Humidity Sensing Study of Polypyrrole (PPy)-Poly (Vinyl Acetate) (PVAc) Composite

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Abstract:- Composites of polypyrrole and polyvinyl acetate were prepared by chemical polymerization method. The composite in the form of a film was used as humidity sensor. Sensitivity to humidity was studied for the films prepared by different concentration of oxidizing agent. It was noted that the sample film which was prepared by high concentration of oxidization showed better sensitivity to humidity.

Keywords: Polypyrrole, humidity sensor.

INTRODUCTION

In general, commercially developed humidity sensors are mainly made of polymer films and ceramics [1]. Ceramics have the advantage of better mechanical, thermal and chemical stability while the polymer films are well suited to fabricate a small, low cost humidity sensor. Most of the sensors are based on porous polymer films thinner than millimeters. Polymer composites and copolymers have also been studied for humidity sensing [2, 3]. Heteroatomic polymers can act as gas and humidity sensors [4]. In particular, polypyrrole based humidity sensors [5, 6, 7] showed variation in initial resistance upon interaction with humidity. For example; PPy-Fe₂O₃ nano-composite [8, 9] showed good sensitivity towards humidity. In both the cases, it was observed that increased percentage of PPy in the composites makes the sensor more sensitive to humidity. Here an attempt is made to study humidity sensing property of PPy-PVAc composite films.

EXPERIMENTAL

Fabrication of Sensor

The chemicals used for synyhesis of PPy-PVAc composite were monomer Pyrrole (E. Merck, Germany), anhydrous FeCl₃(E. Merck, Germany), poly vinyl acetate (PVAc) (AR grade) and methanol (AR grade). The PPy – PVAc composite was prepared by chemical oxidative polymerization using different strength of FeCl₃ and the composite films were obtained by casting polymerized mixture on glass plate[10].

The electrical contacts were made on the PPy – PVAc composite film surface by using silver paste and the films were then used as humidity sensors. The digital camera photograph of one of the sensors is shown in fig.1.

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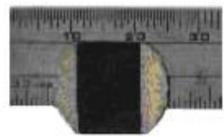


Figure 1 Photograph of PPy-PVAc composite film used as humidity sensor

Nomenclature of the sensors was made on the basis of concentration of $FeCl_3$ used for polymerization. For PPy-PVAc film sensors like S5 and S10, $FeCl_3$ concentration was 0.5 and 1 M respectively.

Scanning electron microscopy

The surface morphology is analyzed by a JSM-6360 scanning electron microscope (SEM) from Department of Physics, Pune University, Pune.

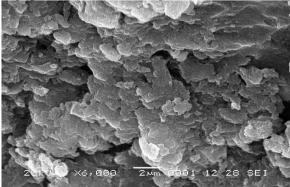
Humidity sensitivity measurement

PPy-PVAc humidity sensor was used as a resistive type sensor. Humidity sensing response of the sensor was studied by increasing humidity from 25 % RH to 90 % RH in steps of 5 % RH at room temperature.

RESULTS AND DISCUSSION

Surface morphology

The surface morphology of the PPy–PVAc composite films was studied using by a JSM -6360 scanning electron microscope (SEM). The SEM images of composite samples S5 and S10 are shown in Fig. 2 (a and b). As seen from surface morphology of S5 and S10 there are some pores on the surface of S10 samples. These sample has average pore diameter in the range of 1 to 2 micro meters.



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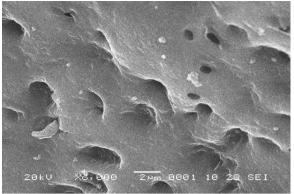
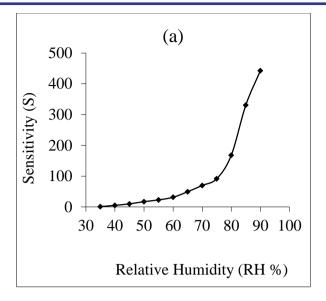


Figure 2 SEM Photographs of PPy-PVAc composite film sensors S5 (a) and S10 (b)

HUMIDITY SENSITIVITY OF COMPOSITE FILMS.

The sensitivity is calculated by using the formula, S=Rd/Rh, where Rd is the dry resistance (value taken at 35%RH) and Rh is the resistance at a particular RH value. Variations of sensitivity with relative humidity (RH) for all the composite samples are shown in Fig.3. From these plots it is observed that sensitivity increases gradually at low humidity levels and beyond some minimum RH it increases at a faster rate. Same type of sensitivity variation was observed in case of PPy-Fe2O3 nano-composites humidity sensors [8, 9]. Like other sensors [11,12], fundamental mechanism of humidity sensing that enables the PPy-PVAc composite film to sense humidity is the physisorption of water on initially chemisorbed layer of hydroxyl ions. The amount of chemisorbed water by polymer depends on several physical and chemical factors such as polymer's polar groups and their number and position on a polymer chain. [13-16]. In case of PPy – PVAc composite C=O group from PVAc and -NH group from PPy plays the main role as active sites for chemisorption. As seen from sensitivity variation with relative humidity, Fig. 3 (a and b), low sensitivity of sensors at low humidity levels (upto 50 % RH) can be attributed to chemisorbed water layer on the surface of PPy-PVAc composite film. The increased sensitivity above 50 %RH can be attributed to physisorbed water layer where protons hop from adjacent hydroxyl ions in water like network formed on film surface. Step increase in sensitivity above 80 % RH is probably due to increase of protons and their mobility in multiple physisorbed water layers. Increase in conductivity with relative humidity due to hopping of protons was reported in earlier study [8].

The effect of strength of FeCl₃ on the sensing performance of PPy–PVAc composites is also studied and it is observed that sensitivity values are higher for S10 than S5. The increase in sensitivity values are attributed to increased content of PPy in the composites with strength of FeCl₃. The large increase in sensitivity for samples S10 may be attributed to porosity of the samples as evident from SEM study. One important change that has been noted in the sensitivity study of samples is that the value of RH above which a sensor becomes more sensible is lowered for S10. That is range of humidity over which a sensor is sensible is seems to be increased for S10.



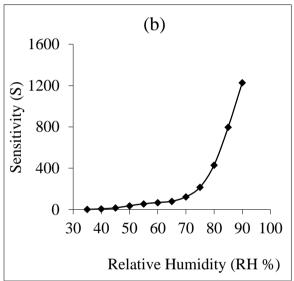


Figure 3 Variation of sensitivity with change in relative humidity for PPy-PVAc composite films S5(a) and S10(b)

RESPONSE AND RECOVERY TIMES

The response time, is the time taken by the sensor during adsorption to reach 90% of the final value for a given relative humidity, and recovery time is the time taken by the sensor during desorption to come to within 10% of the initial value. The response and recovery times for sensor S5 and S10 samples are shown in Fig. 4 (a and b). The response and recovery times for all sensors are shown in Table 1. Decrease in response time for sensor S10 may be attributed to increasing roughness and porosity of the film surface with increase in strength of FeCl₃. The remarkable increase in recovery time for sample S10 is due to increasing porosity of film surface. As reported earlier [9], porous surface absorb more water due to capillary condensation, which during desorption needs more external energy to depart the water molecules from the sample surface. Ultimately, the sensor needs more time to recover back to original state.

Table 1 Response and recovery times for PPy -PVAc composite sensors when alternately exposed to 45 % and 90 % RH.

Sample			Response time (Min)		Recovery time (Min)	
S5 S10			3.3		6.8 8.8	
51	4		2.1	(a)		
Voltage (V)	3					
	2]0 00		
	1					
	0	0		20		40
			Time (Min)			
Voltage (V)	4	7	(b)			
	3					
	2				_ _ _	
	1					1
	0	#				
		0		20		40
				Time (1	Min)	

Figure 4 Time response of PPy-PVAc composite film sensors S5 (a) and S10(b) when exposed alternately to a 45% and 90% RH at room temperature

CONCLUSION

The PPy-PVAc composite films were used as to investigate the humidity properties. The sensitivity was higher for composite prepared with higher concentration of FeCl₃. Also, at higher values of RH all composites showed sharp increase in sensitivity. While composite films prepared with higher strength of FeCl₃ shoed better response over wide range of humidity.

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