Microwave Hall mobility and electrical properties of electrospun polymer nanofibers

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Composite nanofibers from poly(methylmethacrylate)- (PMMA-) conducting polyaniline [PANI(HCl)] were prepared by using the electrospinning technique. The morphology and structural details of the fibers were characterized by SEM and the ac conductivity of the composite fibers found was measured to be $\sim 2.17\times10^{-4}$ S/cm which is very good enhancement compared to that of pure PMMA and conductivity of PANI-PMMA thin films as well. The conductivity is found to increase with increase in the polyaniline content in the composite. Microwave Hall mobility measurements on electrospun nanofibers showed 17 cm^2/V s for the lower loadings. With further increase in the polyaniline content in the composite, the mobility value decreases which is attributed to the increase in carrier-carrier scatterings. © *2011 American Institute of Physics*. [doi:10.1063/1.3556456]

I. INTRODUCTION

Composites derived from both insulating and conducting polymers were found to have advantages in medicine such as controlled drug release,[1] neutral tissue regeneration,[1] electrically conductive scaffolds,[2] etc. Polyaniline (PANI) (a well known conducting polymer) shows a very good potential in microwave absorption,[3] catalytic effects,[4] optoelectronics, and microwave cavity resonance.[5] Furthermore, PANI is unique because of its reversible acid-base doping/dedoping behavior. As microwave-absorbing materials, the nanocomposites derived from PANI and poly(methyl methacrylate) (PMMA) should have low dielectric and magnetic loss.[3] The morphology, size, and specific surface area of the composites also play a vital role in improving their capacities for microwave absorption or electromagnetic shielding. Long *et al.*,[6] explained about conductivity improvement by controlling the morphology and also improved conductivity of composite polymers shows importance toward microwave absorption.[7] In order to effectively regulate the electromagnetic parameters and increase the specific surface area of PANI-PMMA nanocomposites, we have fabricated them via a process called electrospinning, which is a simple, inexpensive, and scalable methodology for one-dimensional nanostructures. Such electrospun polymer composite fibers were found to have applications in electronics and sustainable energy devices.[8,9] These nanofibers can provide very good platform for electron transport pathways in improving electrical conductivity. The main advantage with this method was that we can tune the electrical conductivity of fibers by tailoring the amount of PANI. The nanofibers show a higher specific surface area which is beneficial in improving the properties at microwave frequencies.

This paper reveals the relationship between the PANI content in the composite and the Hall mobility studied at microwave frequencies as functions of composite systems in terms of controlling the morphology and improving the conductivity.

II. EXPERIMENTAL WORK: MATERIALS AND METHODS

Polymethylmethacrylate (PMMA) (Mw 996l000) and polyaniline (PANI) in base form (Mw 35 000) were obtained from the sigma Aldrich, USA. N-methyl-2-pyrrolidone (NMP) (Mw 99.13) was bought from Central Drug House (p), Ltd., New Delhi, India. All the chemicals were used without any further purification.

The HCl doped polyaniline [PANI(HCl)] nanofibers were produced in a two step process as described in Ref. 10. In the first step PMMA was dispersed in NMP then the mixture is agitated using magnetic stirrer for about 48 h. In the second stage PANI (HCl) was added to the above dispersed PMMA-NMP solution at different concentrations (5, 10, 15, and 20% w/w). Then this solution was kept in ultrasonic bath (60 W power was used) for about 1 h. At this stage, the solution was ready for electrospinning. The PMMA-PANI(HCl) solution was taken into a 10 ml syringe with a 23 G needle, the needle and substrate were kept nearly 10 cm apart, the voltage difference maintained of about 7 kV between needle and substrate, solution flow rate 0.5 μl/h, and the speed of the collecting drum kept at 1500 rpm (equivalent to linear velocity of 190 m/s at the drum surface). Fibers were obtained by electrospinning and characterized by scanning electron microscopy (SEM) (JEOL JSM 840A), transmission electron microscopy (TEM) (JEOL 2000FX11), and FTIR spectrospcopy. dc and ac electrical measurements have been carried out on fibers at room temperature. In order to experimentally elucidate the

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charge transport, we employ Hall mobility measurements at microwave frequencies on electrospun nanofibers.

III. RESULTS AND DISCUSSION

A. Fiber morphology

The obtained fibers of composite PMMA-PANI(HCl)-NMP were confirmed by using SEM. Prior to scanning about 30 nm of gold was sputtered on fibers for better contrast then the fiber diameters were estimated. The detailed procedure for obtaining the SEM images of the nanofibers was explained elsewhere[11] and the fiber diameters was evaluated using the UTHSCSA IMAGE TOOL 3.00 program is about 380 nm (standard deviation: 200 nm). The fibers are shown in Fig. 1(a). The fibers seem to be almost aligned and there is a distribution in the diameters which is shown in Fig. 1(a).

Hence, in order to confirm the presence of the PANI particles inside the fibers as well to observe the nature of dispersion, TEM studies were undertaken. TEM images were recorded and confirmed the presence of PANI (HCl) inside PMMA fibers from TEM as shown in inset of Fig. 1(b). A typical TEM image is shown in Fig. 1(b) and the inset shows the fibers at lower loadings (5%) of PANI (HCl).

Thermogravimetric analysis (TGA) (model Pyris 6) was performed on the electrospun fibers to get information about the compositions. Figure 1(c) shows the TGA curves for different compositions of the composite fibers. In all the cases (5, 10, 15, 20 %), HCl and the water contents are getting evaporated at less than 150 °C. The polymer samples decomposed completely above 420 °C. This indicates that the samples are stable up to that particular temperature.

The FTIR spectra for the PANI(HCl)-PMMA fibers having different PANI(HCl) wt. % are shown in Fig. 1(d). The absorption peak at 2945 cm^{-1} is due to the C–H stretching in PMMA. The sharp and intense peak observed at 1722 cm^{-1} is attributed to the C=O stretching in PMMA. The peak at 1387 cm^{-1} is a characteristic peak of intrinsic PANI indicates C–N stretching. The main absorption peak for PANI observed at 1144 and 840 cm^{-1} due to the vibration mode of B–NH=Q (benzene–NH=quinone) or B–NH–B formed in doping reaction. The peak at 1250 cm^{-1} is due to C–O stretching vibration in PMMA and the band at 970 cm^{-1} is due to C–H bending in PMMA. Therefore, the IR results signified that PANI used in the preparation was protonated and a higher doping levels lead to higher conductivity (see below).

B. ac electrical properties

The nanocomposite fibers were studied to investigate the effect of loading of conducting fillers on the electrical conductivity and thus to understand the conduction mechanism in these types of disordered systems. Park *et al.*[12] reported that the dc electrical conductivity of PANI-PMMA ($\sim 10^{-9}$ S/cm) in the form of compressed disks at 10% (w/w) of loadings. This low conductivity of PANI-PMMA indicates that the conductivity is not enough to use in electrical devices; it seems to be enhanced by nanofibers. The nanocomposite fibers were studied to investigate the effect on the loading of conducting fillers and to understand the conduction mechanism in these types of disordered systems.[13] The current-voltage characteristics were performed on electrospun nanofibers using similar conditions[13] and the calculated dc conductivities are plotted in Fig. 2(a). From the figure, the percolation threshold is seen to occur for conducting PANI (HCl) even at less than 5% loadings. As a result, after reaching the percolation limit of conductivity, there was no enhancement for further with increase of PANI (HCl) fraction beyond this limit. However, it is difficult to obtain a reliable resistance value for the attempted conductivity for lower fillings with the existing instrument as it has an upper limit in measuring the resistance. In order to decrease the measured resistance we have attempted the following. We increased the number of fibers across the electrodes, which is refrained due to the fact that we may not be able to count them (to find the total cross-sectional area and hence the conductivity). Also increased numbers may have contact problems with the electrode, as they may fall on top of each other rather than on the electrode. We decreased the distance between the test electrodes. We currently have a facility with which we can fabricate down to 200 μm only and no lower. Due to the above reasons we have not done measurements

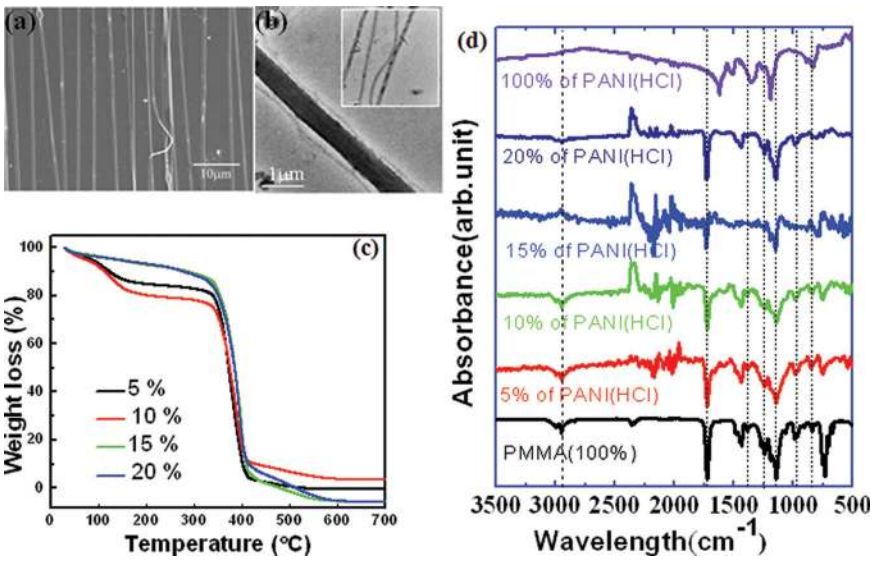

FIG. 1. (Color online) Electrospun nanofibers: (a) SEM images, (b) TEM image. The inset shows the fibers at lower loadings at 5%. (c) TGA, (d) FTIR comparision PMMA with PANI(HCl) loadings.

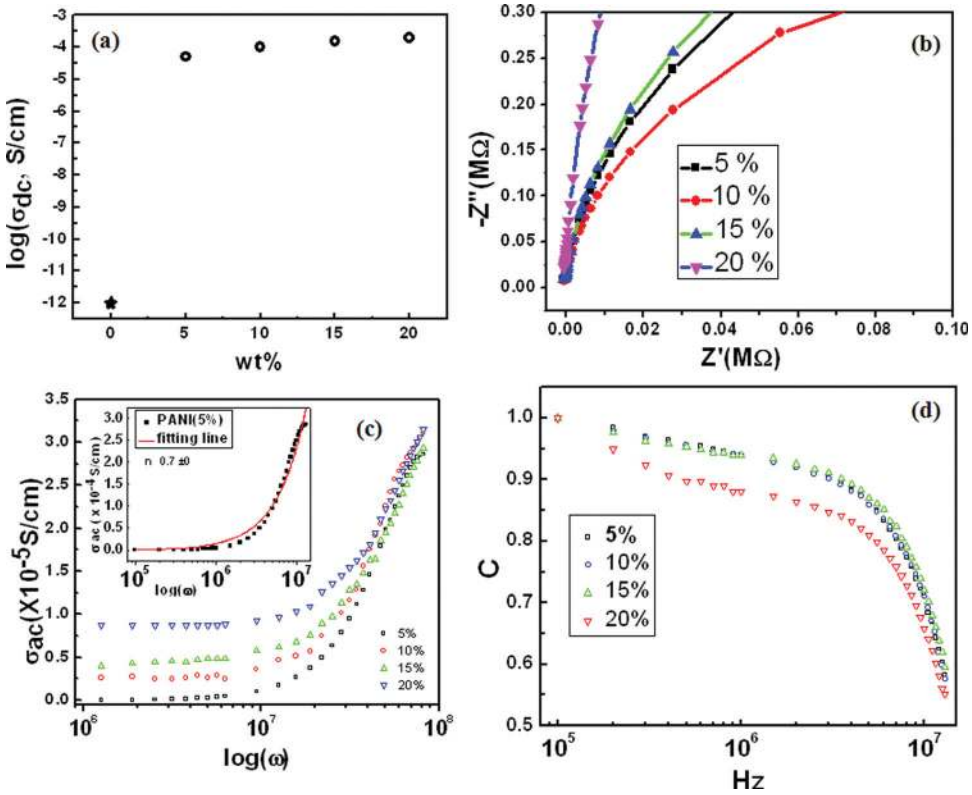

FIG. 2. (Color online) (a) dc conductivity with concentration. An asterisk indicates the conductivity value of PMMA from literature (Ref. 13). (b) ac impedance. (c) ac conductivity and inset shows fitting for power law at 5% concentration. (d) Capacitance for different concentrations.

for lower filling rates of PANI in PMMA. However, the conductivity of the composite nanofibers show 10^{-12}, 4.59×10^{-5}, 1.04×10^{-4}, 1.29×10^{-4}, 2.17×10^{-4} S/cm for the 0, 5, 10, 15, and 20 % (w/w) of PANI (HCl) loadings, respectively. The calculated conductivities are nearly 7 and 5 orders of magnitude improvement when compared to the conductivity of PMMA and PANI-PMMA thin films, respectively. Hence, these nanofibers are superior than the thin films with respect to the electrical properties.

The frequency dependent ac conductivity and ac impedance studies in the frequency range 5 Hz to 10 MHz have been investigated which is shown in Fig. 2(b) and as performed earlier by our group.[10] The conductivity shows an increase with frequency [Fig. 2(c)]. The experimental results showed that the ac conductivity increases with incorporation of PANI(HCl) and with frequency as well. This indicates that the charges are trapped till the critical frequencies.

Beyond the critical frequency, the charges are active, and then the conductivity starts to depending on frequency. It is observed experimentally. Furthermore the conductivities followed power law behavior which is shown in inset of Fig. 2(c). The evaluated exponent n lies between 0.6 to 1.0 and was characteristic behavior for many disordered systems.[14]

From the impedance analyzer one can also measure the capacitance with frequency and shown in Fig. 2(d). The capacitance of the fibers shows almost constant up to the some extent (1 MHz) of frequency then after that limit it drastically decreases with frequency. This was due to the expansion of lattice and excitation of charge carriers present at the imperfection sites or due to orientation of dipoles occurring at high frequencies.[15,16] This is also because of the increasing inability of the heavier dipoles to orient themselves with the rapidly varying applied electric field.[17] Figure 2(d) shows the capacitance variation with the concentration at different frequencies. From the figure, it is clear that the capacitance initially increased up to 10% and then decreased at different frequencies.

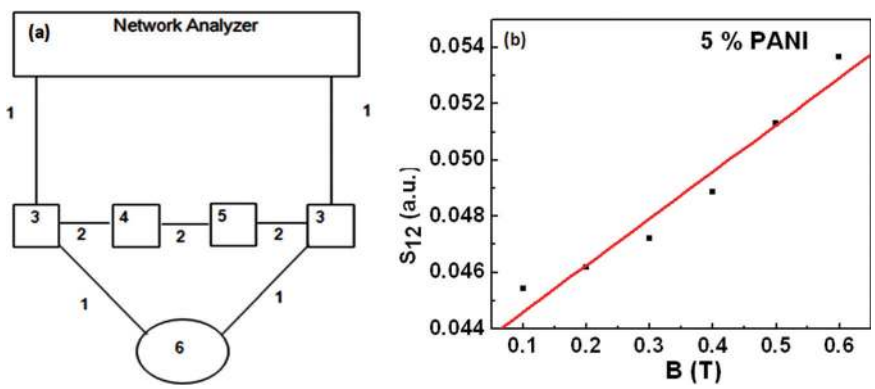

FIG. 3. (Color online) (a) Schematic diagram of microwave Hall effect (MHE). 1: Coaxial cables, 2: rigid coaxial cables, 3: coaxial directional couplers, 4: coaxial step attenuatros, 5: coaxial phase shifter, 6: bimodal cavity. (b) The magnetic field with transmission coefficient proportionality variation.

TABLE I. *Microwave Hall mobility studies for electrospun fibers of PANI(HCl)-PMMA.*

Sample	f_r (GHz)	ρ_{11}	ρ_{21}	Γ_{11}	Γ_{21}	Q_{11}	Q_{21}	S_{12}/ B(a.u./G)	μ_H (cm^2/ V s)
5%	13.955	1.004	1.096	0.002	0.046	1664	1323	2.80×10^{-9}	17
10%	13.953	1.199	1.189	0.090	0.0863	2380	1211	2.92×10^{-9}	8
15%	13.951	1.232	1.295	0.131	0.1285	2332	1117	1.57×10^{-10}	3
20%	13.954	1.225	1.284	0.101	0.124	2145	1070	1.04×10^{-10}	1

C. Microwave Hall mobility

It is difficult to perform carrier mobility measurements using the conventional dc Hall effect for fibers because fixing the gold electrodes on the fibers are a bit complex. Hence, we performed the mobility studies using the microwave Hall effect which is a nondestructive and contactless experimental technique. This gives the information regarding mobility of the carriers at microwave frequencies. The block diagram in Fig. 3(a) shows the experimental arrangement of the microwave Hall effect (MHE) A $TE_{111}P$-band dual mode cylindrical cavity with radius and height of 1.1 and 1.3 cm, respectively, was designed and fabricated. Probe coupling was chosen for the excitation of the cavity. The cavity resonated at 14 GHz and unloaded quality factor was 3109. The detailed explanation of the MHE experimental arrangement is given elsewhere.[18,19] The sample is mounted on a polytetrafluoroethylene sample holder, was placed where both the orthogonal modes have their maximum electric field. One of the modes is excited using the input port of the cavity. The carriers oscillating due to the input microwave power is subjected to an external static magnetic field. This couples the microwave power to the orthogonal mode, the magnitude of which depends on the mobility of the carriers. Thus, the change in the transmission coefficient between the two modes due to the applied magnetic field is related to the mobility of the carriers.

The expression[20] for obtaining the Hall mobility of the composite fiber sample at microwave frequencies is given as follows

$$\mu = \frac{K}{B}\left[\left(1-\frac{Q_{11}}{Q_{10}}\right)\left(1-\frac{Q_{21}}{Q_{20}}\right)(1-\Gamma_{11})(1-\Gamma_{21})\right]^{-1/2} S_{21},$$

where Q_{10}, Q_{20}, Q_{11}, and Q_{21} are the unloaded and loaded quality factors at ports 1 and 2, respectively; Γ_{11} and Γ_{21} are the loaded reflection coefficients of input 1 and output 2 respectively; S_{21} is the change in the transmission coefficient; K (2.08×10^9) is the calibration constant obtained with a standard semiconductor sample; and B is the static magnetic field. This equation is valid only if the skin depth is greater than the thickness of the sample and one can also evaluate the conductivity of the sample if the geometry of the sample is known. The variation of the transmission coefficient with magnetic field is shown in Fig. 3(b) and one can observe that it is linear in nature for all the compositions. As it continues to increase the concentration of PANI (HCl), the mobility decreases, which is clear from Table I. Furthermore the measured microwave Hall mobility of fibers does not depend on any preferred alignment.[21]

The carrier mobility was almost negligible for the polymers. After the addition of PANI (HCl) the mobility of the composite fibers is 17 cm^2/V s. Furthermore, the microwave mobility decreases as the concentration increases. Hence, there must be a critical concentration at which the mobility shows a maximum. It is well known that above the percolation threshold, the conductivity does not proportionally increase with the concentration of PANI (HCl). This happens due to the presence of scattering of the carriers either by other carriers or by the lattice. This dominates even at lower concentrations and, therefore, the percolation threshold for the mobility is lower than that of dc conductivity. Thus, the carrier-lattice scattering may be one of the reasons for the decrease in the mobility of the carriers in the composite.[21]

IV. CONCLUSIONS

PANI (HCl)-PMMA nanocomposite fibers were prepared by electrospinning. The diameters of the fibers were found to be in the range of 380 nm. ac conductivity was estimated by fitting impedance data to a Z-view program. The conductivity was enhanced by nearly seven orders of magnitude from that the conductivity of PMMA. The frequency dependent ac conductivity shows the well-known universal behavior with a frequency independent region at low frequencies and a power law behavior at higher frequencies with an exponent in the range of 0.6 to 1. Hall mobility studies at microwave frequencies were carried on electrospun nanofibers using a nondestructive method. The carrier mobility found to decrease with the increase of PANI (HCl) content. This may be due to the increase in the carrier-carrier scattering.

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