Electrical Properties of Electrospun Fibers of PANI-PMMA Composites

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ABSTRACT

Electrospinning is one of the simplest techniques for obtaining polymer nano fibers. Nanofibers have large surface area to volume ratio and hence have excellent application potential in sensors, filter design etc. Polyaniline (PANI) is the well-known and widely studied conducting polymer, which however, is insoluble in many common organic solvents and hence difficult to process. PANI in its base form is non conductive but it can be made conducting by protonating with an acids such as hydrochloric acid (HCl) or camphor sulphonic acid (CSA). However, it is difficult to electrospin PANI by itself since we need preferably the polymer in solution form. In this study we have formed nanofibers of PANI (CSA) dispersed in Poly Methyl Methacrylate (PMMA) solution in chloroform. The morphology of the electrospun conducting PMMA-PANI composite fibers is studied using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The DC and AC conductivities of these fibers are measured and the results are discussed.

INTRODUCTION

Electrospinning is a process by which fibers with sub-micron diameters can be obtained from an electrostatically driven jet of polymer solution. Invariably, the fibers are collected as a non-woven mat on a metal electrode. These fibers have a high surface area to volume ratio, which makes them suitable for various applications like filtration, scaffolds for tissue engineering, etc., [1]. Polyaniline (PANI) is a well-known conducting polymer, which is difficult to process since it is insoluble in many common organic solvents. However, it has been shown to be useful in many applications including conducting coating on plastic materials for corrosion protection [2]. PANI in the base form non conductive but it is made conducting by doping with some acids such as hydrochloric acid (HCl), camphor sulphonic acid (CSA), etc., [3,4]. For electrospinning, we require a polymer in solution and hence it is difficult to spin PANI by itself. Of course, electrospun fibers of water-soluble PANI blends have been prepared

successfully recently [5]. Here, we have dispersed PANI in Polymethyl methacrylate (PMMA) dissolved in chloroform to make nanofibers. The formation and the diameters of the electrospun fibers depend on the concentration of polymers in the solvent, the applied voltage, the distance between the electrodes and the flow rate of solution [3].

EXPERIMENTAL MATERIALS

Polymethylmethacrylate (PMMA) was obtained from Union Carbides. Dl-Camphor-10- sulphonic acid (purity 98%) was obtained from Alfa Aesar Research chemicals, USA. Chloroform was from Aldrich, India. All the chemicals were used as received.

SAMPLE PREPARATION

Polyaniline (PANI) powder was synthesized chemically by oxidative polymerization of aniline in an aqueous HCl solution. Aniline (0.1 M) was dissolved in 1 M aqueous solution of HCl below 5 °C and an aqueous solution of ammonium peroxydisulphate (0.1 M) was added to the above solution over a period of 30 minutes with vigorous stirring. The mixture was stirred continuously for 2 h. The precipitate was collected by filtration and then washed repeatedly with distilled water. Polyaniline base was obtained when the polyaniline was treated with aqueous solution of ammonia (pH ~ 9) under stirring for 6–8 h and washed with distilled water till washings were neutral to a pH indicator paper. Refluxing it with methyl alcohol, benzene and acetone purified the blue emeraldine base powder obtained after filtration. This process of treatment with organic solvents was repeatedly done till the filtrate was colorless. Finally, the emeraldine base obtained was dried under dynamic vacuum at 60–80 °C for 8 h. This emeraldine base was the starting material for the preparation of conducting polyaniline solution.

PANI–CSA solution was prepared by mixing 1 g (3 m mol) emeraldine base powder, 1.32 g (6 m mol) camphor-10-sulphonic acid and 2 g (14 m mol) Chloromethylphenol (CMP). The mixture was ground thoroughly in a homogeniser in presence of

chloroform as solvent for 2–4 h. The thick solution obtained was filtered and its solubility was 10g/litre and electrical conductivity, 2.5 S/cm. The above PANI solution in chloroform (10g/lit) was used to prepare the required 20% solution of the composite polymer (PANI-PMMA). The concentration of PANI in PMMA was maintained at 10% by weight. The solution was allowed to mix for about 4 hrs using first the magnetic stirrer and then the sonicator. This solution was used to prepare the fibers using electrospinning.

THE PREPARATION OF FIBERS AND CHARACTERIZATION

The experimental apparatus for electrospinning, shown in the fig.1, was built in the lab [6,7]. The polymer solution was taken in a 5ml disposable syringe (Dispovan India) and the diameter of the needle was 0.56mm.
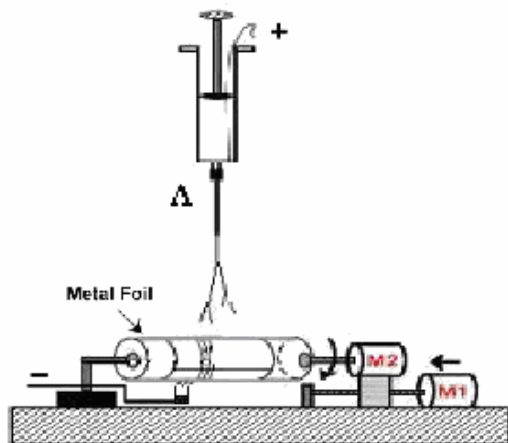

FIGURE 1. The Electrospinning apparatus for producing polymer composite fibers.

Positive terminal of a high voltage variable power supply (0 to 5 kV from APLAB India) was connected to the polymer solution by introducing a very thin copper wire (40 SWG) into the syringe in contact with the solution. The collecting drum, placed about 3.5cm away from the tip of the needle, was wrapped with aluminum foil 0.05 mm thick and was connected to the negative terminal of the power supply (grounded counter electrode). The drum can be rotated at high speed (~2000 rpm) using a small DC motor. The flow rate of the solution was controlled at 0.54ml/hr using a syringe pump (home-made) interfaced to a computer. Fibers were collected with and without rotation of the drum in order to investigate the alignment achieved during rotation. SEM pictures of these fibers were recorded. In order to get an estimate of the diameters of the fibers and the

spacing between the aligned fibers AFM measurements were done. The fibers were characterized by XRD (Shimadzu X-ray Diffrectometer, Model XD-D1 operating at 30 kV and 20 mA (Cu K_∞), Scanning Electron Microscope (LEICA) and Atomic Force Microscope (Dimension 3100, Nanoscope-IV) in contact mode. The current-voltage characteristic was measured using a constant Current Source (Keithley Model 225) and Digital Multimeter (*hp* Model 34401A). The AC impedance measurements in the frequency range of 100kHz to 13MHz were done using *hp* Impedance Analyzers 4192A.

CHARACTERIZATION OF NANO FIBERS

The SEM pictures of the fibers obtained are shown in fig2 (a) and 2(b) without and with the rotation of the drum respectively.
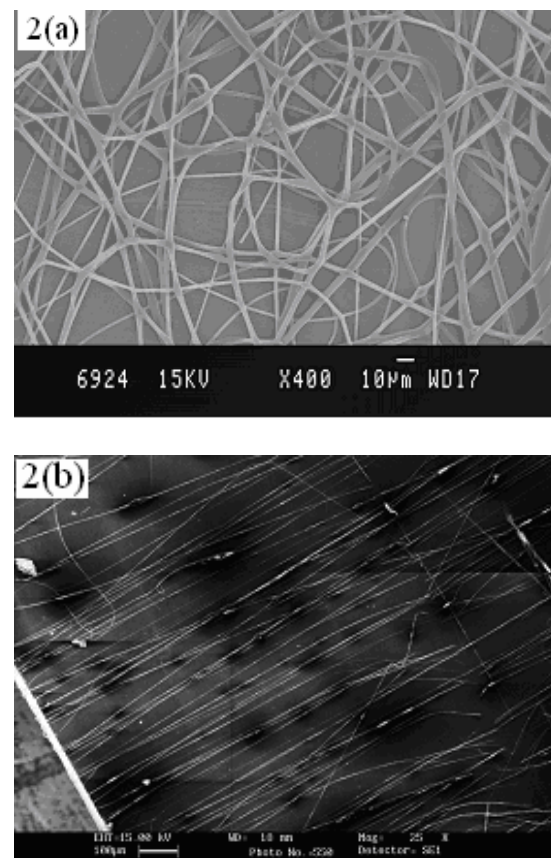

FIGURE 2. Scanning Electron Micrographs for the PANI (CSA)-PMMA Composite fibers (a) with out rotation of drum and (b) with the rotation of drum.

We observe the fibers are formed as random coils in fig2 (a) while they are well aligned along the direction of rotation, when the drum is rotated at high speed (~1000rpm) as shown in Fig 2(b).It shows that the fibers are fractured

this is because of higher rate of collection (high rpm).
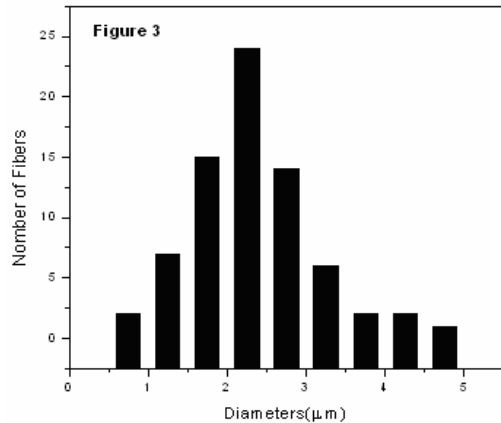

FIGURE 3. Diameter distributions of the fibers of PANI (CSA)-PMMA composites from the SEM pictures.

This was performed to attain good alignment, as we could see from the picture. But actually fibers, which were collected on the electrodes, were not fractured as we have performed at little lower rate of collection. The fibers are of several centimeters in length, having almost uniform diameter throughout their length. However, the diameters show a distribution across different fibers. From the SEM pictures the distribution of diameters of the fibers are plotted using the Image Tool 3.1 as shown in fig.3. The diameters are in the range of 500nm to 5µm. The distribution is Gaussian with the maximum occurring in the range of 2 µm.

The AFM pictures shown in Fig 4(a) & 4(b) also confirm that the fibers are well aligned and diameter measured is in the range of 1 to 2µm. It is difficult in general to obtain exact information about the actual geometry of the fibers from the SEM pictures alone. However, from AFM pictures we can see that the fibers are cylindrical in geometry and not a collapsed tubular structure as observed in a few other cases [8]. It is also seen that the fibers are free from defects such as beads, etc. The spacing between the two parallel fibers is found to be 20µm and it is constant over large distances as seen from the picture.

For the study of XRD patterns, fibers are formed on a glass substrate and later scrapped after drying and then subjected to X-ray diffraction. XRD figures recorded for the films of pure PANI (CSA), pure PMMA and PANI-PMMA composite are shown in Fig.5 (a) to 5(c). The figure 5(d) shows the XRD picture of electrospun fibers of PANI-PMMA composites. It is observed from these pictures that both the Polymers PANI and PMMA

are mostly amorphous, as there are no sharp peaks observed. Intensity peaks having 2θ values around 8, 14, 20 correspond to PMMA [9] while those
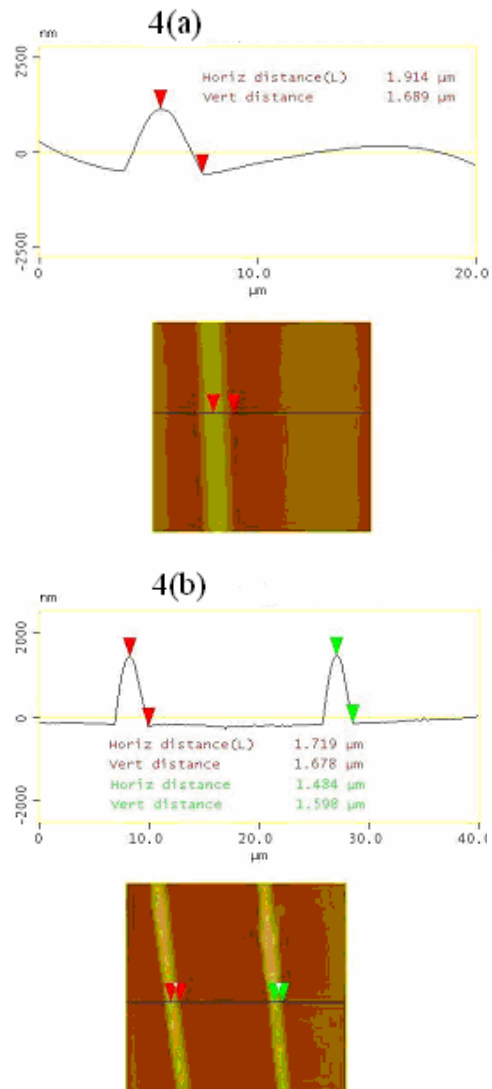

FIGURE 4. The Atomic Force Microscopy pictures for the 10% of PANI (CSA)-PMMA (a) single fiber and (b) two parallel fibers.

around 11, 19, 26 and 56 correspond to PANI [10,11]. Here, the 2θ values of the broad peaks in the figures match closely with some of these values. When we compare the XRD pictures of the film (5(b)) and those obtained for the fibers of the composite (5(d)), we observe that while the film shows almost amorphous behavior the electrospun fiber shows an intense sharp peak around 2θ =26 degrees which is characteristic of PANI. This shows that the electrospinning has improved the crystallinity of the polymer. Zong et al. [12] while

investigating the DSC and XRD data of PLLA nanofibers observed that the polymer chains were non-crystalline, but highly oriented. However, Lee et al. [13] and Reneker et al. [14] reported that the crystalline structure was developed in PCL nanofibers through electrospinning process as well as molecular orientation along the fiber axis. The polymer solution is forced through a narrow orifice during the electrospinning process and during its travel towards the counter electrode most of the solvent molecules evaporate away leaving behind almost solidified polymer. It has been observed that in many situations some of the solvent molecules are still present in the non-woven mat that is obtained at the counter electrode. This slow solidification process along with the partial effect of ordering of the molecules while emerging through the nozzle all help in improving the crystallinity of the electrospun fibers. Renekar et., al., have also observed that on annealing the fibers formed the crystallinity improves. However in the present case even without annealing the fibers show improved crystallinity.

RESULTS AND DISCUSSION

For the measurement of electrical conductivities we need the exact dimensions of the fibers such as diameters and the length apart from the resistance. However, the fibers invariably show a distribution in diameter and are collected randomly in the form of a coil and hence there are only a few reports in the scientific literature on such measurements.

One way to overcome this difficulty is to isolate carefully a single fiber by allowing only a small number of fibers to be formed for a very short time and then form two metallic electrodes by vacuum evaporation for the measurement [6,15]. But isolating a single fiber is indeed a difficult task. Hence in the present experiment the I-V characteristic of a bunch of countable number of aligned fibers was measured and the data obtained is plotted in Fig.6. For this, silver electrodes with a small gap (~1mm) in between, are deposited on the fibers by vacuum evaporation. From the graph it is observed that the behavior is ohmic and from the slope the resistance was found to be ~10MΩ. The number of fibers (~110) and the spacing between the electrodes (1mm) are measured using an optical microscope. The average diameter of the fibers is found to be 2 μm from Fig.3.

Using these, the dc conductivity of the composite fibers is estimated as 0.289 S/m. This value is about three orders less compared to that of pure PANI (CSA) sample (200-400S/m [16]). This is understandable since blending PANI with an insulating polymer would reduce the conductivity. However, if we compare with the conductivity of

pure PMMA obtained from the standard data (~10^{-13}S/m, [17]) there is nearly 12 orders of magnitude
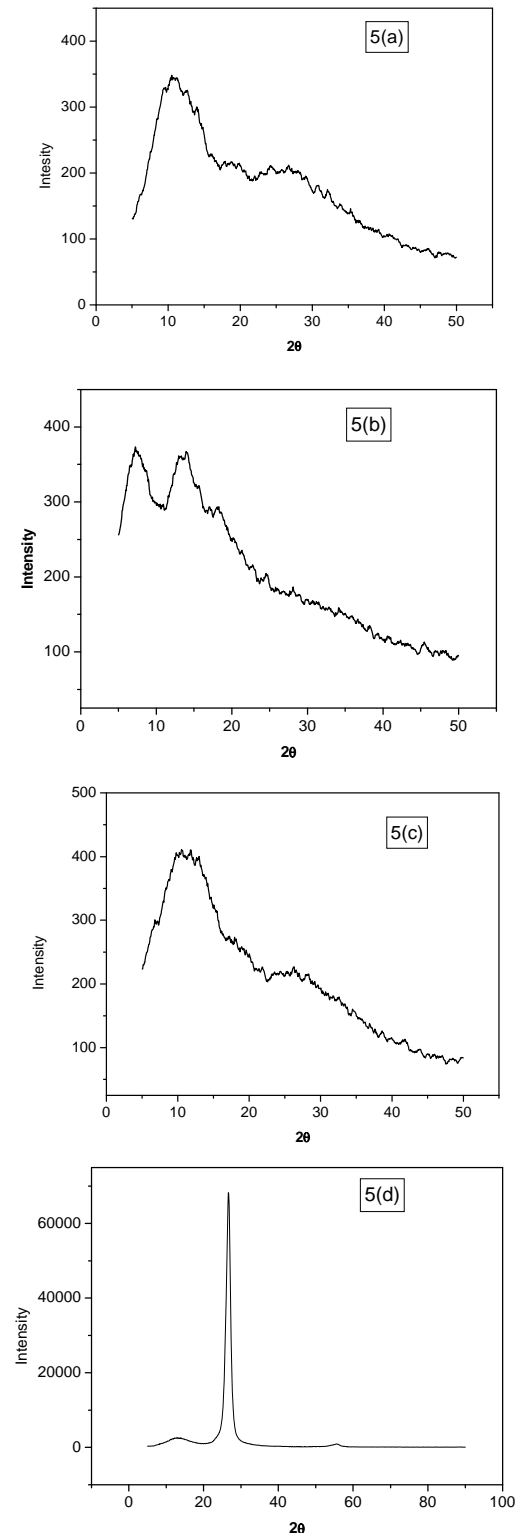

FIGURE 5. The X-Ray Diffractogrames for the (a) PANI (CSA) film, (b) PMMA film, (c) PANI (CSA)-PMMA composite film and (d) PANA (CSA)-PMMA composite fibers.
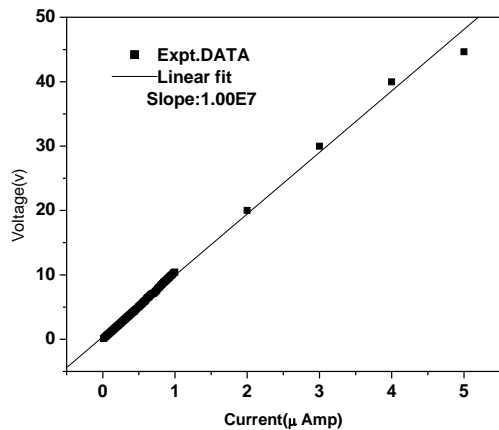
FIGURE 6. The voltage-current characteristic feature for the 10% of PANI (CSA)-PMMA fibers.

increase in the conductivity of PMMA even for an addition of 10% by weight of PANI.

The Real and Imaginary parts of the impedances are plotted against logarithm of frequency in the Fig.7 (a). The complex data was fitted to a semicircle using the Z-View program and the fitting is shown in Fig.7 (b).

From the intercept on the real axis the DC resistance is found to be around 57.8MΩ. This agrees well with the value (10MΩ) obtained from the slope of the I-V characteristics above. The complex conductance σ^* is equal to $1/Z^*$ where Z^* is the complex impedance. In general, we can write $\sigma^* = \sigma'(\omega) + i\sigma''(\omega)$ where σ' and σ'' are the real and imaginary parts of the conductance. J.C.Dyre has shown using his Random Free Energy Barrier (RFEB) model that in many disordered solids including polymers, the $\sigma'(\omega)$ is an increasing function of frequency [18,19]. Any hopping model has this feature. By hopping forwards and backwards at places where the jumping probability is high a quasi particle can contribute to the ac conductivity significantly. The higher the frequency of the electric field the larger is the ac conductivity because better use is made of places with very large jump probability. Thus according to this model the σ' shows a low frequency plateau and for higher frequencies the behavior is like $\sigma' \propto f^n$ where n is close to unity [20,21]. The imaginary part σ'' shows an ever-increasing behavior with frequency.

The plots of σ' and σ'' with frequency in logarithmic scale for the PANI-PMMA fibers is shown in Fig 8. The behavior is similar to that proposed by the Dyre model. This shows that the charge transport is through hopping. Conducting polyaniline islands are distributed among the

insulating regions of PMMA. The electrons are able to hop from one conducting region to another due to the applied time varying electric field, which is responsible for the good conductivity measured for the fibers. Fig.9 shows the plot of capacitance evaluated from the impedance measurements versus the frequency. It is observed that the capacitance is almost a constant around 2pF up to a frequency of 1MHz and then falls slightly below. The variation is not very significant over the range of frequencies. The change in capacitance observed at higher frequencies is similar to that observed in the case of PANI films and can be attributed to the expansion of lattice and excitation of change carriers present at the imperfection sites or due to orientation of diploes occurring at high frequencies [22,23].
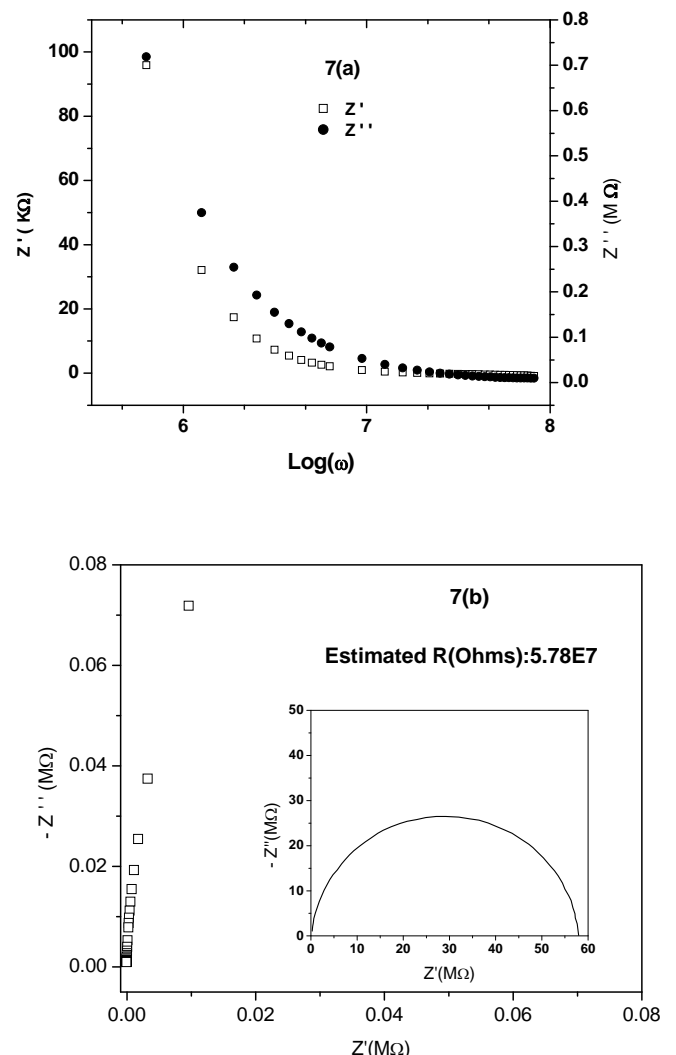

FIGURE 7. The 10% of PANI (CSA)-PMMA fibers (a) The Variation of Real and Imaginary Impedances with Frequency, (b) The Real part of Impedance Verses the Imaginary part of impedance.
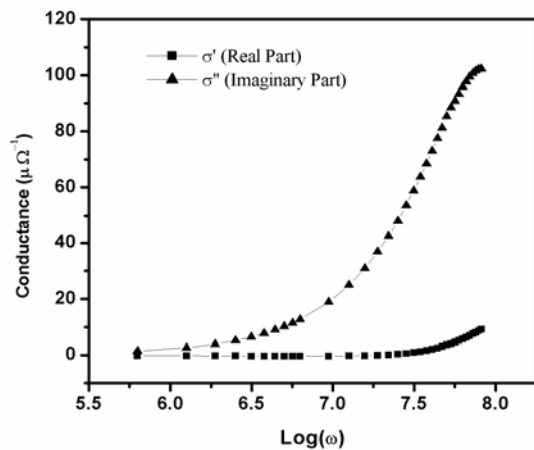
FIGURE 8. The Real and Imaginary conductance variations with the logarithmic frequency for 10% of PANI (CSA)-PMMA fibers.
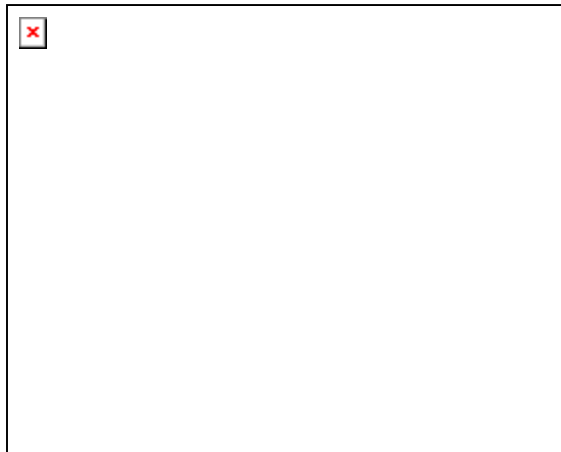

FIGURE 9. The Capacitance for the 10% of PANI (CSA)-PMMA composite fibers with logarithmic frequency.

CONCLUSIONS

PANI (CSA)-PMMA composite fibers were prepared using Electrospinning. The fibers were characterized using SEM; AFM, XRD and the I-V characteristics and AC impedance measurements were carried out. Very good aligned fibers with diameters in the range of 500nm to 5μm were obtained. The dc conductivity was estimated to be around 0.28 S/m. The complex conductance plots show that the system under study is a highly disordered one as predicted by the Dyre's model. These fibers would find application in gas sensing.

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