Humidity sensor using epoxy resin containing quaternary ammonium salts

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Abstract

Humidity-sensitive epoxy monomer, glycidyl trimethyl ammonium chloride (GTMAC) was selected as the humidity-sensing resin. Polypropylene glycol diglycidyl ether (PPGDGE) and methyl tetrahydrophthalic anhydride (MTPHA) were used as a comonomer and a curing agent, respectively. The humidity-sensitive membranes were composed of GTMAC, PPGDGE and MTPHA. When impedance characteristics of the epoxy resins containing quaternary ammonium salts were measured, the impedance decreased linearly with an increase in the content of GTMAC in its semi-logarithmic graph. The impedance changed from $10^7$ to $10^3$ $\Omega$ between 30 and 90\%RH, which was required for a common humidity sensor. Temperature dependence, frequency dependence and response time were also measured. The humidity-sensitive characteristics of the sensor did not change even after soaking in water. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of organic polymers for sensing humidity is well-known, and various devices incorporating organic polymer humidity sensing elements have been suggested [1]. Resistance of the humidity sensor is measured for the most common form of polymeric humidity sensor. In spite of the availability and the improvements of new polyelectrolytes in recent years, polymeric humidity sensors still suffer from a variety of significant disadvantages including large hysteresis and instability in high humidity. Most significantly, these disadvantages become increasingly severe at elevated temperatures and high levels of relative humidity [2].

Various modifications of polyelectrolytes have been attempted to improve the water durability [3–10]. The methods of cross-linking with multifunctional monomer and copolymerization with hydrophobic monomer have been frequently employed for the preparation of the water-resistant humid membrane [11–14]. Many polymers were examined in an effort to produce a sensor, which would provide high accuracy measurements with a long service life at high temperature and humidity condition [1]. Epoxy resins were widely used as a structural matrix resin for composite and a chemically resistant coating. However, epoxy resins have rarely been met for the humidity sensing materials.

In this article, we have prepared a water-resistive humidity sensor using epoxy resin consisting of glycidyl trimethyl ammonium chloride (GTMAC), polypropylene glycol diglycidyl ether (PPGDGE) and anhydride curing agent, and the impedance characteristics on gold–alumina electrode were investigated and evaluated.

2. Experimental

2.1. Chemicals and instrument

GTMAC (Aldrich Chem. Co.) was freeze-dried before use to remove water. Methyl tetrahydrophthalic anhydride (MTPHA) and PPGDGE ($M_n$ ca. 380, Aldrich Chem. Co.) were used without further purification. Dimethylsulfoxide (DMSO) was purified by distillation under reduced pressure after azeotropic distillation with benzene using a Dean–Stark separator.

The humidity and temperature controller (Tabai Espec Model PL-2G, –40 to 150°C, 30–95\%RH) was used for the
measurement of relative humidity at constant temperature. The impedance was measured with an LCR meter (Model EDC-1635, 0.1 Ω–20 MΩ) and an impedance analyzer (HP 4192A). Gold electrode (thickness of electrode: 8–10 μm) was printed on the alumina substrate (10 mm × 5.08 mm × 0.635 mm). Soldering pad of lead wire and over-coat were formed by using silver–palladium alloy and glass paste, respectively. The surface resistance of gold electrode was found to be <0.04 Ω using four-point probe measurement system.

2.2. Fabrication of humid membrane

Epoxy monomer GTMAC (3.03 g, 20 mmol) and MTPHA (2.31 g, 14 mmol) were dissolved in anhydrous DMSO (21.3 g) at room temperature. The mixture was applied on the gold electrode by injecting 5 μl of solution with a micro-syringe. The curing reaction was carried out by heating the fabricated sensors in an oven at 100°C for 30 min and at 150°C for 30 min. After the curing reaction was completed, the samples were immersed in ethanol for 30 min and dried under vacuum at 50°C for 12 h. Other epoxy humidity sensors with different content of PPGDGE were prepared by the similar procedures described above.

2.3. Measurement of impedance characteristics

The characteristics of impedance versus relative humidity (RH) of the humidity sensors were measured for an absorption process, from 30 to 90%RH, and for a desorption process, from 90 to 30%RH, respectively, at 1 V, 1 kHz and 25°C. The temperature dependence was measured at 15, 25 and 35°C at 1 V and 1 kHz. The frequency dependence was obtained by applying frequency of 100 Hz, 1 kHz and 10 kHz at 1 V and 25°C. Response time was determined over saturated salt solution of MgCl₂·6H₂O for 33%RH and KNO₃ for 94%RH at 25°C in its equilibrium state. Water-resisting property was examined by measuring resistance change after soaking the samples in water.

3. Results and discussion

Epoxy resins have been widely used as various coating materials by blending them with curing agents to form epoxy resin with a variety of compositions. Conventional epoxy/anhydride systems are cured at ambient temperature or can be cured at elevated temperature. As a curing accelerator for epoxy/acid anhydride system, tertiary amine, phosphine, quaternary ammonium halide or phosphonium halide have been used. Therefore, GTMAC containing quaternary ammonium salt and MTHPA system can be cured without curing accelerator.

The humid membrane was composed of GTMAC and MTHPA. The acid anhydride curing agent was used at 70 mol% concentration of epoxy functionality. The epoxy humidity-sensitive membrane was also fabricated with GTMAC, various content of PPGDGE and MTHPA via copolymerization reaction for the improvement of the flexibility as well as the control of the resistance characteristics as shown in Scheme 1.

Epoxy copolymers with PPGDGE showed a good adhesion to the gold electrode and alumina substrate. A schematic view of the electrode is shown in Fig. 1. A pair of interdigitated gold electrodes with a thickness of 8–10 μm

![Scheme 1. Synthesis of humidity sensitive epoxy copolymers.](image-url)
were formed on the alumina substrate. An appropriate voltage source of 1 V is connected between the electrodes. The voltage is preferably ac with a frequency of at least 100 Hz to avoid interference with the electrical signal passed by the polymer due to any small gaps between the electrodes and humid membrane.

The compositions of the humidity-sensitive membrane were GTMAC/PPGDGE/MTHPA = 100/0/70, 80/20/70 and 70/30/70. Impedance characteristics versus relative humidity of the sensor were measured using a thermostatic humidity chamber controlled by mixing dry and wet air. The sensor was connected to an impedance measurement system at 1 V and 1 kHz. The impedance of the humidity sensors composed of only GTMAC changed in the range of 1.7 MΩ–5.1 kΩ between 30 and 90%RH, which is the suitable impedance range for the common humidity sensor. The typical impedance characteristic curves of epoxy resin humidity sensor of GTMAC at 25°C and 1 kHz are shown in Fig. 2. Notably, the sensitivity of the sensor (change in impedance versus change in relative humidity) in the test temperature-humidity range covers three orders of magnitude, which is higher than other known polymeric humidity sensors. The hysteresis between absorption process and desorption process was also measured in the range of 30–90%RH. The two dotted lines display the range of ±2.0%RH. The results indicate that the sensing element described exhibits hysteresis of <2%RH. In the case of the epoxy resin humidity sensors, a pathway of the desorption process was located at the lower position of the loop. This fact demonstrated that the rate of desorption of the absorbed water in the humid-membrane is slower than that of the absorption.

The copolymer derived from GTMAC/PPGDGE/MTHPA = 80/20/70 showed a good linearity as illustrated in Fig. 3. Resistance of the humidity sensor increased gradually with an increase in the content of PPGDGE units in the copolymers. The membrane of GTMAC/PPGDGE/MTHPA = 80/20/70 showed lower impedance than that of...
GTMAC/PPGDGE/MTHPA = 70/30/70. The impedance decreased with an increase in the amount of epoxy resin containing quaternary ammonium salts in the polyelectrolyte, which might be due to the enhancement of the dissociation of ammonium ion and an increase of the carrier ion such as chloride anions dissociated by absorbed water.

The complex impedance plot (Cole–Cole plot) is a semicircle. The resistance for the sensors was determined as the intercept to the real axis, assuming a simple equivalent circuit of a parallel combination of the resistance and the capacitance. The resistance values of the sensors consisting of GTMAC/PPGDGE/MTHPA = 80/20/70 at 50%RH showed 245, 132 and 98 kΩ at 15, 25 and 35°C, respectively. Several other parameters such as thickness of the membrane and content of salt considerably influence on the resistance of polymeric humidity sensor. The concentration of the epoxy resin solution is directly related to the thickness of the fabricated humid membrane. The impedance decreased with an increase in the concentration of the humidity-sensitive epoxy resin as shown in Fig. 4. For example, the high concentration of the epoxy resin containing quaternary ammonium salts in the solution resulted in a drastic reduction in resistance. However, it was found that the sensitivities of the humidity sensor such as hysteresis and response time decreased with an increase in the thickness of humid-membrane.

The impedances of the humidity sensors were plotted on relative humidity as a function of relative humidity at 15, 25 and 35°C, at an operating frequency of 1 kHz as shown in Fig. 5. The curves showed a good linearity when plotted on a semi-logarithmic scale between 30 and 90%RH and negative temperature coefficients. In general, the ion transport in polyelectrolyte is strongly dependent upon the operating temperature. At higher temperature, the impedance was decreased because of the improved movement of the carrier ion. The dependency of humidity change upon temperature can be calculated from the following equations in the
humidity range of 30–90%RH as shown in Fig. 5:

\[
\text{\%RH/C = } \frac{[\text{\%RH}(a) - \text{\%RH}(A)]}{10} \text{ or } \frac{[\text{\%RH}(A) - \text{\%RH}(a')]}{10}\C
\]

The average value of temperature dependency coefficient was \(-0.5\%\text{RH}/^\circ\text{C}\) between 15 and 35\(^\circ\text{C}\). Therefore, the compensation of temperature is necessary for the application to a humidity sensor.

The impedance of the sensor was also dependent on the applied frequency in the range of 100 Hz–10 kHz between 30 and 90%RH. When the impedance dependence on the applied frequency was measured at 100 Hz, 1 kHz and 10 kHz, the impedance decreased with an increase in the applied frequency as shown in Fig. 6. However, the impedance versus relative humidity tends to deviate slightly from linearity in the high humidity region. This phenomenon is occasionally found in the cases of the polymeric humidity-sensitive polyelectrolytes.

Response time is one of the significant features for the estimation of the humidity sensors. Constant humidity bottles were used for the measurement of response time. Fig. 7 showed a response time of the humidity sensor, in which the relative humidity is plotted against time in seconds. For the 33 and 94%RH environment, the saturated solution of MgCl\(_2\cdot6\text{H}_2\text{O}\) and KNO\(_3\) solution at a temperature of 25\(^\circ\text{C}\) were adopted, respectively. The response time between 33 and 94%RH were measured by transferring the humidity sensor in equilibrium at 33%RH to the other chamber in equilibrium at 94%RH. The curves showed 55 s of response time from 33 to 94%RH for an absorption. The desorption process showed a similar results.

The sensor is occasionally dewed during the measurements at high humidity environment. When the durability against water was examined after soaking in the water for 2 h, there was no change in impedance, as shown in Fig. 8. This result indicates that the humidity-sensitive film has an excellent durability against water and dewdrops.
4. Conclusion

New epoxy resin containing quaternary ammonium salts was used as a humid-membrane for the humidity sensor. The impedance characteristics of the sensor varied from 5.4 kΩ to 1.7 MΩ between 30 and 90%RH for the humidity sensor composed of virgin GTMAC epoxy resin. The impedance of the humidity sensors consisting of copolymers of GTMAC with PPGDGE increased with a decrease in the content of GTMAC. Temperature coefficient between 15 and 35 °C is −0.5%RH/°C and the response time is 55 s between 33 and 94%RH. The humidity sensor is an applicable water-resistive humidity sensor suitable for the severe conditions.

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References


Biographies

Myoung-Seon Gong obtained a BS degree in Chemical Technology in 1978 from Seoul National University, South Korea, and a PhD degree in 1983 from Korea Advanced Institute Science and Technology, South Korea, for work on Polymer Chemistry. Since 1983, he has been employed in the Department of Chemistry, Dankook University (Cheonan, Korea) as a professor. His main field of current scientific interest is thermally stable polymers, humidity sensors and ion conducting polymers.

Chil-Won Lee is a chemistry student at Dankook University. He received a BS degree in Chemistry from Dankook University (Cheonan), Korea, in 1998. He expects to receive his MS degree with Polymeric Humidity Sensors and Materials. His interest includes electronic sensor and their application.

Hee-Woo Rhee received his BS degree in Chemical Engineering from Seoul National University, South Korea, in 1978 and PhD degree in Polymer Engineering from University of Connecticut, USA, in 1987. From 1980 to 1983, he was associate researcher in Korea Institute of Science and Technology (KIST). From 1987 to 1993, he was senior researcher scientist in KIST. Since 1993, he has been with Department of Chemical Engineering at Sogang University, South Korea, where he is an associate professor. His research interests are in area of low-k materials for Cu-chip, electroluminescence, LCD, LPB and conducting polymer materials.