Chitin–polyaniline blend as humidity sensor

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ABSTRACT

A new processable and humidity sensitive chitin–polyaniline blend has been developed. Polyaniline is blended with chitin by solution blending method. The free standing films of blends are stable under ambient condition. The characterization of the blends is done by UV–vis absorption spectrum, FTIR, conductivity studies, thermogravimetric analysis and SEM. Conductivity of the self-doped blends increases from less than $\approx 10^{-7}$ S/cm to 2.15×10^{-5} S/cm, depending on the percentage of polyaniline in the blend. When these blends are doped with HCl conductivity rises to $\approx 9.68 \times 10^{-2}$ S/cm. Spectroscopic analysis shows interaction between chitin and polyaniline and the electronic states are similar to those of the emeraldine and protonically doped forms of polyaniline. These blend films are used for the construction of resistive based humidity sensor. A linear response of resistance with humidity is observed. It shows a small hysteresis and its response is stable even after 75 cycles of humidity exposure. Effect of electron beam irradiation on the humidity response has also been studied. Sensitivity is improved upon irradiation and doping. Further effect of thickness and electrode separation on humidity response is also studied. Response time for the humidity sensor is less than 30 s. The constructed humidity sensor shows good results in the 10–100% humidity and in the temperature range of 20–60 °C.

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1. Introduction

Humidity sensors have gained increasing applications in industrial processing and environmental control [1]. For manufacturing highly sophisticated integrated circuits in semiconductor industry, humidity or moisture levels are constantly monitored in wafer processing. There are many domestic applications, such as intelligent control of the living environment in buildings and laundry, cooking control for microwave ovens, etc. In automobile industry, humidity sensors are used in rear window defoggers and motor assembly lines. In medical field, humidity sensors are used in respiratory equipment, sterilizers, incubators, pharmaceutical processing, and biological products. In agriculture, humidity sensors are used for green-house air-conditioning, plantation protection (dew prevention), soil moisture monitoring, and cereal storage. In general industry, humidity sensors are used for humidity control in chemical gas purification, dryers, ovens, film desiccation, paper and textile production, and food processing [2].

The conventional materials used for sensing humidity are electrolytic metal oxides, alumina thin films and ceramics [3]. Polymeric humidity sensors have been widely studied in research and applied in industry for more than 30 years. Polymer based thin film humidity sensors have the advantage of high processability that allows for simple fabrication of a range of geometry including smaller sensor designs. The development of humidity sensor based on conducting polymers has gained a considerable momentum in the last decade [2–5]. Various polymers have been used to prepare humidity sensors. From their basic principle they are classified in to two categories:

(i) Based on electrical properties: (a) change in capacitance; (b) change in electrical resistance.
(ii) Based on gravimetric change in the materials such as the quartz crystal oscillator.

The first category is divided into two types, the electric resistance type and the capacitor type. Hydrophilic polymers are used for resistance type humidity sensors while; hydrophobic polymers are preferred for capacitance type sensors, where either capacitance or resistance based parameters have been found to change with water ingress. But problems such as overall size and processability of sensing materials restrict their applications in certain areas [5]. A useful approach to overcome these limitations involves blending conducting polymers (CP) with conventional polymers. These blends are designated to combine the desired properties of both components, i.e., electrical conductivity of the CP along with processability and physical properties of the matrix polymer [5,6].

Among the conducting polymers, polyaniline (PANI) has attracted attention of most of the researchers, due to the combi-

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nation of unique properties like simple preparation and doping procedure, good environmental stability, relatively high conductivity and low cost and also due to their wide spectrum of applications [7,8]. Humidity sensitive nature of PANI and its derivative is well known for a long time [2,9–11]. Although it is verified that PANI and its derivative are sensitive to humidity, the response is very low due to weak hygroscopicity, at most one order of magnitude change in conductivity and hence PANI alone cannot be used for humidity sensor application [2,9,12]. In order to improve the humidity sensitivity of PANI, researchers have combined it with hygroscopic polymers like PVA [2,13–15]. Even then the major draw back is the processability of PANI. In order to improve the processability of PANI, several methods are reported in literature. Blending PANI with conventional polymer is one of them. Recently we have blended polyaniline with chitin using DMA and LiCl as solvent [6]. In this paper we report the development of low-cost, highly processable humidity sensors from chitin–polyaniline blend and the effect of 8 MeV electron beam on the humidity response of the blend.

2. Experimental

2.1. Materials and chemicals

Chitin from HIMEDIA, Mumbai, with molecular weight 400,000 g/mol, N,N-dimethyl acetamide (DMA; AR grade) and LiCl (AR grade) from SRL, and ammonium peroxy disulphate (APS; GR grade) from MERCK were used as received. Aniline GR grade from MERCK was distilled under reduced pressure before use.

2.2. Blend preparation

PANI is prepared by chemical oxidative polymerization of aniline by using ammonium peroxy disulphate (APS) as an initiator in aqueous acidic medium. So obtained PANI were treated with 0.5 M ammonium hydroxide for 16 h, in order to get emeraldine base form. Blends of chitin and polyaniline with polyaniline 30%, 50% and 70% (30P, 50P and 70P) were prepared by mixing chitin solution (0.5 vol%) and polyaniline emeraldine base solution (0.5 vol%) in DMA and LiCl. Details of blend preparation is reported in our earlier publication [6]. Blend solutions were irradiated with electron beam for different doses using 8 MeV electron beam at Microtron center Mangalore University. Specifications of electron beam used for irradiation is as follows, beam energy 8 MeV, beam current 25–30 mA, pulse repetition rate 50 Hz, pulse width 2.5 μs, dose rate of 60 kGy/h (Fricke dosimetry) and sample is kept at a distance of 30 cm. Free standing films of blends were cast on glass petridishes and dried at 70 °C. The films were peeled off and washed with water, then with acetone and dried at 60 °C for 24 h before being used for further studies.

2.3. Physical characterization

The blend solutions were diluted and UV–vis absorption spectra were recorded between 300 and 800 nm using Shimadzu spectrophotometer (model UV-3101 PC). FTIR spectra of the blend films were recorded using PerkinElmer Spectrophotometer (model 1000) employing the KBr pellet technique. SEM photographs were taken for surface of samples coated with gold using Scanning Electron Microscope (Model: JEOL JSM 5800CV). Thermogravimetric analysis was carried out using PerkinElmer, Diamond TG/DTA machine, in nitrogen atmosphere, from room temperature (25 °C) to 600 °C at a heating rate of 10 °C/min. The variation of resistance with humidity is measured using Keithley electrometer connected with humidity sensor (Keithley model 6517-RH) using alternating polarity technique, in order to avoid polarization effect. When this
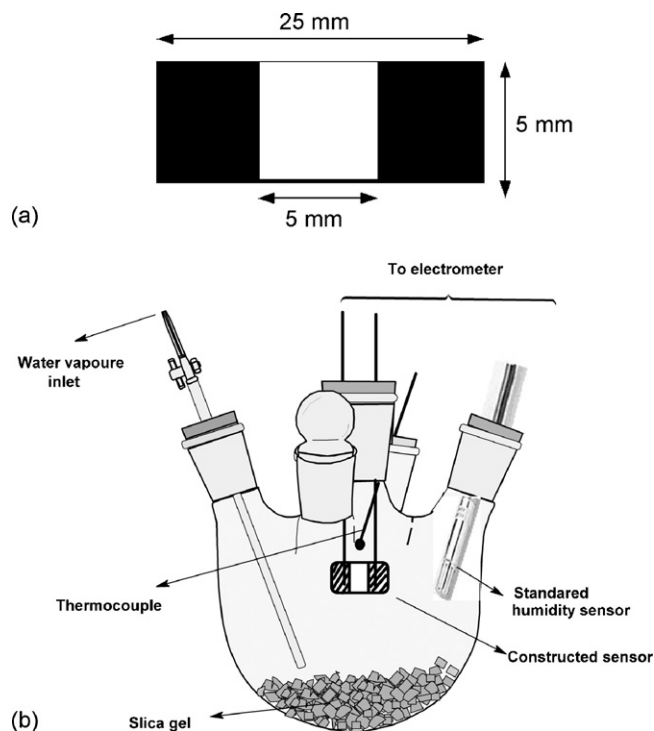

Fig. 1. (a) Sensor layout and (b) humidity measurement setup.

test is run, the voltage source will alternate between two voltages at timed intervals. Current measurements are taken at the end of each of these alternations and after calculation of I_{calc} resistance values are computed. Hence resistance reading will not have any time dependent effect. Three samples with the same experimental conditions and with the same irradiation were studied for each blend. For same sample measurements were repeated at least 10 times.

2.4. Sensor construction and set up for the measurement of humidity

The blend film was cut in to small strips of 2.5 cm × 0.5 cm in size. 0.5 cm × 0.5 cm area was masked and the electrode on the film was applied by using quick drying and highly conducting silver paste (sensor layout is shown in Fig. 1(a)). Two thin copper wires were connected to electrode using silver paste. Thickness of the film used for sensor construction is 40 μm. Constructed sensor is placed inside the humidity chamber. Set up consists of 500 ml five neck flat bottomed flask. From center neck, sensor constructed is inserted and two copper wire connections from the sensor are connected to the keithley electrometer. In one of the side neck standard humidity sensor is inserted (supplied with keithley electrometer operating range is from 0 to 100% RH). The standard and constructed humidity sensors are placed in such way that they are at a same level and as near as possible. K type thermocouple connected to keithley electrometer is inserted in one of the neck in order to monitor the temperature in side the humidity chamber. Water vapour tube is connected to another neck and last neck is used to introduce silica gel by a special arrangement in order to control the humidity level inside the chamber. All the humidity measurements experiments are carried out at 25 °C. The humidity inside the chamber is increased by introducing water vapour and decreased by introducing silica gel.
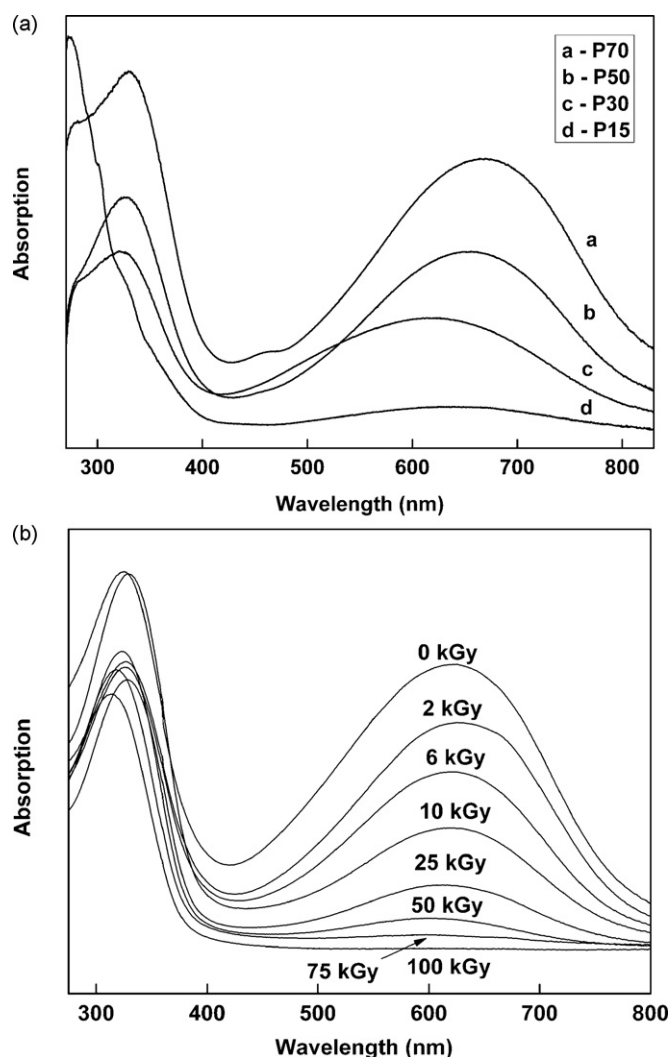
Fig. 2. UV–vis spectra of (a) blends and (b) irradiated 30P blend.

3. Results and discussion

UV–vis absorption spectra of unirradiated chitin–polyaniline blend solutions show absorption peaks at ≈330 and ≈630 nm (Fig. 2(a)). These peaks are similar to the absorption peaks observed for polyaniline, the absorption peak at ≈330 nm corresponds to π–π^* transition of the benzenoid ring. The peak at ≈630 nm is assigned to polaron band transition. As the composition of polyaniline in the blend increases, the polaron band transition absorption peak shifts to higher wavelength side. The intensity of absorption peak at ≈630 nm decreases as irradiation dose increases and shifts to lower wavelength (Fig. 2(b)). This indicates the conversion of EB in to leucoemeraldine base (LEB) during irradiation. The conversion of EB to LEB on irradiation has been reported by Wolszczak et al. [16].

IR spectrum of unirradiated and irradiated blends show all significant peaks of chitin and polyaniline (Fig. 3(a)). The peaks at $\approx1519\,cm^{-1}$, $\approx1431\,cm^{-1}$, $\approx1259\,cm^{-1}$, $\approx1153\,cm^{-1}$ and $\approx835\,cm^{-1}$ are characteristic of polyaniline. In the IR spectrum of chitin, the peak observed at $\approx1669\,cm^{-1}$, is related to carbonyl groups. But in the case of blend, this peak is shifted to $\approx1650\,cm^{-1}$. This is due to the interaction between chitin and PANI [6]. It is found that after irradiation the peak at $\approx1650\,cm^{-1}$ is shifted further to lower wavenumber. This shows that interaction is retained even after irradiation (Fig. 3(b)). The details of interaction between
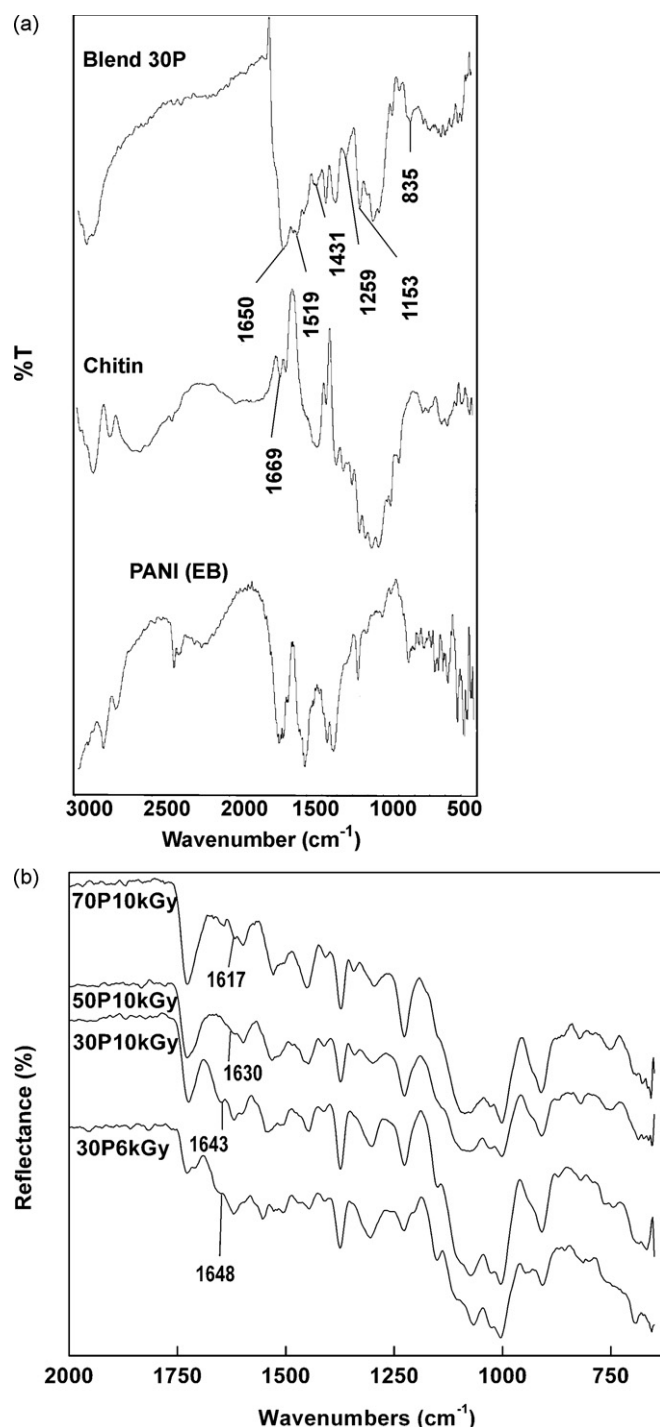

Fig. 3. (a) FTIR of chitin, EB and blend. (b) FTIR of irradiated blends.

chitin and polyaniline in the blend is discussed in our earlier publication [6] and blend is miscible. Miscibility of the blend is further confirmed from the homogeneous and co-continuous phase morphology in SEM (Fig. 4).

Fig. 5 shows the TGA thermograms, initial weight loss is due to the residual solvent or moisture present in the polymer. Blends are stable up to 250 °C and stability of the blend slightly increases as the PANI content in the blend increases.

The DC conductivity of blend films increase as the composition of PANI increases in the blend (Table 1) and is reported in our earlier publication [6]. This is because more and more LiCl gets doped with polyaniline from the LiCl used as solvent for
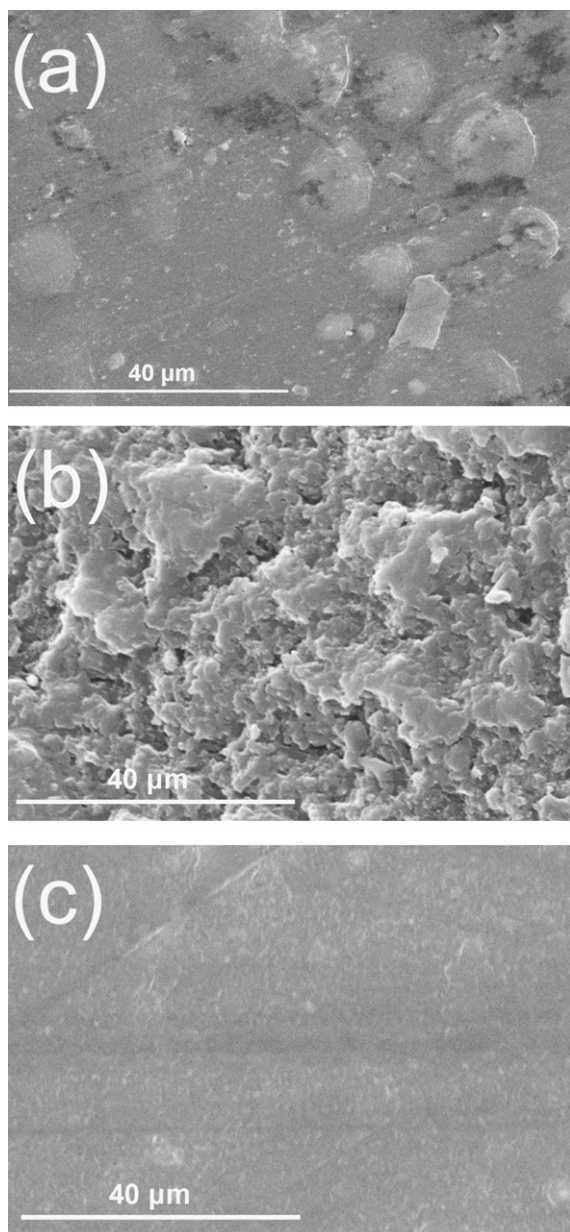
Fig. 4. SEM images of (a) chitin, (b) PANI, and (c) blend (30P).

chitin. Doping of EB with LiCl is already reported by Saprigin et al. [17,18] and they obtained the maximum conductivity of the order of 10^{-8} S/cm. In the present case, highest conductivity obtained for unirradiated blend is 2.15×10^{-5} S/cm. This is due to the interaction between chitin and PANI [6]. On irradiation the conductivity increases further and highest conductivity observed is 2.36×10^{-4} S/cm (Table 1). This is due to more and more delocalization of charge carriers during irradiation. Further it should be noted that conductivity in the case of 50P and 70P blends, initially increases with increase in dose and then starts decreasing. During irradiation, as the composition of the PANI increases in the blend, the percentage of conversion of EB to LEB is more. But the self-doped (Li$^+$) LEB is less conducting than self-doped EB and therefore conductivity starts decreasing at higher dose. It has been reported that, LEB is not so conducting as that of EB form. In addition to this we have doped these irradiated blends with 1 M HCl. A small amount of increase in the conductivity is observed depending on the percentage of EB form present in the blend.
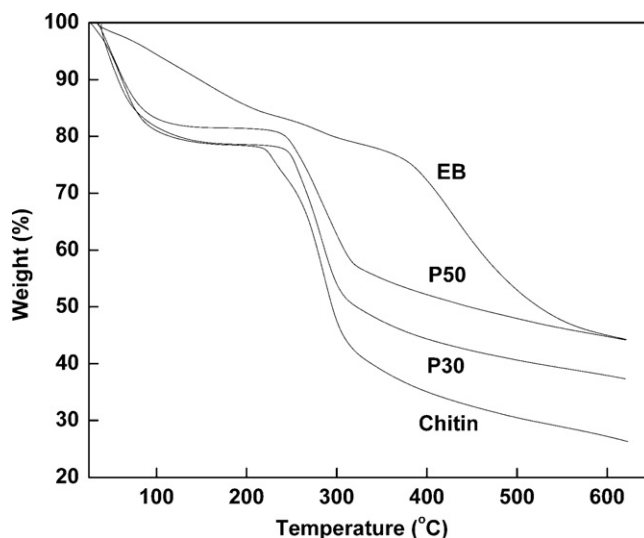

Fig. 5. TGA curves of chitin, EB and its blends.

Fig. 6 shows the temperature dependent conductivity of blend (30P) and the observed conductivity increases with temperature. The increase in conductivity would be due to the increase in the efficiency of charge transfer between the polymer chains and the dopant LiCl with temperature. Further, at room temperature a small increase in the conductivity is observed, which shows that the present blend is hygroscopic in nature. One-dimensional variable range hopping as the most probable conduction mechanism in the case doped and undoped blends, because the electrons hop more easily along chains due to well overlapping electronic states of the same chains. The details of conduction mechanism in the undoped and doped blends are discussed in our earlier publication [19].

Variation of resistance of chitin–polyaniline blend as a function of relative humidity (%RH) is presented in Fig. 7, log of resistance decreases almost linearly with increase in humidity. The decrease in the resistance or increase in conductivity can be attributed to the mobility of the dopant ion which is loosely attached to the polymer chain by weak vander walls forces of attraction. At low humid-

Table 1
Conductivity of various blend samples.

Sample ID[a]	DC conductivity (S/cm)	
	Undoped	1M HCl doped (24 h)
30P0kGy	8.3×10^{-7}	2.6×10^{-3}
30P1kGy	2.78×10^{-6}	1.22×10^{-5}
30P2kGy	1.05×10^{-5}	3.25×10^{-5}
30P4kGy	1.64×10^{-5}	3.10×10^{-5}
30P6kGy	6.47×10^{-5}	1.00×10^{-4}
30P8kGy	1.27×10^{-4}	1.51×10^{-4}
30P10kGy	1.68×10^{-4}	3.19×10^{-4}
50P0kGy	1.79×10^{-6}	4.72×10^{-2}
50P1kGy	6.85×10^{-5}	–
50P2kGy	1.26×10^{-4}	7.81×10^{-4}
50P4kGy	2.27×10^{-4}	6.17×10^{-4}
50P6kGy	2.36×10^{-4}	4.19×10^{-4}
50P8kGy	5.90×10^{-5}	1.21×10^{-4}
50P10kGy	9.96×10^{-6}	1.86×10^{-5}
70P0kGy	2.15×10^{-5}	9.68×10^{-2}
70P1kGy	9.31×10^{-5}	–
70P2kGy	1.34×10^{-4}	–
70P4kGy	8.58×10^{-5}	–
70P6kGy	3.24×10^{-6}	–
70P8kGy	7.15×10^{-6}	–
70P10kGy	8.04×10^{-6}	–

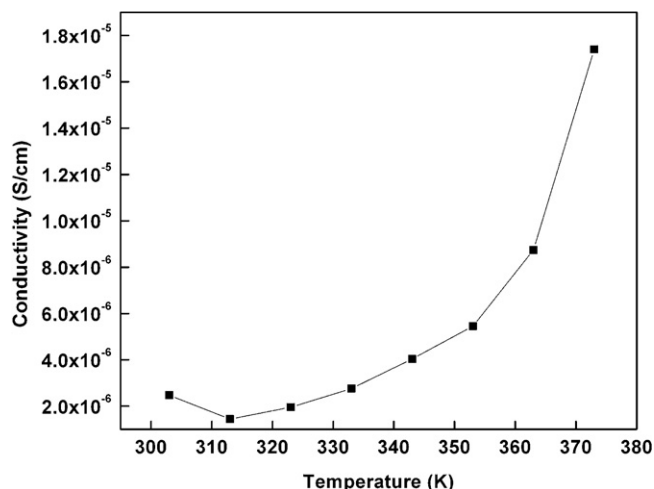[a] Prefix and postfix number to P refers to percentage of PANI and irradiated dose, respectively.

Fig. 6. Temperature dependent conductivity.

Reduced form   Oxidized form

Fig. 8. Two forms of PANI.

ity, the mobility of dopant ion is restricted due to coiled structure of polymer chain under dry condition. On the other hand, at high humidity, the polymer absorbs water molecules, and the polymer chains get hydrated. As a result, swelling up of polymer chains takes place, followed by the uncurling of polymer chain into straight chains that are aligned with respect to each other. This geometry of the polymer is favorable for enhanced mobility of dopant ions or/and the charge transfer across the polymer chains and hence increase in conductivity [20]. The almost linear response of resistance or conductivity with percentage of relative humidity can be used in amplifier circuits for converting the measured values in to measurable %RH values.

It is also reported that water increases the electrical conductivity of PANI through an increase in the interchain electron transfer and/or by increasing the mobility of dopant ions [21]. Due to polymerization by strong oxidant like APS, the PANI structure contains two basic forms: non-oxidized (reduced –NH–) and oxidized structures (–N=) (Fig. 8). Apparently, the PANI synthesized in this way may be regarded as p-type doping. Due to the un-bonded electron pair on the nitrogen atom, both forms can be protonated: $NH \rightarrow NH_2^+$ and $N \rightarrow NH^+$. According to a buildup model [2,9–12], the electron transferring (hopping) from the protonated reduced form (NH_2^+) to the protonated oxidized form (NH^+) is the dominant

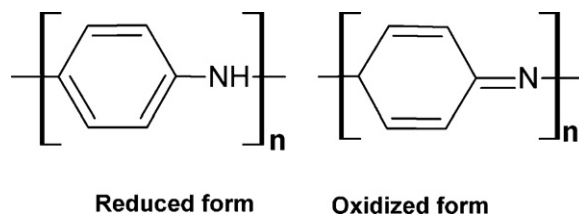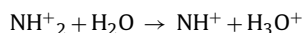conduction mechanism in PANI. The electron hopping is conditioned by a preliminary transfer of a proton, since NH_2^+ unit can not lose an electron with out first losing a proton. As evidenced by NMR experiment, such a proton transfer from or to the polymer take place in the presence of water molecules [12]. The proton transfer is shown as follows:

$$NH^+_2 + H_2O \rightarrow NH^+ + H_3O^+$$

Thus absorbed water plays an important role in the conductivity. The humidity sensing property of PANI to water vapour can be regarded as electron hopping assisted by proton exchange.

Fig. 9 shows the effect of doping on the humidity response of the blends. Figs. 7 and 9 show that, the variation of logarithm of resistance with humidity is almost linear in nature.

The effect of electron beam irradiation on the humidity response of blends is shown in Fig. 10. Irradiated sample also shows, linear response in humidity and better linearity with irradiation dose, but slightly deviates from linearity at higher doses. The optimum linear response is obtained for 6 kGy irradiation dose.

The linear response for humidity is not sufficient for a material to use it as humidity sensor. The other factors are hysteresis, reproducibility, stability or mechanical property of polymer with repeated exposure to water, sensitivity and response time. Sensitivity of humidity sensor has been defined as the change in resistance ($\Delta \log R$) of sensing element per unit change in relative humidity (RH%), i.e.,

$$S = \frac{\Delta \log R}{\Delta RH\%}, \quad \Omega/RH\% \tag{1}$$

The sensitivity computed using above expression shows that blends have good sensitivity over the entire range of humidity (Table 2). The sensitivity of the blend samples varies from 200 Ω to 1 MΩ. But in order to understand the variation of sensitivity
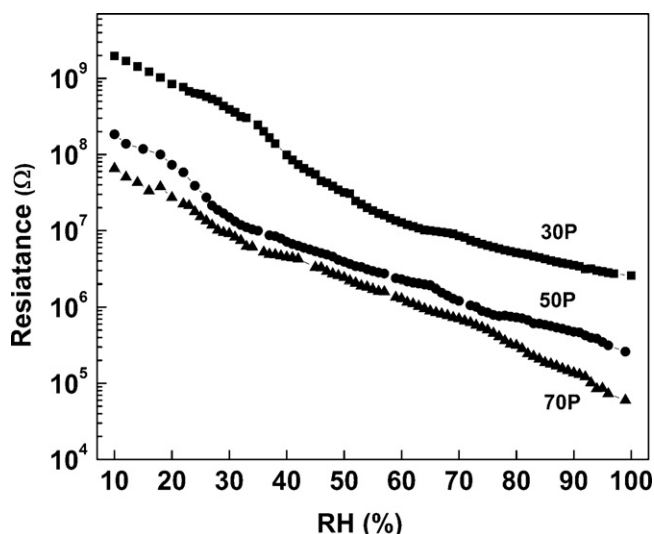
Fig. 7. Plot of log R vs. RH for blends.
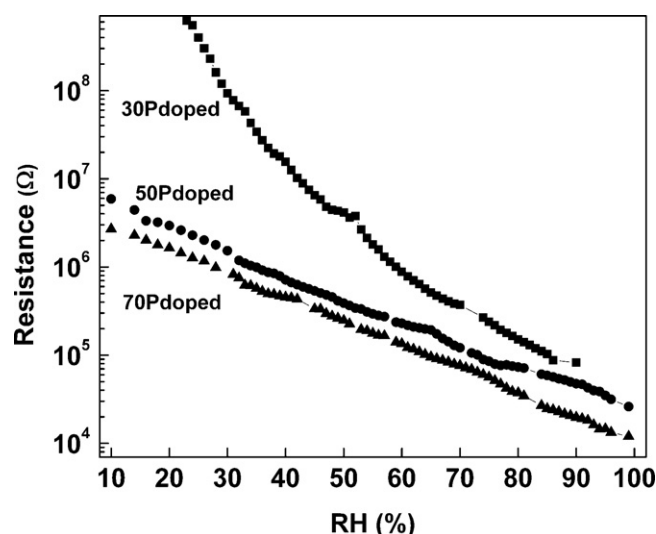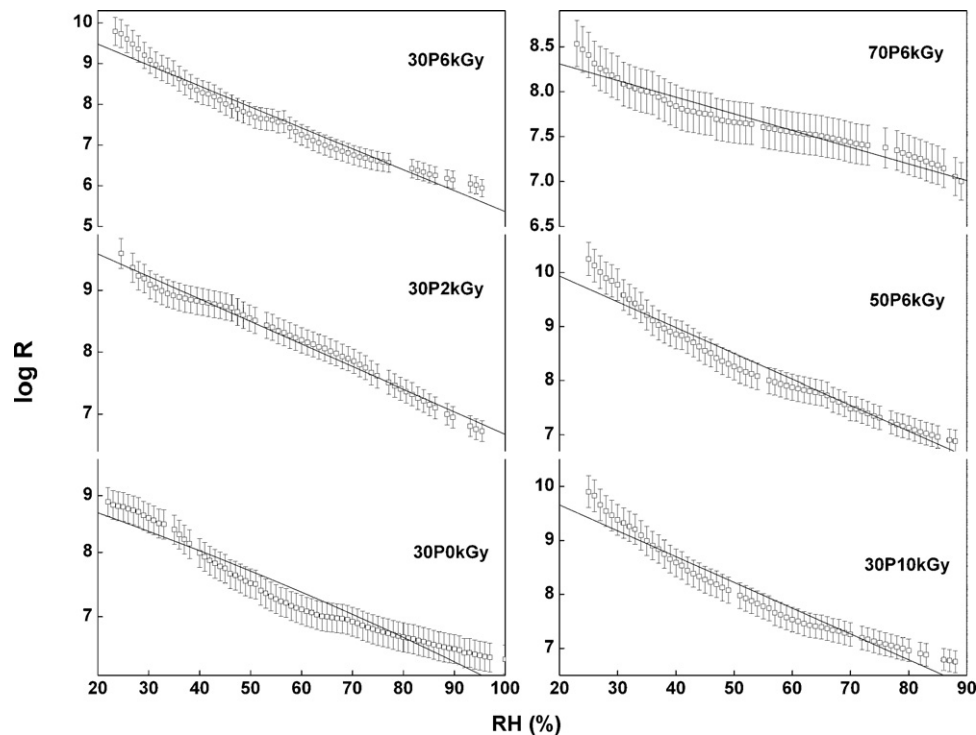

Fig. 9. Plot of log R vs. RH for doped blends.

Fig. 10. Plot of log R vs. RH for irradiated blends.

Table 2
Sensitivity of blend sample.

Sample ID	Sensitivity
30P	2.88
50P	2.64
70P	2.45
30Pdoped	5.34
50Pdoped	6.35
70Pdoped	6.70
30P2kGy	4.3
30P6kGy	6.09
30P10kGy	7.12
50P6kGy	5.72
70P6kGy	5.21

over the entire range of humidity, percentage of sensitivity is plotted against RH. The percentage of sensitivity (*PS*) for detection of humidity of the materials is defined as

$$PS = \left| \frac{\log R_{\text{dry air}} - \log R_{\text{humid air}}}{\log R_{\text{dry air}}} \right| \times 100 \qquad (2)$$

The variation of sensitivity plotted for different samples is presented in Fig. 11. Sensitivity of the blend increases almost linearly with increase in humidity level. The sensitivity of the blend also improved upon doping and irradiation. This may be due to the enhancement of mobility of charge carriers due to increase in the conductivity of blend due to irradiation or doping. Sensitivity of the blend decreases as the composition of the PANI in the blend increases (Table 2). Further sensitivity of the irradiated blend
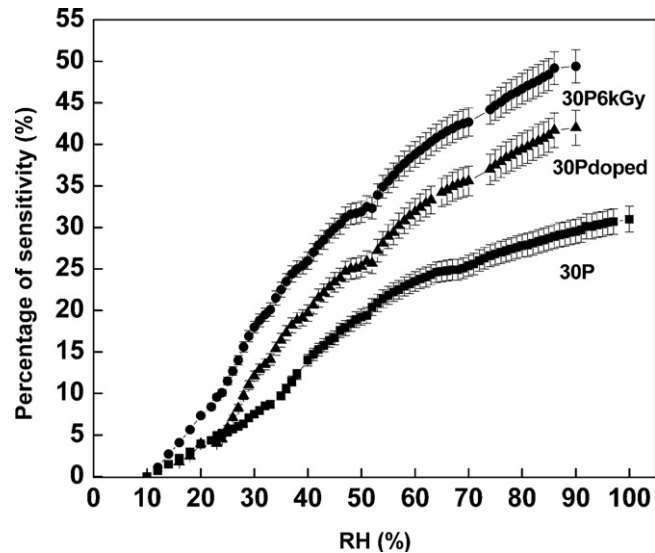

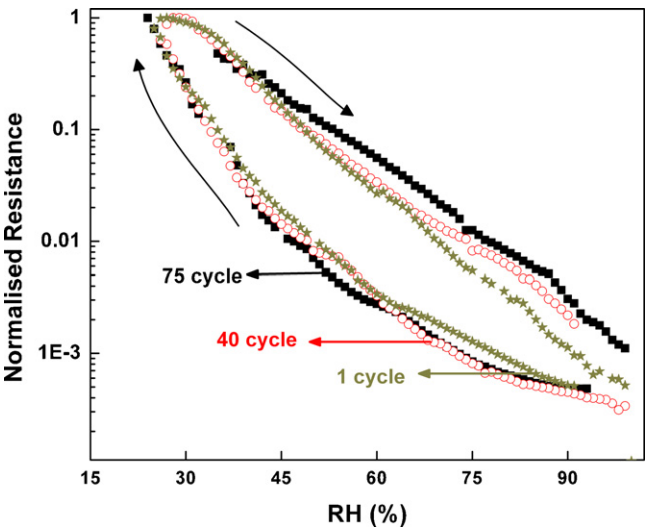**Fig. 11.** Variation of sensitivity with change in relative humidity.

Fig. 12. Characteristic response of 30P blend for various cycle of exposure.

Table 3
Variation of hysteresis loop area for 30P blend sensor.

Number of cycles	Loop area (Ω%)
1	18.22
3	18.23
5	18.25
10	18.71
25	19.03
40	19.204
75	20.31

depends on the percentage of emeraldine base present in the blend and conductivity of the blend (see supplementary information).

Fig. 12 shows the characteristic response of 30P blend for the different humidity cycles. The response can be reproduced even after 75 cycles. The response shows hysteresis, this may due to the hygroscopic nature of the LiCl present in the blend and thickness of the blend film used. When humidity is lowered from higher to lower, because of the hygroscopic nature of LiCl present in the blend, water is not so easily released from the blend. When humidity is raised from lower to higher level, water vapour will take some time to penetrate into the polymer, due to the thickness of the polymer blend used for the construction of the sensor. Hence resistance of the polymer is slightly higher compared to other part of the cycle.

In order to understand the stability and reproducibility of humidity sensitivity of the blend, area inside the loop is computed and is presented in Table 3. No significant increase in the area of the hysteresis loop is found even after 75 cycles (Table 3) and characteristic response is same. The area of the hysteresis loop for different samples is presented in Table 4. As PANI content increases the area inside hysteresis loop decreases and after doping with 1 M HCl area further reduces and almost becomes negligible.

Fig. 13 shows the humidity response of the sensor for different time. Humidity of the chamber is switched between 15% RH and 100% for each 5 min. Time response of humidity sensor is studied for 60 min and response remains same. As seen in the figure, the steady resistance or conductivity reverts always to original one when the humidity is restored to the former state, indicating that the humidity sensing process is extremely reversible. During humidification as well as desiccation there is a small time delay in reaching steady state or equilibrium resistance. Undoped blends show slower response compared to doped and irradiated blends. Response time is found to vary between 30 and 190 s and improves on doping and irradiation due to the improvement in the sensitivity. As the percentage of PANI increases in the blend response time of the blend increases. Almost all sensors constructed are mechanically stable even after 75 cycles of humidity exposure (Table 4). In addition to this the sensor response is reproducible even after 1 year.

Table 4
Response time, stability and durability of the blends.

Sample	Loop area (Ω%)	Response time (s)		Durability of the sensor (after 75 cycles humidity exposure)
		Humidification	Desiccation	
30P	18.22	120	60	Stable
50P	18.02	150	75	Stable
70P	15.98	190	100	Stable
30Pdoped	3.9	60	45	Stable
50Pdoped	2.2	125	45	Breaks after 57 cycles
70Pdoped	1.8	–	–	Breaks after 6 cycles
30P2kGy	15.90	105	55	Stable
30P6kGy	16.65	75	45	Stable
30P10kGy	22.44	45	30	Breaks after 48 cycles
50P6kGy	8.1	125	55	Stable
70P6kGy	9.76	155	80	Breaks after 69 cycles
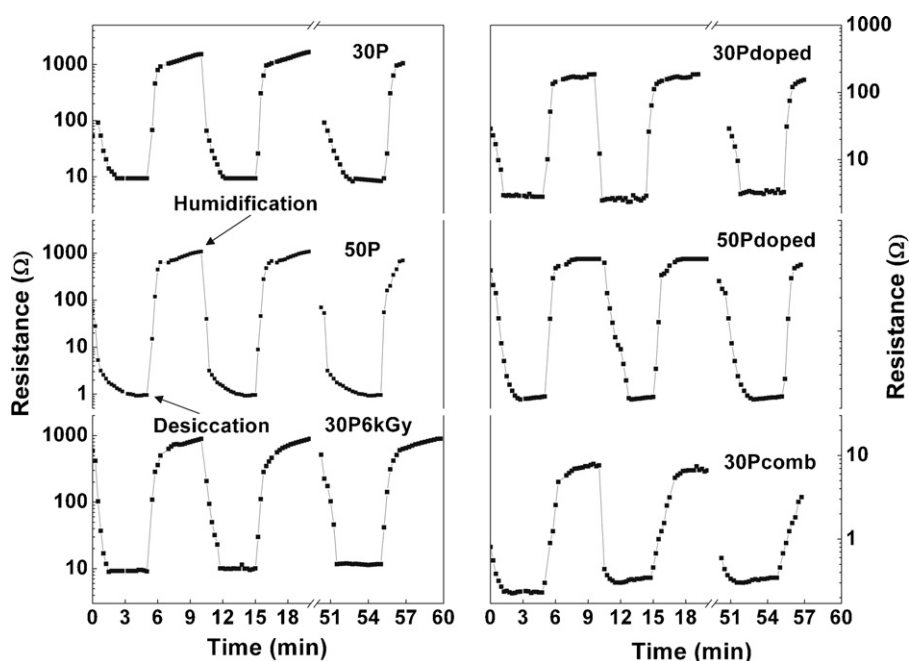
Fig. 13. Resistance variation of sensor as function of time (for each 5 min humidity is switched).
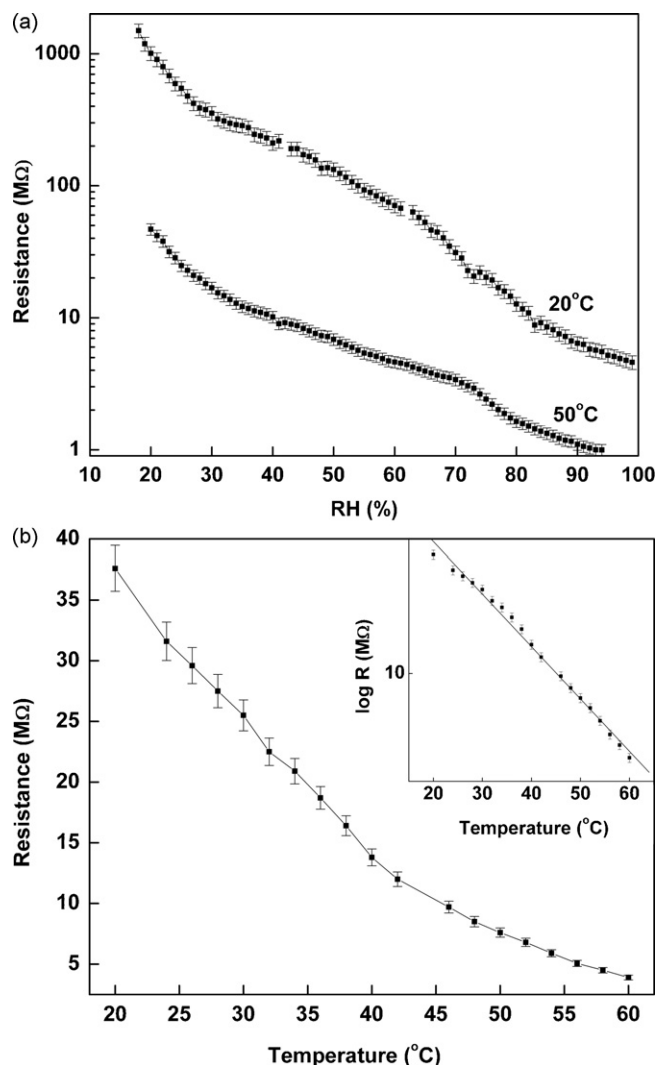
Fig. 14. (a) Effect of temperature on the variation of resistance with humidity and (b) variation of resistance with temperature for a particular humidity.

Fig. 15. (a) Variation of resistance for lower thickness ($\approx$7 μm) sensor and (b) humidity response of lower thickness sensor with time.

Fig. 14 shows the effect of temperature on the 30P blend sensor. As the temperature increases, the conductivity of blend increases and $\log R$ vs. RH plot shows better linear response (Fig. 14(a)). In order to understand the variation of resistance with respect to temperature, resistance is recorded for various temperatures at 60% RH. The resistance decreases exponentially with temperature (Fig. 14(b)). Logarithm of resistance with temperature shows a linear response. Since the standard sensor used for the study has got operating limit from 20 °C to 60 °C, the study is limited to 20–60 °C.

From the above results one can say that chitin–polyaniline blend can be used as a humidity sensor, but with limitations like high resistance, slow response time and hysteresis. However by modifications in the sensor layout and by reducing the thickness of the blend film used for the construction of the sensor, these limitations can be overcome. To demonstrate this we have used comb electrode structure for sensor in order reduce the separation (1 mm) between two electrodes. By reducing separation of the electrodes, resistance of the sensor is reduced by 3 orders (Fig. 13). Also in order to increase the response time, thinner ($\approx$7 μm) film is used for the construction of the sensor.

Sensors constructed with thinner film show almost no hysteresis with humidity cycling (Fig. 15(a)) and faster response time (Fig. 15(b)). When thickness of the film is lower, it can absorb or desorb the moisture and reach the equilibrium at a faster rate. From the
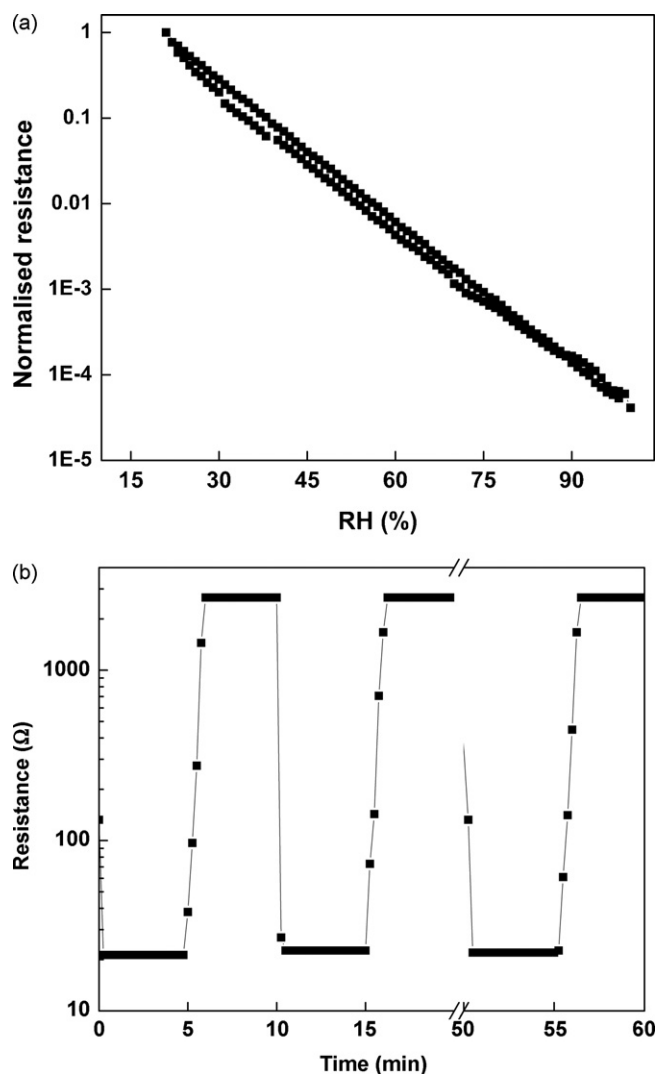
response plot (Fig. 15(b)), response time is found to be less than 10 s during humidification and less than 30 s during desiccation. Further these sensors are stable even after 1 year (see supplementary information). All the above results suggest that chitin–polyaniline blend is a promising material for the humidity sensor and even micro-humidity sensors can be constructed using sophisticated technology.

4. Conclusions

Self-doped blends of chitin and polyaniline with various compositions are prepared by solution blending technique and are irradiated with electron beam of various doses. The free standing films of blends are stable under ambient condition. The red shift and absorption shoulder at $\approx$430 nm clearly indicates that as percentage of polyaniline increases, conductivity of the blend increases. FTIR study shows interaction between chitin and polyaniline in the blend. Further, from SEM studies miscibility of chitin-PANI blend is confirmed. Blends show good thermal and environmental stability even after 3 years (see supplementary information). Conductivity achieved through self-doping with LiCl used as solvent, is 2.15×10^{-5} S/cm. The conductivity achieved is high enough to make them interesting materials. The DC conductivity further improves on irradiation. When these blends are doped with HCl

conductivity rises to $\approx 9.68 \times 10^{-2}$ S/cm. Blends show almost linear response to humidity. The characteristic response of the blend can be reproduced even after 75 cycles of humidity exposure. A small amount of hysteresis is seen. The response and sensitivity of blends are improved upon irradiation and doping. The hysteresis and response time can be reduced by reducing the thickness of blend films. The constructed humidity sensor shows very good results in the 10–100% humidity range and operating temperature range is found to 20–60 °C. Further it should be noted that, sensor has got very good durability against water and humidity response can be reproduced with sensor even after 1 year. Hence it proves to be a competent material as humidity sensor.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2010.05.044.

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