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Polymeric Humidity Sensors with Nonlinear Response: Properties and Mechanism Investigation

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ABSTRACT: A class of humidity sensors with switching property based on several hydrophilic polymers [poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), and hydroxyethyl cellulose (HEC)] were researched. These polymers were selected as the sensing materials because the polar groups in the molecules (amide, hydroxyl, and ether bond) could interact with water molecules. The sensors all show nonlinear response to relative humidity (RH) under AC voltage. The impedances of the sensors remain almost unchanged at low RH and decrease sharply at certain humidity (about 75, 65, and 55% RH for PVP, PVA, and HEC sensors, respectively). The switching points and sensitivities of the sensors could be adjusted by changing the operating frequency, polymer blending, or doping with hydrophilic materials. The complex impedances of the sensors demonstrate that the electronic contribution is dominant at low RH, and the ions make a significant contribution for increasing RH levels. The different sensing properties of the polymers are attributed to their different hydrophilic properties and ionic contributions at high RH. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 2056–2061, 2013

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INTRODUCTION

Humidity sensors have attracted the attention of many researchers in past years.[1,2] Different kinds of materials have been used as sensing materials of humidity sensors, such as organic polymers,[1,2] ceramics,[3,4] and composite materials.[5–8] Many polyelectrolytes were reported for preparing resistive-type humidity sensors.[9–12] Polymeric humidity sensors have received much attention due to their advantages of easy preparation, simple measurements, good stability, and no need of heat cleaning.[13–15]

Above sensors based on amphiphilic polymers could give an impedance change with a wide humidity range. And generally speaking, the polymeric humidity sensors which show good linear curves from low to high humidities are ideal. However, humidity sensors with switching property are needed to monitor and control the relative humidity (RH) within a certain range in some conditions. Such as storage, plant growing, and electronic product manufacturing, etc. Until now, few researches have been done to develop switching type humidity sensors.

Conductive polymers composed with hydrophilic polymers and carbon material have been used to monitor high RH.[16–18] The ensitive composite film contains conductive filler and a polymer matrix with swelling-shrinkage properties. The resistance of the composites increases sharply at high RH attributed to the swelling of hydrophilic matrix, which increases the distance between conductive particles and decreases the electrical conductivity of the composites.[18] This kind of sensor could work in high RH environments for condensation control.

In this study, humidity switching sensors based on several hydrophilic polymers [poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), and hydroxyethyl cellulose (HEC)] were researched. The chemical structures of the polymers are shown in Figure 1. The three types of polymers obtain different polar groups in the molecules (amide, hydroxyl, and ether bond), which could form hydrogen bonds with water molecules. And because of their different interactions with water molecules, the hydrophilic properties of the polymers are different. The humidity switching properties of these sensors are different with the sensors based on polymer/carbon composites introduced above. The impedances of the sensors hardly change at low RH, and decrease sharply at certain humidity. The switching properties and mechanism of the sensors were investigated.

MATERIALS AND METHODS

Sensor Preparation

PVA with a degree of polymerization of 1750 and an alcoholysis degree higher than 98% was from Sinopharm Chemical

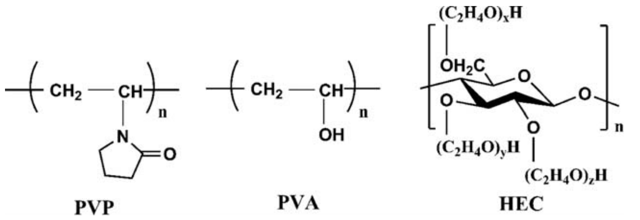

Figure 1. The chemical structures of polymers (PVP, PVA, and HEC) used for humidity sensors.

Reagent. HEC (800–1500 mPa s, 2% in water at 20°C) and PVP (molecular weight = 30,000) were from Aladdin Chemical.

The sensitive films were prepared by a solution process similar as our published article.[19] In a typical procedure, PVP was dissolved in distilled water with the concentration of 100 mg/mL to form a uniform solution. Then the suspension was casted onto clean ceramic substrates (10 mm × 8 mm × 0.8 mm) by dip coating with a thickness of ~10 μm, where an interdigitated array of Ag–Pd electrodes had been previously screen-printed. Aging treatments of the sensors were under 1 V AC with the frequency of 1000 Hz for 6 h to improve the stability and durability.

Measurements

The humidity switching properties of the sensors were investigated by recording the electrical response of the sensors at 1 V AC under different RH at about 20°C. The atmosphere of RH are produced by different saturated salt solutions in their equilibrium states including LiCl for 11% RH, $MgCl_2$ for 33% RH, $Mg(NO_3)_2$ for 54% RH, NaCl for 75% RH, KCl for 85% RH, KNO_3 for 95% RH, and H_2O for 100% RH. The uncertainty of the RH values is about ±1%.

RESULTS AND DISCUSSION

Humidity Switching Properties

The impedances of the sensors based on PVP, PVA, and HEC under 1 V AC (1000 Hz) at different RH are shown in Figure 2. These sensors all show nonlinear response to RH. The impedances of the sensors are close at low RH (about 1600 kΩ) and begin to decrease at certain humidity with increasing RH. It is worthy to note that the switching humidity points are about 75, 65, and 55% RH for PVP, PVA, and HEC sensors, respectively [Figure 2(a)]. And as shown in Figure 2(b), the sensitivities [defined as the ratio of initial impedance of the sensor (at 11% RH) to that at a certain RH] of these sensors at high RH are very different (49, 171, and 363 at 100% RH for PVP, PVA, and HEC, respectively). It is obvious that HEC sensor shows the lowest switching humidity point and highest sensitivities at high RH, which are opposite with that of PVP sensor. The much different humidity switching properties of the sensors are related to the hydrophilic properties of the polymers, which would be discussed later. These results demonstrate the above sensors based on hydrophilic polymers may be used for monitoring certain range of RH.

Adjustment of Switching Properties

The obtained polymeric sensors showed different humidity switching properties with certain humidity switching point. In order to realize a wide range of switching points, different methods were used to regulate the humidity switching properties based on PVP sensor (the humidity switching point of PVP sensor is about 75% RH under 1 V AC, 1000 Hz), which is beneficial for realizing a wide range of switching points.

The impedance of PVP sensor at different operating frequencies (1 V AC) at about 20°C was researched and the results are shown in Figure 3. The impedance of the PVP sensor depends on frequency in low RH, and is independent of frequency at high RH. The impedance of the sensor at low RH decreases as the frequency increased, and the curves show very different humidity switching properties as the frequency changed. The switching humidity increases from ~50% RH for 50 Hz to ~85% RH for 10 kHz, and the sensitivity at 100% RH is about

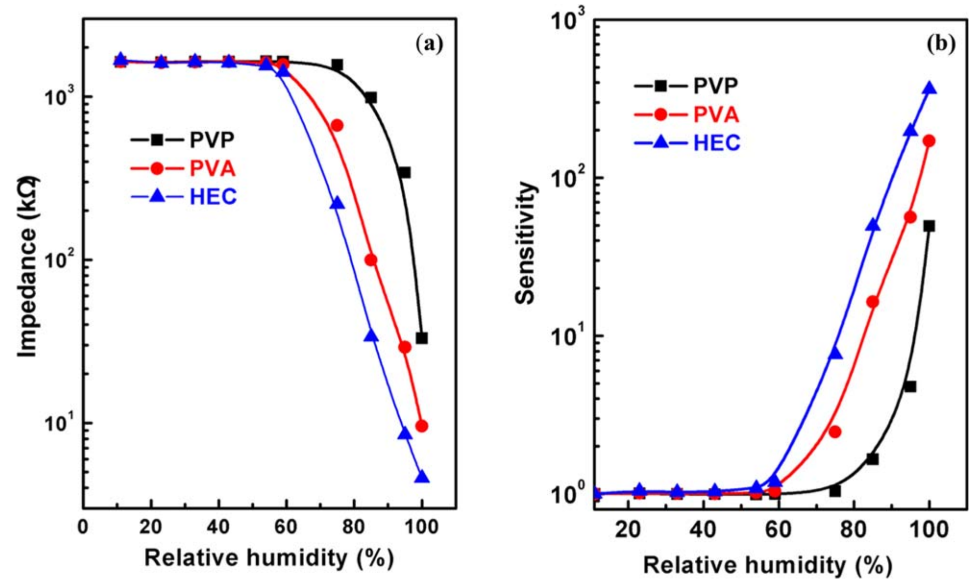

Figure 2. The impedances (a) and sensitivities (b) of sensors based on PVP, PVA, and HEC under 1 V AC (1000 Hz) at different RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

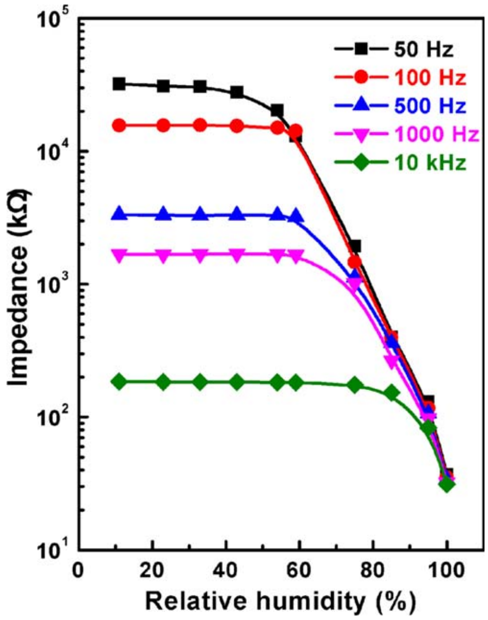

Figure 3. The impedances of PVP sensor at different RH under different frequencies (1 V AC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

865 and 6 under 50 and 10 kHz, respectively. Since the sensor is not stable under low frequency and not sensitive if the frequency is too high, we confirmed the operation condition of AC 1 V, 1000 Hz in the following experiments.

As above sensors show different humidity switching points, sensors based on the mixtures of polymers may be used for controlling the switching properties. The humidity sensing curves of sensors based on different ratios of PVP and PVA mixtures were shown in Figure 4. As the content of PVA in sensing materials increases, the switching point shifts towards low RH and the sensitivities at high RH increase (the sensitivity is 49, 107, and 138 for 0, 25, and 50 wt % of PVA, respectively). Therefore, switching properties of PVP sensor could be tuned easily by mixing with certain amount of PVA as the sensing material. The tune of switching points between 65% RH (for pure PVA sensor) and 75% RH (for pure PVP sensor) could be realized by blending PVA and PVP with a certain ratio in principle.

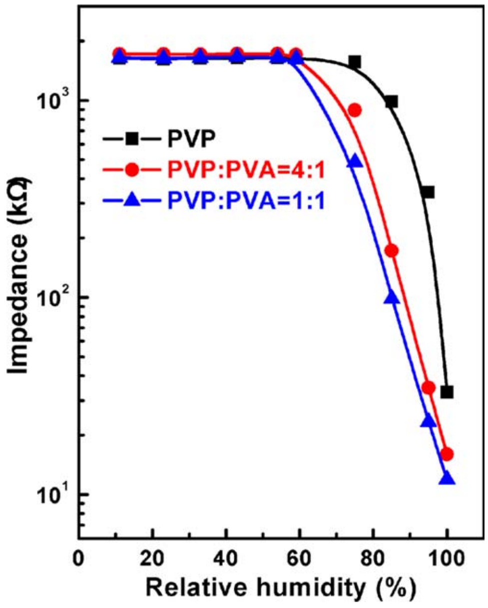

Figure 4. The impedances of sensors based on PVP/PVA composite films at different RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

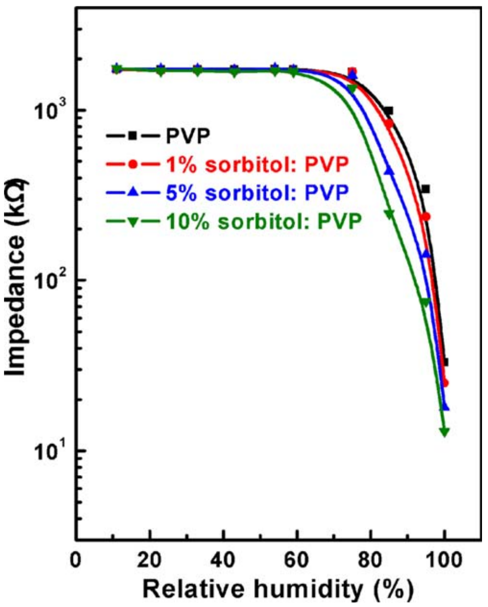

Figure 5. The impedances of sorbitol/PVP sensors with different contents of sorbitol at different RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sensors based on PVP doped with different contents of sorbitol (1, 5, and 10 wt %) were fabricated and the humidity sensing properties are shown in Figure 5. As the sorbitol content increases, the switching points shift towards low RH and the sensitivities at high RH increase at the same time. This result is related to the highly hydrophilic characteristic of sorbitol (a large amount of hydroxyl in the molecules), which could interact with water molecules and absorb more water molecules on the surface of sensing film. For 10 wt % sorbitol/PVP sensor, the humidity switching point is about 65% RH and the sensitivity is 135 at 100% RH.

Response and Recovery Property

Response and recovery time is an important parameter for polymeric humidity sensors. PVP sensor was researched as an example. Figure 6 shows the response and recovery property of PVP sensor corresponding to the water adsorption and desorption process. The time taken by the sensor to achieve 90% of the total impedance change is defined as the response or recovery time.[20] For PVP sensor, the response and recovery time between 11% and 95% RH is about 37 s and 10 s, respectively. This is rather short compared with the sensors based on amphiphilic polymers, especially for the recovery time, which is usually dozens or hundreds of seconds.[21,22] The rapid response and recovery property of PVP sensor is beneficial for practical RH detection and control.

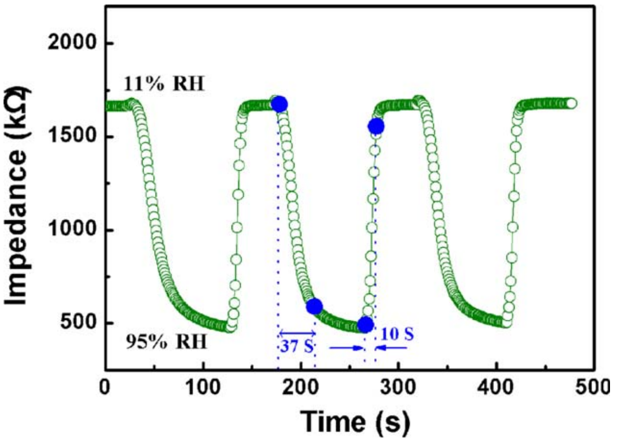

Figure 6. Response and recovery curve of PVP sensor between 11 and 95% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Humidity Sensing Mechanism

Figure 7 shows the relationship between capacitance and humidity of PVP sensor under the AC voltage of 1 V with frequencies from 50 Hz to 100 kHz at about 20°C. The capacitance of the sensor almost does not change under all frequencies at humidities lower than 70% RH. While the capacitance increases with the humidity from ~70% RH for 50 Hz and 100 Hz and 80% RH for 1000 Hz (inset of Figure 7), and the capacitance increases much more rapidly with lower frequency. When the frequency reaches a high value, the capacitance becomes very small and hardly changes with humidity. According to the adsorption theory, adsorption of water molecules takes place in two processes. The chemisorbed layer completes first, then many more physisorbed layers form at higher RH.[23] In a low humidity environment, only a little amount of water molecules are adsorbed, and the capacitance is independent of the frequency, which can be considered as an ideal capacitor. When more water molecules are adsorbed, leak conductance appears, and the capacitance increases with RH.[24] In addition, the capacitance is in inverse proportion to the frequency. In our experimental results, the capacitance was little affected by RH when the frequency was over 1000 Hz.

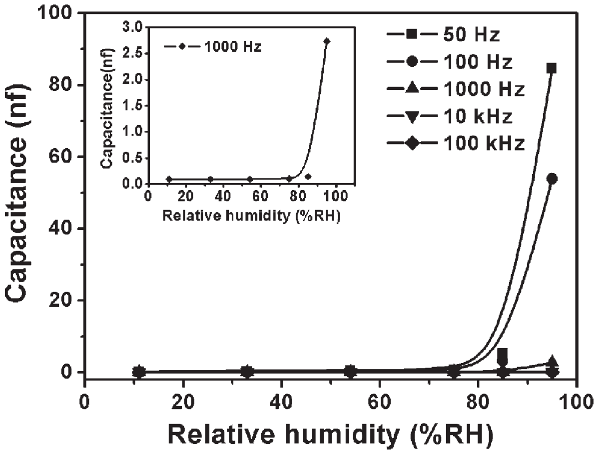

Figure 7. Capacitance-humidity curves of PVP sensor at different frequencies. Inset shows the amplified capacitance–humidity curve at 1000 Hz.

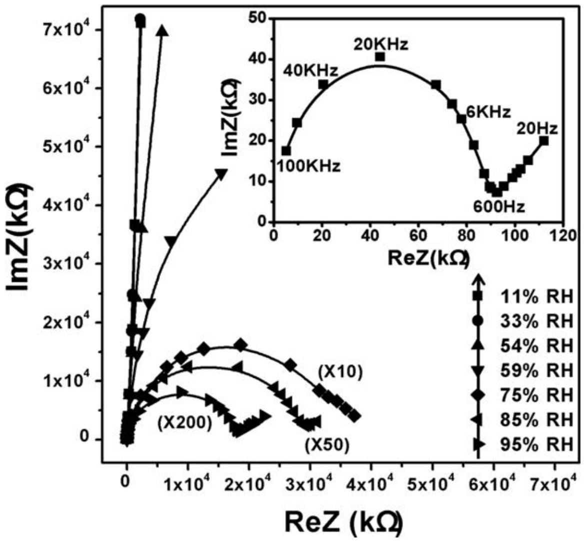

Figure 8. Complex impedance plots of PVP sensor under different humidity environments. ImZ, imaginary part; ReZ, real part. Inset shows the amplified complex impedance curve at 95% RH.

Complex impedance plots could be used to research the humidity sensing behaviors of materials.[13,25] The complex impedances of the sensors were measured at 1 V with the operating frequency from 20 Hz to 100 kHz and the RH from 11% RH to 95% RH at about 20°C. The real part and imaginary part were magnified on the same plane to compare several complex impedance plots conveniently. The typical complex impedance plots of PVP sensor are shown in Figure 8. The curve is a part of a semicircle at low RH (11, 33, and 54% RH), and the region of the semicircle increases to become a complete semicircle at 75% RH. Before this humidity point, the intrinsic electrons are the main contributors to the conduction. When the humidity was further increased, a little straight line appears after the semicircle in the low frequency range. This straight line was considered to be mainly due to the contribution of ions (H^+ and H_3O^+) to the conduction.[13] Therefore, the complex impedance plots demonstrate the conductance of the polymer is the totality of the electronic and ionic contribution. The electronic contribution is dominant at low RH, and the ions make a significant contribution for increasing RH levels. According to the ion transfer mechanism,[26] $H_2O + H_3O^+ = H_3O^+ + H_2O$, the initial and final state are the same, so the transfer of ions is quite easy. The quick transfer of ions results in a sharp decrease of the impedance. And, because the polarization frequency of electrons and the ions are different, the effective ionic contribution drops with increasing frequency, which is remarkable under the frequency range used in our work (50–10 kHz), as shown in Figure 3.

It is worthy to note that the humidity point where the straight line appears in the complex impedance plots of PVP sensor coincides with the humidity switching point in Figure 2, from where the impedance decreases sharply with increasing RH. And the results demonstrate the contribution from ions

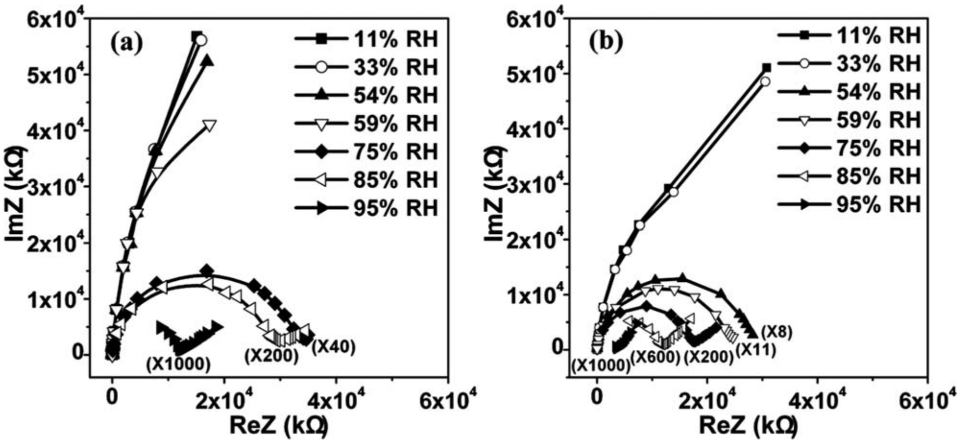

Figure 9. Complex impedance spectra of (a) PVA sensor and (b) HEC sensor under different humidity environments.

increases the conductivity of the film and results in decreased impedance. Similar results were observed in the complex impedance spectra of PVA and HEC sensors (Figure 9). The humidity points where the straight lines appear in the complex impedance plots of PVA and HEC sensors also coincide with the humidity switching points shown in Figure 2. According to the above data, the three polymeric humidity sensors work with a similar mechanism, while the ionic contributions at high RH are different. So, the impedances of the sensors at low RH are similar, and the humidity switching points and the sensitivities at high RH are different because of the different ionic contributions, which come from the different hydrophilic properties of the polymers.

CONCLUSION

Simple-structure polymeric humidity sensors based on hydrophilic polymers were fabricated and their humidity switching properties were researched. The sensors show nonlinear response to RH with different humidity switching points between 55 and 75% RH. The switching properties of the sensors could be adjusted by controlling the operating frequency, polymer blending, or doping with hydrophilic materials. Complex impedance results demonstrate the electronic contribution is dominant at low RH, and ions make a significant contribution for increasing RH levels, which coincides with the impedance responses of the sensors at different RH. This type of sensor is more beneficial to monitor and control certain range of humidity atmospheres than common humidity sensors.

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