JOURNAL OF MATERIALS SCIENCE **35** (2000) 2005–2008

The switch-type humidity sensing properties of polyacrylic acid and its copolymers

SHUIZHU WU, FENGXIAN LI, YINLAN ZHU, JIARUI SHEN
Department of Polymer Science & Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China
E-mail: mcfzeng@scut.edu.cn

In this paper, switch-type humidity sensors based on PAA (polyacrylic acid) and its copolymers were examined. The humidity sensing properties of these polymers, such as hysteresis, response time, water resistivity and long-term stability were investigated. The factors which influence the humidity sensors' inflection point were investigated experimentally as well. The results show that, the inflection point of the humidity sensors varies with the content of crosslinking agent and the sample composition. In particular, humidity sensors based on Sample E and B show good property and stability. © *2000 Kluwer Academic Publishers*

1. Introduction

There is a strong need for reliable and accurate humidity sensors in applications such as meteorology, agriculture and manufacturing. In some situations, switch-type humidity sensors are required in which the electrical resistance–relative humidity curve has an obvious inflection point or switch point. Different inflection points are required for control or measurement in low-humidity and medium-humidity ranges, as well as in dew point applications [1–5]. We present in this paper the properties and characteristics of several switch-type humidity sensors based on polyacrylic acid (PAA) and its copolymers. The influencing factors, such as the content of the crosslinking agent and the effects of different components on the inflection points of the humidity sensors, are investigated experimentally. In addition, hysteresis, water resistivity, response time, temperature coefficient and long-term stability of these humidity sensors are studied as well. These could provide useful information for future applications.

2. Experimental

2.1. Synthesis

Polyacrylic acid and the acrylic acid-acrylamide (70 mol % acrylic acid and 30 mol % acrylamide) copolymer (AAC) were synthesized by the solution polymerization method at 70 °C for 8 h with ammonium persulfate as the initiator. PEG (polyethylene glycol) 2000 ($M_n = 2000$) and PEG 400 ($M_n = 400$) are of AR grade.

2.2. Preparation of the humidity sensors

Sample compositions were as follows:

Sample	Composition
A	PAA + 3 mol % PEG 2000 + 5 mol % LiOH
B	PAA + 3 mol % PEG 2000
C	AAC
D	AAC + 3 mol % PEG 2000
E	AAC + 3 mol % PEG 400

Toluene-2, 4-diisocyanate was used as the crosslinking agent. The above solutions were coated on the surface of an alumina substrate having a pair of comb-shaped gold electrodes, after that the coated alumina substrate was placed in oven at 65 °C for 4 h. Afterwards, it was rinsed with ethyl alcohol, and vacuum dried at 80 °C for 24 h. Finally it was placed in vacuum at 60 °C for another 24 h.

2.3. Measurement

A LCR meter of Ando Electrical Co. Ltd. was used for the measurement of electrical characteristics of the humidity sensors. The electrical resistance of the sample at 1 kHz was measured at selected relative humidities (RH) using saturated salt solutions at 25 °C.

Ionic mobility was evaluated from direct-current measurements on the cells with ion-blocking platinum electrodes. DC 2.5 V was first applied to the cells for 60 min in one direction in order to form space charges at the vicinity of the electrodes. Subsequently, the polarity of the applied voltage was reversed. The time dependence of the monitored current showed a peak at the time of flight t of ionic carriers from one electrode

0022–2461 © *2000 Kluwer Academic Publishers*

TABLE I The effects of the content of crosslinking agent (Sample E)

Content of the crosslinking agent (mol %)	Inflection point (RH)
100	No humidity sensitivity
40	Around 85%
30	Around 90%
5	Poor water resistivity

to the other. Ionic mobility μ can be estimated as follows:

$$\mu = \frac{d^2}{Vt}$$

where d is the sample thickness, and for the simplification of the analysis, V is assumed to be identical to the applied voltage [6–8].

3. Results and discussion

3.1. The effects of the crosslinking agent

The humidity sensors based on Sample B and Sample C exhibit the inflection point around 60–65% RH (relative humidity) and 75–80% RH respectively on the electrical resistance-humidity curve.

The effects of the crosslinking agent on the inflection point (switch point) of Sample E (with 3 mol % PEG 400) are shown in Table I. It can be easily seen that, with 100 mol % of the crosslinking agent, the copolymer exhibits no humidity sensing property. As the content of the crosslinking agent decreases, the inflection point of the copolymer increases. But, when the content of the crosslinking agent is under 5 mol %, the copolymer's water resistivity is so poor that, after being immersed in water for only a few minutes, the copolymer swells significantly and the humidity sensor is damaged.

These experimental phenomena can be explained as follows: With relatively higher content of crosslinking agent, most of the hydrophilic groups on the copolymer participate in the crosslinking reaction, so the sample is less humidity sensitive. As the crosslinking agent content decreases, more hydrophilic groups are left on the polymer, so the sample is more humidity sensitive. When the content of crosslinking agent is too low (less than 5 mol %), then the water resistivity of the sample is so poor that the sample is easily destroyed in water. Hence, all samples in the experiment used 30 mol % of the crosslinking agent, unless otherwise specified.

3.2. The effects of the copolymer composition

Figs 1 and 2 show the relationship between the electrical resistance of the samples and humidity. Generally, the impedance decreases with increasing relative humidity, which is similar to previous studies [9–14]. As shown in Fig. 1, Sample B displays an inflection point around 60–65% RH. With the addition of 5 mol % LiOH, namely Sample A, the inflection point shifts to the left at around 50–55% RH.

TABLE II The hysteresis of the humidity sensors based on different samples

Sample	Hysteresis (RH%)
A	4
B	2
C	3
D	1
E	0.2

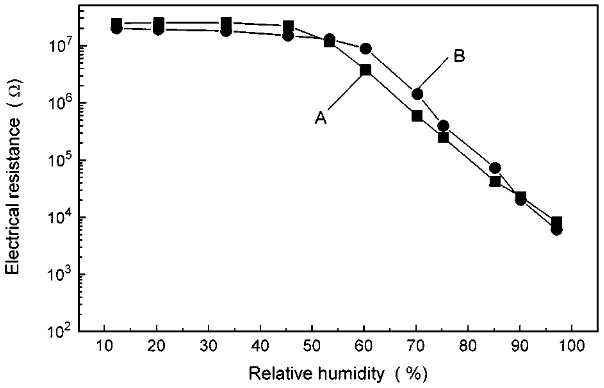

Figure 1 The relationship between electrical resistance and relative humidity for Samples A and B.

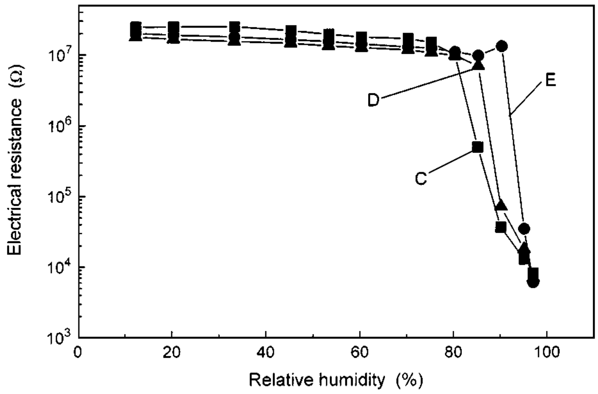

Figure 2 Electrical resistance versus relative humidity for Samples C, D and E.

Fig. 2 shows that, the inflection point of Sample C (acrylic acid-acrylamide copolymer) occurs around 75–80% RH. With the addition of 3 mol % of PEG 2000 (namely Sample D), the sample's inflection point shifts to the right at around 85% RH. With the addition of 0.5 mol % of PEG 400 (Sample E), the sample's inflection point shifts to around 90% RH.

As shown in the above figures, in all samples the impedance decreases as the relative humidity becomes higher, namely in the absorption process. However, it is found that, when the impedance is measured from high humidity to low humidity, namely in a desorption process, slight hysteresis is found. The hysteresis of the humidity sensors based on these samples is shown in Table II. It is found that, the hysteresis of the humidity sensor based on Sample A is the largest, at about 4 RH, whereas the humidity sensor based on Sample E has the smallest hysteresis. This is probably because, Sample E

TABLE III The response time of the humidity sensors

Sample	Response time (s)	
	Absorption	Desorption
A	39	120
B	35	30
C	30	5
D	120	35
E	25	5

TABLE IV Long term stability

Sample	Sensor output shift (% RH)	
	40 °C, 1000 h	Room temperature, 3 months
A	±15	±8
B	±7	±4
C	±10	±5
D	±5	±2
E	±4	±1

has quite good absorption and desorption capabilities; as for Sample A, since it contains Li^+ and Li^+ has relatively small radius, hence once it absorbs water, desorption won't occur easily.

The 90% response time τ (which is defined as the required time for the sensor output to reach 90% of the difference between initial and final humidity value) of the humidity sensors is shown in Table III. For the case of water absorption, resistance was measured at 97% RH as a function of time immediately after the sample was conditioned at 25 °C and 12% RH for 25 min. For the case of water desorption, a similar measurement was carried out, but at 12% RH immediately after the sample was conditioned at 25 °C and 97% RH for 25 min. It can be seen that, except for Sample A, the response time for the desorption process of all the samples is shorter than that for the absorption process. While the response time for desorption of the humidity sensor based on Sample A (PAA with LiOH) is much longer than that for absorption, this is probably because, Li^+ radius is relatively small, once it absorbs water, desorption doesn't occur easily. This experimental phenomenon also coincides with the result obtained in the above-mentioned hysteresis experiment.

For the above crosslinked copolymers, the impedance decreased a little as the measurement temperature increased. The temperature dependence of the sensors was 0.5% RH/°C and was reversible. This effect of temperature on the copolymer can be considered to be due to an increase in the activity of the ionic groups of the copolymer as the temperature increased. It was also confirmed that these sensors can be used at temperatures up to 150 °C. Above 150 °C, the impedance increased irreversibly.

For all five samples, we used the polarity reversal method [6–8], and tested the time dependence of the monitored current after the application of a constant DC voltage for an appropriate time and the reversal of the applied voltage polarity. It was found that, at higher humidity (92% or 97% RH), one obvious current peak was observed, while at lower humidity (12% RH), the current peak became ambiguous. Hence, it is considered that, at higher humidity, ionic conductivity exerts more influence upon the electrical characteristics of the copolymer. While at lower humidity, electronic conductivity (tunneling effect) gradually becomes significant.

3.3. Water resistivity and long-term stability

The humidity sensors' water resistivity is shown in Fig. 3. After being immersed in water for up to 4 h, the humidity sensing property of Sample E doesn't change at all, this sample displays excellent water resistivity, while the humidity sensing property of Samples A and C show some changes.

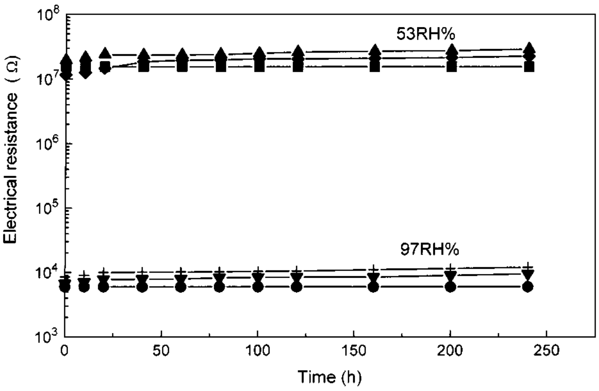

Figure 3 Electrical resistance versus time at different humidities: (—■—, —●—) Sample E; (—▲—, —▼—) Sample C; (—◆—, —+—) Sample A.

The long-term stability of the humidity sensors was tested by placing these sensors in an indoor environment for over 3 months at room temperature or at 40 °C for 1000 h at 97% RH. The results are shown in Table IV. Good stability was exhibited, in particular, the sensor drift of Sample E was small at ±4 RH after 1000 h of exposure to 40 °C, 97% RH. This stability under hot and humid conditions is essential for a wide variety of applications. The humidity sensors' long-term stability in decreasing order is as follows: Sample E > Sample D > Sample B > Sample C > Sample A.

4. Conclusions

The humidity sensing properties of PAA and its copolymers, such as the hysteresis, response time, water resistivity, inflection and long-term stability were investigated experimentally. The results show that, the inflection point of the humidity sensors varies with the content of the crosslinking agent; and with the adding of Li^+, the inflection point of the polymer shifts to the left. The humidity sensor based on Sample E shows the best hysteresis, response time, water resistivity and long-term stability.

Acknowledgement

The authors would like to thank the financial supports of the Key Scientific & Technological Program of Guangzhou City and Guangdong Natural Science Foundation of China.

References

1. V. MATKO and D. DONLAGIC, *Sensors and Actuators* **A61** (1997) 331.
2. Y. SAKAI, Y. SADAOKA, M. MATSUGUCHI and H. SAKAI, *ibid.* **B24/25** (1995) 689–694.
3. M. HIRATA, S. INOUE and R. YOSOMIYA, *Die Angew. Makromol. Chemie* **131** (1985) 125–134.
4. H. AN, M. HIRATA, R. YOSOMIYA and Y. XIN, *ibid.* **150** (1987) 33–44.
5. P. R. STORY, D. W. GALIPEAU and R. D. MILEHAM, *Sensors and Actuators* **B24/25** (1995) 681–685.
6. M. WATANABE, K. SANUI and N. OGATA, *J. Appl. Phys.* **57**(1) (1985) 123.
7. M. WATANABE, M. RIKUKAWA, K. SANUI and N. OGATA, *ibid.* **58**(2) (1985) 736.
8. E. TSUCHIDA, N. KOBAYASHI and H. OHNO, *Macromolecules* **21** (1988) 96.
9. J. M. PEREZ and C. FREYRE, *Sensors and Actuators* **B42** (1997) 27.
10. T. KUROIWA, T. MIYAGISHI, A. ITO and M. MATSUGUCHI, *ibid.* **B24/25** (1995) 692.
11. K. D. KREUER, *Solid State Ionics* **97** (1997) 1.
12. S. A. HASHMI, *ibid.* **96** (1997) 209.
13. J. H. PARK, *J. Mater. Sci.: Mater. In Electronics* **5** (1994) 300.
14. G. SBERVEGLIERI, R. ANCHISINI, R. MURRI, C. ERCOLI and N. PINTO, *Sensors and Actuators* **B32** (1996) 1.

Received 28 September 1998
and accepted 24 May 1999