Synthesis, Characterization, and Electrochemical Properties of Poly(ethylene oxide)-Based Polyaniline Electrolyte Complex

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ABSTRACT: The polymer electrolyte based poly(ethylene oxide) complexed with conducting polyaniline (PANI) has been prepared in different weight percentages. The complexation is confirmed by Fourier transform infrared spectroscopy (FTIR).The change in morphology is studied by using scanning electron microscopy. The DC conductivity measurements are carried out using Keithley digital multimeter. It is seen that DC conductivity shows exponential behavior for all PEO : PANI complexes. It is observed that among all the PEO : PANI complexes, 50 wt % of PEO in PANI shows highest conductivity. Electrochemical cell parameters for battery applications at room temperature also have been determined. The samples are fabricated for battery application in the configuration of Na:(PEO : PANI):(I$_2$ + C + sample), and their experimental data are measured using Wagner polarization technique. The cell parameters results in an open-circuit voltage of 0.4 V and a short-circuit current of 902 μA for PEO : PANI (50 : 50) composite. Hence, these composites can be better candidates for the polymer electrolyte studies. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1652–1656, 2012

Key words: PEO; polyaniline; FTIR; SEM; DC conductivity and battery applications

INTRODUCTION

Over the last few decades, there have been extensive research activities in conducting polymers because of their potential applications in various fields such as batteries, super capacitors, chemical sensors, electrochromic displays and electric devices.[1] Compared to conventional secondary batteries, these batteries made from conducting polymers offer several advantages such as high energy, density, high voltage, low density and shape multiplicity. Moreover, conducting polymer-based electrodes are neither soluble nor do they undergo passivation during oxidation. Furthermore, there is no precipitation during charging/discharging. Hence, conducting polymers are excellent candidates for use as electrodes in battery applications.[2] Among the various conducting polymers, polyaniline (PANI) has been the most widely studied due to the ease of synthesis, controllable electrical conductivity and an excellent environmental stability.[3,4] These properties of PANI have prompted researchers to use it in rechargeable batteries. PANI-based batteries have several advantages as they are very stable, low cost and can be easily handled even in the presence of moisture.

The poly(ethylene oxide) (PEO): LiX-based polymer electrolytes have received extensive attention for its potential capability to replace traditional liquid electrolytes, but the ionic conductivity is observed at higher temperatures only (higher than the melting points). It is found that at higher temperatures, the system has poor mechanical strength and is ineffective. The addition of plasticizers has also shown to enhance conductivity.[5–6] It is also reported that addition of some fillers into PEO-based electrolytes increases their conductivity.[7–8]

Furthermore, nowadays, composites or blends have also proved to be an alternate and effective route for improving properties. In the present work, the authors report the synthesis, characterization, and electrochemical properties of PEO-based PANI electrolyte complex.

EXPERIMENTAL

Materials and methods

PEO (relative molecular mass of 5×10^5) was obtained from Shanghai Research Institute of Chemicals, China and is dried under vacuum at 50°C for
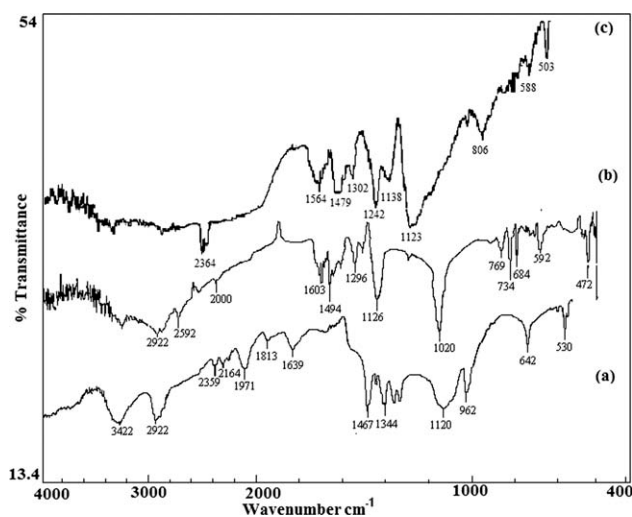
Figure 1 FTIR spectra of (a) PEO, (b) PANI, and (c) PEO: PANI composites 50 wt %.

24 h before use. The PANI was prepared in our laboratory by the standard chemical oxidation method.[9]

PEO : PANI composites (PP-composites) were prepared by stirring in anhydrous acetonitrile for 5–6 h to form homogeneous solutions/gels at different weight percentages (PP1-10 wt %, PP2-20 wt %, PP3-30 wt %, PP4-40 wt %, and PP5-50 wt %, respectively). The gels were poured into glass plates in a dry room fume hood and left for 12 h to remove the majority of the acetonitrile. The composites were then further dried at 60°C under vacuum for 24 h. The composites were later stored in the dry room at 22°C for several weeks before characterization.

Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded on a Perkin–Elmer 1600 spectrophotometer in KBr medium and scanning electron microscopy (SEM) has been carried out for PEO : PANI composites on Phillips XL 30 ESEM. The electrochemical properties of these composites have been studied using Keithley Electrometer meter-6514.

RESULTS AND DISCUSSION

Fourier transmission infrared spectroscopy

Figure 1 (a) shows that the FTIR spectra of pure PEO. In the pure PEO, the predominant peaks are found at 3422 cm^{-1}, 2922 cm^{-1}, 2359 cm^{-1}, 2341 cm^{-1}, 2237 cm^{-1}, 2164 cm^{-1}, 1971 cm^{-1}, 1813 cm^{-1}, 1639 cm^{-1}, 1467 cm^{-1}, 1344 cm^{-1}, 1282 cm^{-1}, 1242 cm^{-1}, 1120 cm^{-1}, 962 cm^{-1}, 842 cm^{-1}, and 530 cm^{-1}. A large broad band appears centered at 3442 cm^{-1} of spectrum corresponds to the hydration of PEO, as it is highly hydrophilic. It is observed from the figure that PEO has a large broad band of CH$_2$ stretching between 2950 cm^{-1} and 2840 cm^{-1}. However,

this band is found to split into two at 2922 cm^{-1} and 2359 cm^{-1} corresponding to asymmetric CH$_2$ stretching ($n(CH_2)_a$) and symmetric CH$_2$ stretching ($n(CH_2)$s), respectively. It is also noticed that two clear CH$_2$ vibrational modes appear in PEO at 1467 cm^{-1}, which corresponds to asymmetric CH$_2$ bending (d(CH$_2$)a) and 1344 cm^{-1}, which corresponds to symmetric CH$_2$ wagging and some C—C stretching (w(CH$_2$)s + n(CC)).

Figure 1 (b) shows the FTIR spectra of pure PANI. The predominant peaks are appeared at 2922, 2592, 2000, 1603, 1494, 1296, 1126, 1020, 769, 734, 684, 592, and 472 cm^{-1}. It is observed that the formation of PANI is confirmed by noticing the predominant peaks at the wave number of 1603 cm^{-1} corresponding to C=C stretching of quinine ring, 1494 cm^{-1} for C=C stretching of benzonoied ring, 1296 cm^{-1} for C—N stretching, 1126 cm^{-1} due to C—O—C stretching of excess oxidant, 1020 cm^{-1} for S—O vibration, 769 cm^{-1} and 734 cm^{-1} for C—H vibration of Para coupling benzonoied and benzene rings, C—H bending is at 684 cm^{-1}, 592 cm^{-1} corresponding to aromatic ring and 472 cm^{-1} is stretching at out of the plane.

Figure 1(c) shows the PEO : PANI composites spectra. The peaks appeared in the spectrum are 2364.94 cm^{-1}, 1564 cm^{-1}, 1479.96 cm^{-1}, 1302 cm^{-1}, 1242.27 cm^{-1}, 1138 cm^{-1}, 806 cm^{-1}, 588 cm^{-1}, and 503 cm^{-1}. It was observed that the intercalation of PANI within PEO shows the similar type of effect on PEO structure and in return on PEO crystallinity. The wave number found at 3552 cm^{-1} is absent in the composites and this is due to the interaction between the ether-oxygen of PEO segments and the free O—H groups of PANI via hydrogen bonding. It is seen that C—H stretching band appears at 2364.94 cm^{-1}, which is slightly shifted to the higher frequencies, and this clearly indicates that there is strong interaction between the PANI and PEO. This was further confirmed as the intensity band of (n(C—O) at 1603 cm^{-1} for pure PANI and 1344 cm^{-1} in pure PEO, respectively, are shifted to lower frequency in PEO : PANI composites, and the band of (n(O—H) at 1581 cm^{-1} in PANI and 1342.58 cm^{-1} in PEO is intense. The predominant peaks appeared in composites are at 2364.94 cm^{-1}, 1564 cm^{-1}, 1479.96 cm^{-1}, 1302 cm^{-1}, 1242.27 cm^{-1}, 1138 cm^{-1}, 806 cm^{-1}, 588 cm^{-1}, and 503 cm^{-1}, which confirmed the formation of PEO : PANI composites.

Scanning electron micrograph studies

Figure 2(a) shows the SEM image of pure PEO and it is found to be highly macrocrystalline, elongated rodlike structure, and has considerable intergranular distance between the two grains. It is also clearly seen from the image that the PEO grains have less interaction with each other. The average grain size
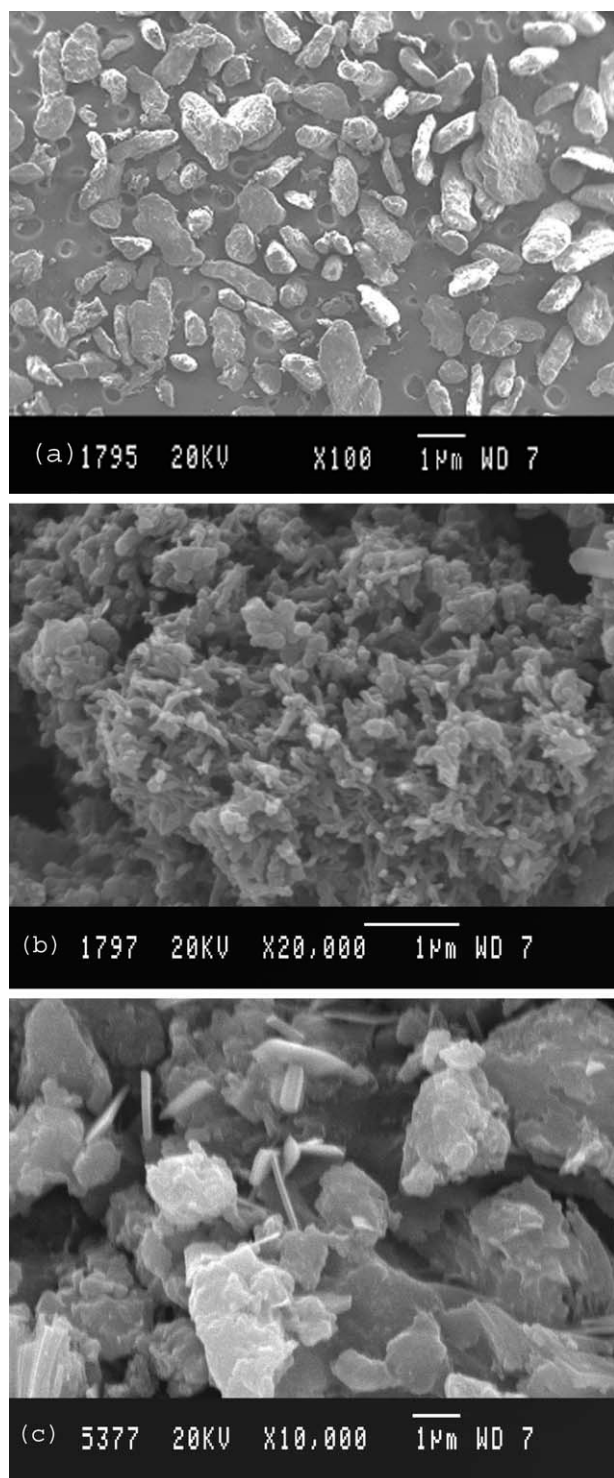
Figure 2 Scanning electronic micrograph (SEM) image of (a) pure PEO, (b) pure PANI, and (c) PEO : PANI composites.

was calculated by using the linear intercept formula and it is found to be 35–40 μm.

Figure 2(b) shows the higher resolution SEM image of pure PANI, and it is seen to be mesoporous and highly agglomerated granular in shape. The average grain size was found to be 4–5 μm. The grains are

found to be well interconnected with each other, which indicate that they have enough binding energy to combine with neighbor grains or molecules.

Figure 2(c) shows the SEM images of PEO : PANI composites, and it is found to have highly agglomerated chainlike structure. The crystallinity of the PEO is seen to decrease with the addition of PANI in it. The average grain size is found to be 350–400 nm.

The significant change in the morphology of PEO : PANI composites are observed as PANI weight percentage is increased in PEO matrix. This may be due to the hard PEO matrix becoming a rubbery like filament networking with PANI fibers, which cause the elongation of the matrix in length. It is also clearly observed that the grain size of the PEO decreases with increase in PANI concentration in the base matrix.

DC conductivity

Figure (3) shows that the σ_{dc} conductivity of PEO and PEO/PANI composites at various weight percentages as a function of temperature. It is observed that conductivity of the composites increases with increase in temperature ranging from 50 to 220°C. Among all the composites, PEO : PANI composites of 20 wt % shows higher conductivity. This clearly indicates that the conductivity is not only the motion of ions (PEO) but also hopping of charge carriers like polarons and bipolarons from one island to another.

It is also suggested here that the thermal curling effects of the chain alignment of the PANI lead to the increase in conjugation length and that bring about the increase of conductivity. Also, there will be molecular rearrangement on heating which make the molecules favorable for electron delocalization. The conductivity varies directly with the temperature obeying an expression of the following form.
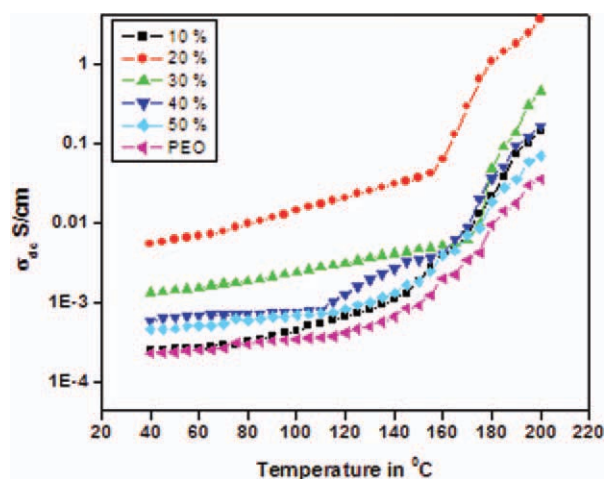

Figure 3 The σ_{dc} conductivity of PEO and PEO/PANI composites at various weight percentages as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
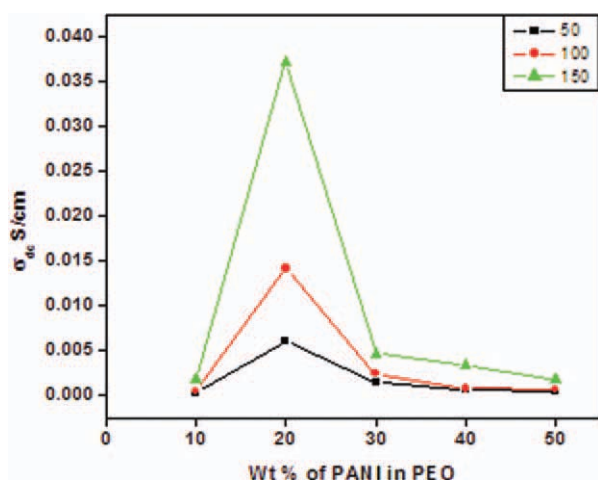
Figure 4 The variation of DC conductivity as a function of different weight percentages of PANI in PEO matrices at three different temperatures (50,100, and 125°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{[1/4]}] \qquad (1)$$

where σ is the conductivity, T is the temperature, and σ_0 is the conductivity at characteristic temperature T_0. Conductivity varying with various values of the exponent (e.g., $T^{-1/4}$, $T^{-1/3}$, and $T^{-1/2}$) has been reported, and different models have been used to interpret this data.

Figure (4) shows the variation of dc conductivity as a function of different weight percentages of PANI in PEO matrix's at three different temperatures (50, 100, and 125°C). It is observed that in all the composites, the conductivity decreases from 10 to 20 wt % and further it increases from 30 to 50 wt%. The increase in conductivity is due to the variation in distribution of PANI, which may be supporting for more number of charge carriers to hopp between favorable localized sites causing increase in
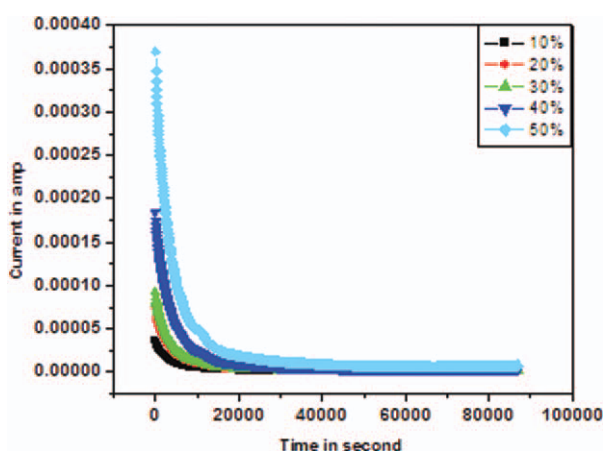

Figure 5 The variation of current with time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
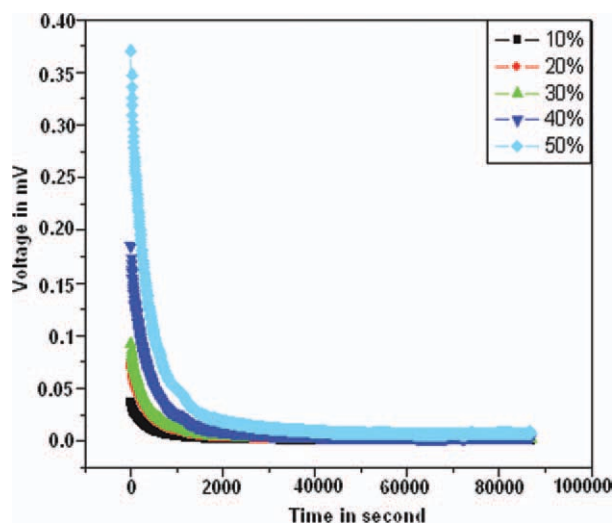

Figure 6 The variation of voltage with time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conductivity. The decrease in conductivity may be attributed due to the trapping of charge carriers. This can be well supported by VRH model.

Electrochemical cell parameters

Electrochemical cells have been fabricated based on PEO : PANI polymer electrolytes and their discharge curves determined under a constant load. There is an initial rapid decrease in polarization current as a function of time (Fig. 5 and 6), and this may due to the formation of a thin layer of polarons and bipolarons at the electrode interface. This suggests that the charge transport in PEO : PANI composite is predominantly ionic. This indicates that the PEO : PANI composites have an electrochemical stability and are thus suitable for application in solid-state batteries. As the PANI content increases in PEO, there is an increase in the polarization current and in the voltage stability. With the addition of more than 50% PANI in PEO matrix, however, shows gradually decrease in the stability. The cell parameters results in an open-circuit voltage (OCV) of 0.4V and a short-circuit current (SCC) of 902 μA for PEO: PANI (50 : 50) composite. These data demonstrate the potential application of these electrolytes in solid-state batteries. This may be confirmed by characterization and conductivity studies.

Sreepathi et al.[10] have reported the cell parameters for PEO+ NaYF$_4$ and PEO + KYF$_4$ polymer electrolytes, Sreekanth et al.[11] for PEO + NaNO$_3$ polymer electrolyte, Kim et al.[12] for PEO with ethylene carbonate and poly(ethyl glycol dimethyl ether).

CONCLUSIONS

The composites of PEO : PANI have been prepared using acetonitrile. From the studies of FTIR spectra,

it is found that the ionic property is predominant, and this is also supported by DC conductivity studies. The surface of various weight percentages of these composites changes from ellipsoidal to square like morphology. The DC conductivities studies also reveal the presence of polarons as well as ions as charge carriers. The cell parameters results in an OCV of 0.4 V and a SCC of 902 μA for PEO : PANI (50 : 50) composite. Hence, these composites can be better candidates for the polymer electrolyte studies.

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