On the Prospects of Polyaniline and Polyaniline/MWNT Composites for Possible Pressure Sensing Applications

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ABSTRACT: This work highlights the prospects of applications of doped polyaniline (PANI) and Polyaniline–MultiWalled Carbon Nanotube (MWNT) composites with different dopants in pressure sensing devices. PANI and its nanocomposite samples in the form of pressed pellets show orders of change in electrical conductivity with applied pressure in the range 0–30 MPa, even for very small applied bias of a few milli-volts. The percentage variation of electrical conductivity with applied pressure is strikingly large for PANI and its composite samples. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 138–142, 2010

Key words: Polyaniline; nanocomposites; conducting polymers; MWNT; matrix

INTRODUCTION

Conducting polymer nanocomposites have the distinction of being hybrids belonging to a class of advanced composite materials that can be used for very interesting applications. These composites generally have two components: a polymer matrix and a filler. The filler can be an inorganic powder, such as a metal or a ceramic, or an organic material such as carbon (carbon black or a fullerene) or an intrinsically conducting polymer. It is found that the properties of the hybrid materials get modified when one of the fractions occur in the nanometric scale.[1] Carbon nanotubes both single walled and multiwalled have been a subject of extensive research because of their unique physical, chemical, and structural properties, which have been exploited for their use in field emitters,[2] nanoelectronic devices, sensors,[3] actuators,[4] etc. Blends of carbon nanotubes with conducting polymers resulting in the formation of composites have now received a great deal of attention.

These composites exhibit the properties of their constituents with synergetic effects and are promising candidates for use in organic light emitting diodes,[5] photovoltaic cells,[6] batteries,[7] and supercapacitors.[8]

Polyaniline, an interesting conducting polymer, has been known for more than a century, and is still of interest both academically and industrially. Because of its unique processibility together with the availability of relatively inexpensive monomer and high yield of polymerization, it has become one of the most technologically important polymeric materials. Neutral (or undoped) polyaniline exhibits conductivity of the order of 10^{-10} S/cm; but doping with an acid results in a significant increase in its conductivity (up to 10–11 orders of magnitude). The process of doping causes the delocalization of the charge and spin along the backbone of the polymer, there by enhancing its conductivity. It is reported that carbon nanotubes (CNT) in the polyaniline (PANI) matrix, in the doped and the neutral form, act as dopant thereby increasing the electrical conductivity of the matrix.[9]

This work describes the synthesis and characterization of acid doped polyaniline and its composites with multiwalled carbon nanotubes (MWNT) obtained by *in situ* polymerization. Attempts have been made to study the variation of DC electrical conductivity with applied pressure, and thus, to assess the prospects of application of these materials in pressure sensing devices.

EXPERIMENTAL

Synthesis of acid doped PANI and PANI-MWNT composite

The chemical oxidative polymerization[10,11] of monomer aniline was done in the acidic medium of 1*M* camphor sulphonic acid (CSA) and orthophosphoric acid (OP), with ammonium persulphate (APS) as oxidant. APS was added immediately to the solution and stirred for 5 h. The resultant solution was
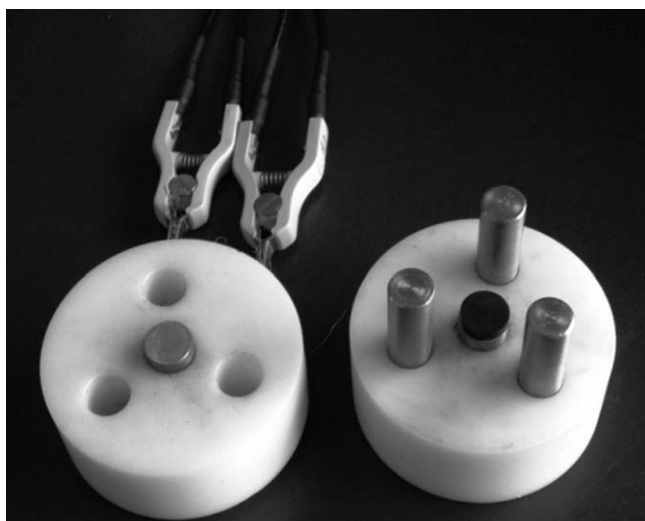
Figure 1 Sample holder used in the experiment to measure the change in conductivity with applied load using 2-probe method.

filtered and washed with water and acetone. The powder thus obtained was dried in hot air oven at 50°C for 4 hr and pelletized under a pressure of 9 tones. Pellets of 13 mm diameter and a few mm thickness were made using a die.

Naphthalene-2-sulphonic acid (NSA) doped PANI was synthesized by dissolving APS in deionized water and then adding slowly to a cooled 1 : 1 mixture of aniline and NSA.[12] The mixture was stirred for 24hrs at 0–5°C. The precipitate was washed with deionized water, methanol, and ethyl ether several times and then kept for drying at room temperature for 24 h. The powder was pelletized to get 13 mm diameter pellets.

PANI-MWNT composites were also synthesized by the same procedure as described above. MWNT, purchased from Conyuan Biochem, Taiwan, was mixed with aniline in the acidic medium and then kept for *in situ* polymerization.

Structural characterization

X-ray Diffraction, Fourier Transform Infrared, and Raman spectroscopic techniques were used to carry out the structural characterization of the samples. The XRD studies of the samples were done using Rigaku X-ray diffractometer using Cu-Kα radiation. FTIR and Raman investigations were performed using Jasco V-70 UV-VIS-NIR and Jobin Yvon Horibra LABRAM-HR microraman spectrophotometer with 488 nm argon laser as source, respectively. The spectra were analyzed to assure the presence of MWNT in the composite samples and structurally characterize the samples.

The pellets of 13 mm diameter and 1.5–2 mm thickness were made at room temperature using a

homemade die under a pressure of 9 tons in a table-top hydraulic pellet press. The quantity of the sample, applied pressure, and pressing time were optimized and maintained the same for all the samples. The variation of DC electrical conductivity with applied pressure of the pellet samples was studied using a homemade sample holder (Fig. 1) connected to Keithley 2400 source meter automated using Lab-VIEW software. Calibrated loads were applied on top of the sample holder and the change in conductivity for each sample with the loads was analyzed using a dedicated program developed in LabVIEW. An average of 10 conductivity values was taken as the conductivity of each of the pellets. The bias applied was in the range of 1–10 millivolts.

RESULTS AND DISCUSSION

Structural characterization

Figures 2, 3, and 4 show the XRD patterns of acid doped PANI and their composites with multiwalled carbon nanotubes.

PANI shows amorphous peaks at around 11° and 19° and a sharper peak at 25°. MWNT has a highly crystalline peak at 25°, which is much more intense and sharper than that of PANI at the same position. PANI-MWNT shows the crystalline peak of MWNT at 25° with high intensity and sharpness. The amorphous peaks of PANI at 11° and 19° appear sharper in the XRD spectrum of PANI-MWNT confirming the formation of the composite. The appearance of the graphite-like diffraction peak at 25°, which is common to both PANI and MWNT, indicates the presence of long range π-conjugation, in all the samples. This peak is very much sharper in MWNT because of much enhanced π-conjugation in MWNT.
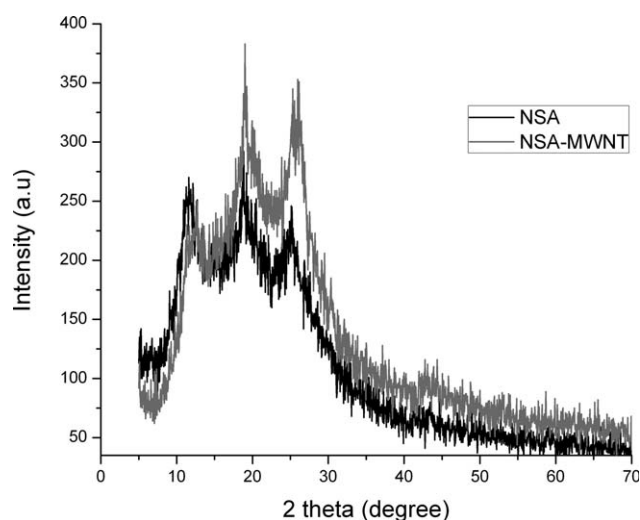

Figure 2 XRD of NSA doped PANI and its composite with MWNT.
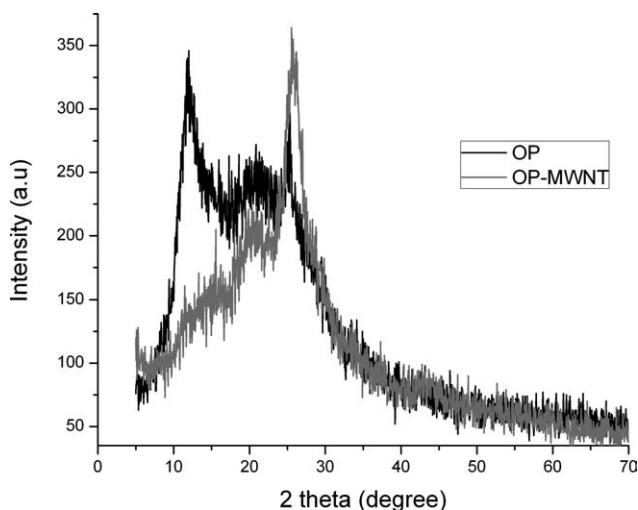
Figure 3 XRD of OP doped PANI and its composite with MWNT.

These observations are common to all the three acid doped PANI samples and their composites.

The FTIR spectra of CSA, OP, and NSA doped PANI are shown in Figure 5.

In OP doped PANI, peaks are observed at 1473 cm^{-1} (C = C stretch of the benzenoid unit of PANI) and at 1052 cm^{-1} (quinoid unit vibration of doped PANI) as reported before.[13,14]

In CSA doped PANI, the peak at 1240 cm^{-1} corresponds to the C—N stretch vibration and the one at 684 cm^{-1} denotes the C—H out of plane bending.[15] The peaks at 1566 cm^{-1} and 1487 cm^{-1} correspond to the C=C stretching deformation of quinoid and benzenoid rings,[16] respectively, and the one at 1301 cm^{-1} is attributed to the C—N stretching of secondary aromatic amine.[17] The vibrations of —SO$_3$H group[18] are observed at 508, 582, 790, and 1039
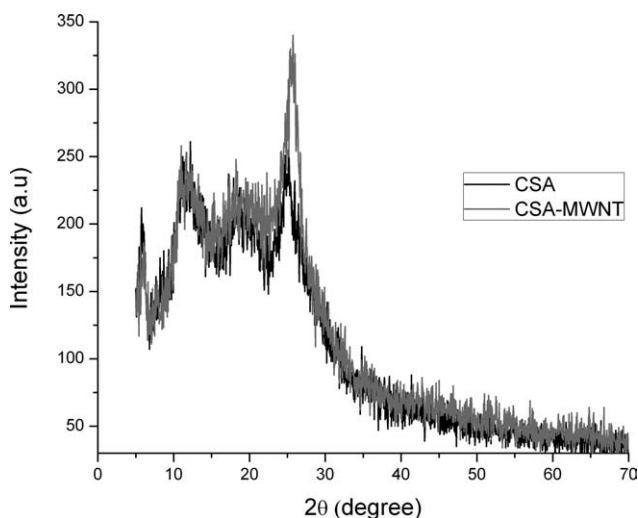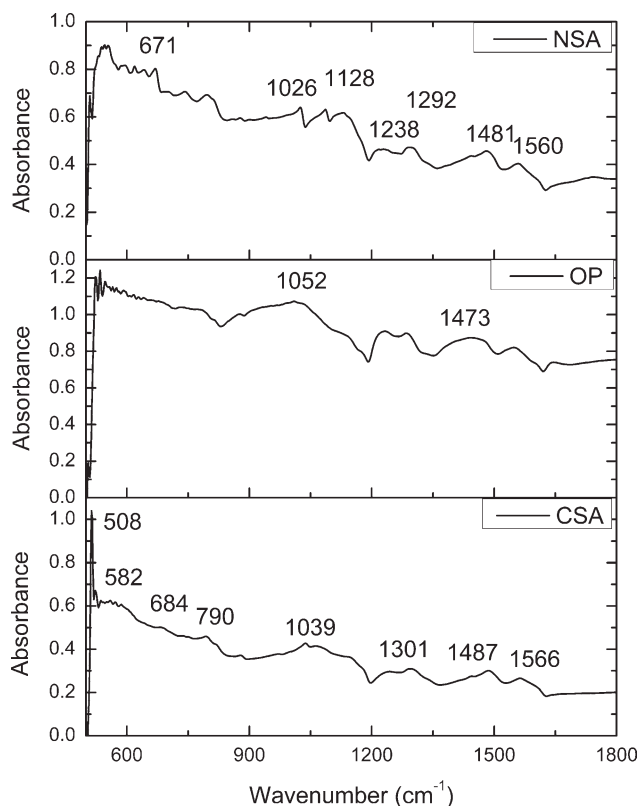

Figure 5 FTIR spectra of CSA, OP, and NSA doped PANI.

cm^{-1}, which signifies the presence of the dopant CSA.

Characteristic peaks of NSA doped PANI are observed at 1560 cm^{-1}, 1481 cm^{-1}, 1292 cm^{-1}, 1238 cm^{-1}, 1128 cm^{-1}, and 800 cm^{-1}. When compared with EB form of PANI, a small red shift can be observed for these bands.[12,19] There is also broadening of the bands and change in the relative intensity. The enhancement of the oscillator strength of the backbone-related vibrations because of a vibronic coupling with the π-electron charge oscillation along the chain[12,20] can be a possible reason for this. There is also similar observation in PANI–HCl, indicating that the backbone structure of PANI–NSA tubules and PANI–HCl are similar. A slight difference exists at 1026 cm^{-1} and 671 cm^{-1}, which is absent in the FTIR of PANI–HCl, and this can be attributed to the absorption of —SO$_3^-$,[12,18] which confirms the presence of the dopant NSA.

The presence of MWNT in the PANI/MWNT composites could not be established from the FTIR investigations. However, the Raman spectra of the composite samples clearly indicate the presence of MWNT as explained below. In Figure 6, the Raman spectra depict the G-mode vibrations[21] of MWNT (graphite like) at 1346, 1347, and 1344 cm^{-1} for the NSA, OP, and CSA doped composites, respectively. Similarly the D-mode vibrations of MWNT are
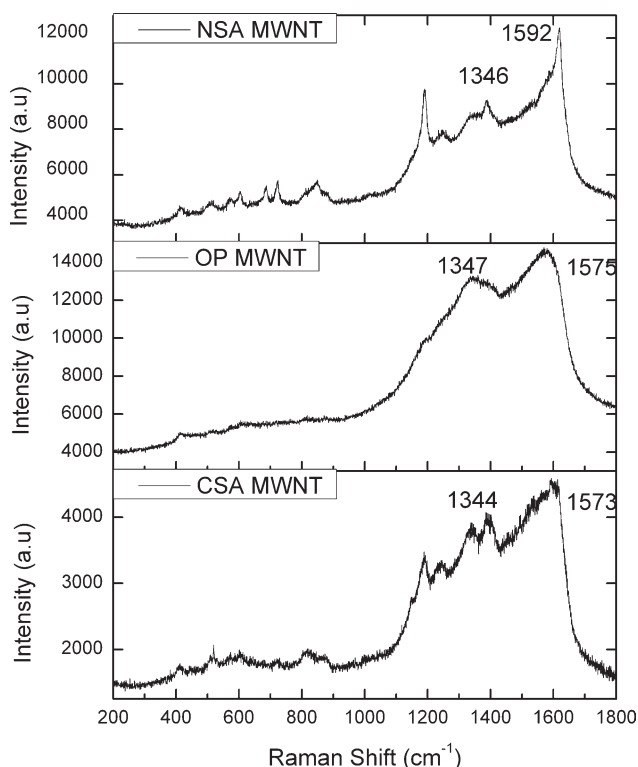

Figure 4 XRD of CSA doped PANI and its composite with MWNT.

Figure 6 Raman spectra of PANI/MWNT composites.

observed at 1575, 1573, and 1592 cm^{-1}, respectively, for NSA, OP, and CSA doped composite samples. Thus, the presence of MWNT in all the three composite samples can be established.

Electrical characterization

It is observed that there is appreciable change in the dc conductivity of the samples with applied pressure.

The percentage variation of conductivity of each sample with applied pressure is calculated using the equation,

$$\% \text{ variation} = \frac{100 \times (\sigma_1 - \sigma_0)}{\sigma_0} \qquad (1)$$

where σ_1 is the conductivity with maximum load and σ_0 is the conductivity with no load.

A graph drawn with applied pressure along the x-axis and % variation in conductivity along the y-axis for different samples is shown in Figure 7.

From Figure 7, it is clear that there is appreciable change in conductivity with applied pressure for all the samples investigated. It is also observed that with the application of pressure, there is an increase in electrical conductivity up to a maximum of two orders of magnitude.

The variation of conductivity with pressure for each sample depends upon the dopant used and the

presence of MWNT. The highest conductivity of 10.5 S/cm is observed for the NSA doped MWNT composite of PANI. However, the maximum percentage variation is observed for the CSA doped PANI sample without MWNT.

The electrical conductivity in doped PANI is mainly because of (1) the ability of the charge carriers to move along the polymer backbone and (2) the ability of the charge carriers to hop between the polymer chains,[22] which contribute toward the intra-chain (σ_{inter}) and interchain conductivity (σ_{intra}),[23] respectively.

$$\sigma = \sigma_{inter} + \sigma_{intra} \qquad (2)$$

The interchain conductivity is because of the expanded coil like conformation of PANI chains, whereas intrachain conductivity is because of the higher crystallinity of PANI.[24]

When pressure is applied on the surface of the PANI samples, the dispersed conducting particles are forced to touch each other, resulting in the formation of conducting channels, thus increasing the electrical conductivity.[25] It is also widely accepted that the conductivity of PANI pellets would increase with the applied pressure because of the removal of voids inside the pellets. Therefore, the observed conductivity is mainly the interchain conductivity of PANI and PANI MWNT composite samples. The conductivity reaches a peak value when there is maximum contact, which is somewhere above 30 MPa. In this work we could not apply pressure above 30 MPa, and hence, could not observe any saturation in conductivity.

From Table I it is clear that the conductivity is higher for the composite samples, whereas the percentage variation in conductivity with applied pressure is higher for the doped PANI samples
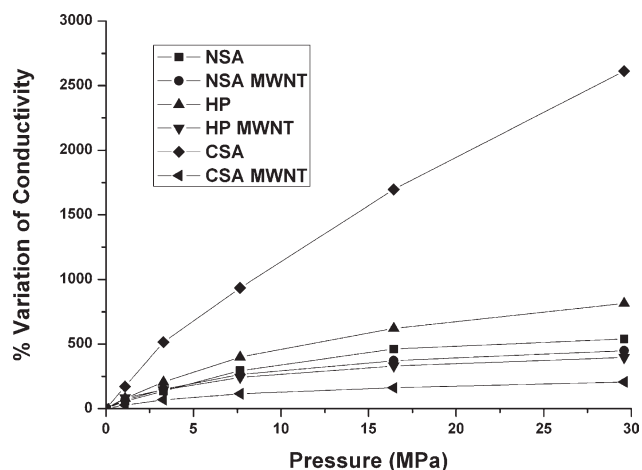

Figure 7 Percentage variation of conductivity with applied pressure for various samples.

TABLE I
Conductivity of the Samples Without Any Load and
with the Maximum Load Applied

Sample	Conductivity without applied pressure (S/cm)	Maximum conductivity with pressure (S/cm)
CSA	0.020348	0.552122
OP	0.119437	1.09329
NSA	0.487236	3.11276
CSA/MWNT	0.339168	1.04144
OP/MWNT	1.082814	5.36433
NSA/MWNT	1.91649	10.5094

compared with the composite samples. MWNT is a good electrical conductor. It acts as a bridge between the isolated conducting regions in PANI matrix. It also covers the voids in the pellets on the application of even a small pressure, and hence, prominent changes in conductivity are not observed by applying higher pressures. That is why the percentage variation of the conductivity with applied pressure in the composite samples is not prominent when compared with that in doped PANI samples. In general, doped PANI samples consist of isolated conducting regions separated by insulating regions. On the addition of MWNT, the isolated conducting regions get connected to some extent, facilitating the formation of conducting channels. Thus, there is appreciable enhancement in electrical conductivity. On applying pressure, further enhancement in the number of connected regions occur. However, the formation of conducting channels get maximized for a particular optimum pressure, and hence, further increase in pressure does not make any significant difference in the distribution of conducting channels. Hence, there is no significant percentage variation in electrical conductivity with applied pressure in the composite samples compared with the doped PANI samples.

CONCLUSIONS

Appreciable enhancement in electrical conductivity is observed for both doped PANI and PANI-MWNT composite samples on applying pressure. The observed sensitive dependence of electrical conductivity on applied pressure can be utilized for pressure sensing applications in various fields.

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