA fibers with the variation of frequency.

## CONCLUSIONS

Conducting PMMA-PANI(HCl) composite fibers were prepared by electrospinning. The diameters of the fibers were found to be in the range of 1 to 0.6 $\mu$ m. From the AC impedance measurements the conductivities were found to increase with the concentration. There is a 12-order magnitude increase in the dc conductivity of pure PMMA when even less than 5% of PANI is added. The frequency dependent ac conductivity shows the well-known universal behavior with a frequency independent constant value at low frequencies and at higher frequencies shows a power law in frequency with an exponent in the range of 0.6 to 1.

## REFERENCES

- [1] Y. Cao, A. Andreatta, A.J. Heeger, P. Smith, "Influence of chemical polymerization conditions on the properties of polyaniline" *Polymer*, vol 30, pp.2305-2311, 1989
- [2] E.M. Genies, A. Boyl, M. Lapkowski, C. Trintavis, "Polyaniline: A historical survey" *Synth. Met.* vol 36, pp. 139-182. 1990
- [3] L.Dan, JX Huang, RB Kaner "Polyaniline Nanofibers: A Unique Polymer Nanostructure for Versatile Applications" *Accounts of chemical research*, vol 42, pp.135-14, 2009.
- [4] F. Lux, "Properties of electronically conductive polyaniline: a comparison between well-known literature data and some recent experimental findings" *Polymer*, vol 35 pp. 2915-2936,1994
- [5] E. T. Kang, K. G. Neoh, K. L. Tan, "polyaniline: a polymer with many interesting intrinsic redox states" *Prog. Polym. Sci.* vol 23, pp. 277-324, 1998.
- [6] W. Xianyan; D. Christopher; L. Soo Hyoun; K. J. Senecal, K. Jayant; L. A. Samuelson, "Electrospinning technology: A novel approach to sensor application" *J. Macromolec. Sci. part A: Pure and Appl. Chem*, vol 39, pp. 1251-1258, 2002
- [7] S. Nain, M. Sitti, A. Jacobson, T. Kowalewski, C. Amon, "Dry Spinning Based Spinneret Based Tunable Engineered Parameters (STEP) Technique for Controlled and Aligned Deposition of Polymeric Nanofibers" *Macromol. Rapid commun.*, vol 30, pp.1406-1412, 2009
- [8] J. X. Huang, R. B. Kaner, "A General Chemical Route to Polyaniline Nanofibers" *J. Am. Chem. Soc.* vol 126, pp.851-855, 2004.
- [9] E. Smit, U. Buttner, R. D. Sanderson, "Continuous yarns from electrospun fibers" *Polymer*, vol 46, pp.2419-2423, 2005.
- [10] J. Doshi, D.H. Reneker, "Electrospinning process and applications of electrospun fibers" *J. Electrostat.* vol 35, pp. 151-160, 1995
- [11] P. W. Gibson, H. L. Schreuder-Gibson, D. Riven, "Electrospun fiber mats: Transport properties" *AIChE J.* vol 45, pp.190-195, 1999.
- [12] V. Thavasi, G. Singh, S. Ramakrishna, "Electrospun nanofibers in energy and environmental applications" *Energy&Environ. Sci.*, vol 1, pp.205-221, 2008.
- [13] B. Sundaray, V. Subramanian, T. S. Natarajan, "Electrospinning of continuous aligned polymer fibers" *App.Phys. Lett.* vol 84, pp. 1222-1224, 2004
- [14] L. Yarin, S. Koombhongse, D. H. Reneker, "Taylor cone and jetting from liquid droplets in electrospinning of nanofibers" *J. Appl. Phy.*, vol 90, pp.4836-4846. 2001
- [15] L. Yarin, S. Koombhongse, D. H. Reneker, "Bending instability in electrospinning of nanofibers" *J. Appl. Phy.* Vol. 89, pp. 3018-3026, 2001.
- [16] J. J. Feng, "The stretching of an electrified non-Newtonian jet: A model for electrospinning" *Phys. of Fluids* vol 14, pp.3912-3926, 2002.
- [17] D. H. Reneker, I. Chun, "Nanometre diameter fibres of polymer, produced by electrospinning" *Nanotechnology*, vol 7, pp.216-223, 1996.
- [18] Sundaray, V. Subramanian, T. S. Natarajan, "Electrical conductivity of a single electrospun fiber of poly(methyl methacrylate) and multiwalled carbon nanotube nano composite" *App. Phys. Lett.*, vol 88, pp. 143114, 2006.
- [19] Della Santa, A, Mazzoldi, C. Tonci, D, De Rossi "Passive mechanical properties of polypyrrole films: a continuum, poroelastic model" *Matenals Science and Engineering C.* vol 5, pp.101-109, 1997.
- [20] J.B. Yadav, R.K. Puri, V. Puri, "Improvement in mechanical and optical properties of vapour chopped vacuum evaporated PANI/PMMA composite thin film" *Appl. Surf. Sci.*, vol, 254, pp. 1382-1388, 2007.
- [21] Charles, R. C. Weast, S. M. Selby, *Handbook of Chemistry and Physics*, Chemical Rubber Company, Cleveland, OH, 1960.
- [22] T. C. Girija, M. V. Sangaranarayanan, "Investigation of polyaniline-coated stainless steel electrodes for electrochemical supercapacitors" *Synth. Met.* vol, 156, pp. 44-250. 2006

[23] J. C. Dyre, "The random free-energy barrier model for ac conduction in disordered solids" J. Appl. Phys. vol, 64, pp. 2456-2468, 1988.

**AUTHORS' ADDRESSES**

**Veluru Jagadeesh Babu**

**Appukuttan Srikumaran Nair, Ph.D**

**Seeram Ramakrishna, Ph.D**

Healthcare and Energy Materials Laboratory

National University of Singapore

Singapore - 117576

SINGAPORE

**Vasantha Kumari**

**B.S. Abdur Rahman**

Crescent Engineering College

G.S.T. Road

Vandalur, Chennai - 600 048

INDIA

**G.J.Subha**

Department of Rubber and Plastics Technology

Chennai - 600044

INDIA

**V. S. Pavan Kumar**

**T.S. Natarajan**

Indian Institute of Technology

Department of Physics

Madras, Chennai - 600 036

INDIA