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Humidity sensor composed of a microporous film of polyethylene-graft-poly-(2-acrylamido-2-methylpropane sulfonate)

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SUMMARY

Inside a microporous polyethylene film, 2-acrylamido-2-methylpropane sulfonic acid was graft polymerized by ultraviolet irradiation. A humidity sensor was fabricated by depositing gold electrodes on both sides of the grafted film. The impedance was measured as a function of humidity for the acid and alkali salts of sulfonate. The sensor has long term stability and is resistant to water.

INTRODUCTION

In recent years, there is an increasing demand for electrical humidity sensors. Since Dunmore (DUNMORE 1938) investigated the humidity sensor that utilized a polymer film containing LiCl, various types of hydrophilic polymers have been used for humidity sensors (KINJO et al. 1983, SADAOKA et al. 1984, 1986a, 1986b, SAKAI et al. 1984a, 1984b, 1986, 1987). When the hydrophilic polymers absorb water vapor, the conductivity of the polymers increases. However, in order to make humidity sensors that use hydrophilic polymers, we must solve one problem, that is, the polymers should neither dissolve in water nor swell with water at high humidities.

Copolymerization with a hydrophobic polymer is one of the methods to make a hydrophilic polymer insoluble in water (KINJO et al. 1983, TAKAOKA et al. 1983). Hijikigawa et al. have reported a humidity sensor made of polystyrene sulfonate crosslinked with N,N-methylene bisacrylamide (HIJIKIGAWA et al. 1983). We have developed a water resistant humidity sensor by simultaneous crosslinking and quaternizing of polyvinylpyridine with 1,4-dibromobutane (SAKAI et al. 1987).

Graft polymerization is also a promising method to make a water resistant humidity sensor. We have prepared the polytetrafluoroethylene-graft-polystyrene sulfonate (SAKAI et al. 1986) and the polytetrafluoroethylene-graft-quaternized polyvinylpyridine (SAKAI et al. 1987) as the materials for humidity sensors. These materials proved to be excellent polymers for humidity sensors, since they are insoluble in water and their a.c. impedance is highly dependent on humidity. In the present study, we have synthesized a graft copolymer of another combination of trunk and branch polymers using ultraviolet irradiation in place of γ-rays. In order to make homogeneously grafted films, microporous polyethylene film was chosen as the trunk polymer in which 2-acrylamido-2-methyl propane sulfonic acid(AMPS) was grafted. The a.c. impedance of this grafted film was measured as a function of relative humidity. The properties of the alkali salts of the graft film were compared with that of the original acid formed film.

EXPERIMENTAL

The microporous polyethylene film was HIPORE 2000 produced by Asahi Kasei Kogyo Co. Ltd. The thickness and the porosity was 100 μm and 70%, respectively. The average and maximum pore diameter of this film was 0.15 μm and 0.4 μm, respectively.

2-acrylamido-2-methylpropane sulfonic acid(Nitto Kagaku Kogyo Co. Ltd.) and benzophenone (Wako Pure Chemical Industries, Ltd.) were used without further purification.

HIPORE film was impregnated with benzophenone by immersing the films overnight in methanol solution containing 10 wt% benzophenone. The amout of benzophenone in the film was estimated gravimetrically to be 30-40%. The films were put in glass tubes along with 15% aqueous solution of AMPS monomer and then degassed by repeated freeze-thaw cycles. The sealed tubes were irradiated with a high pressure mercury lamp(500W) at room temperature. After a given time, the films were washed with a large excess of methanol to remove the homopolymer and benzophene and then dried under vacuum. The grafting ratio was calculated by dividing the increase in weight of the film by the weight of the original film. Some of the grafted films were neutralized with an aqueous solution of lithium hydroxide, sodium hydroxide or potassium hydroxide and then washed with water.

Sandwich type sensors were fabricated by vacuum depositing the gold electrodes(4x4mm) on both sides of the films. The sensor was fixed in a vessel in which the humidity and temperature were controlled (Shinyei SRH-1R). The impedance of the sensor was measured with an LCZ meter (Yokogawa Hewlett Packard 4276A and 4277A).

RESULTS AND DISCUSSION

The impedance was measured as a function of humidity with the films of various grafting ratios. One example of impedance dependence on humidity for a grafted film is shown in Fig.1. The impedance decreased four or five orders of magnitude as the relative humidity increased from 10 to 90%. In Fig.2, the impedance was plotted against the graft ratio at various relative humidities. The figure shows that at all humidities the impedance decreased with an increase in grafting ratio.

The sulfonic acid of the poly AMPS branch of the graft polymer was neutralized to form alkali salts. Their impedance were compared at various humidities in Fig.3. The impedance is low in the order of H<K<Na<Li. This order is the same as the case of PTFE-graft-polystyrenesulfonate (SAKAI 1986).

Response curves of conductance for the rapid change of humidity with these alkali and acid forms of the graft film were obtained. The humidity was changed as follows: 30% → 60% → 90% → 60% → 30% as shown in Fig.4 and 5. The response time is the shortest for the acid type (less than 2 minutes),

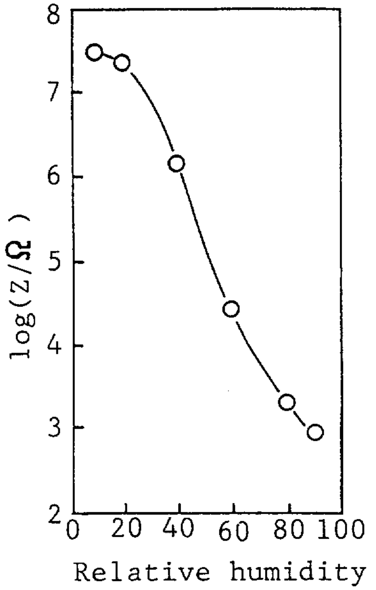

Fig. 1: Impedance dependence on humidity for PTFE-graft-poly AMPS film. Grafting ratio is 0.315.

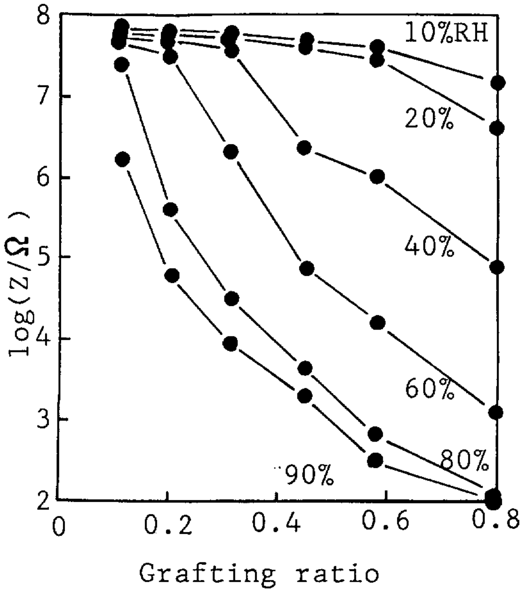

Fig. 2: Plot of the logarithm of Impedance against the grafting ratio at various humidities.

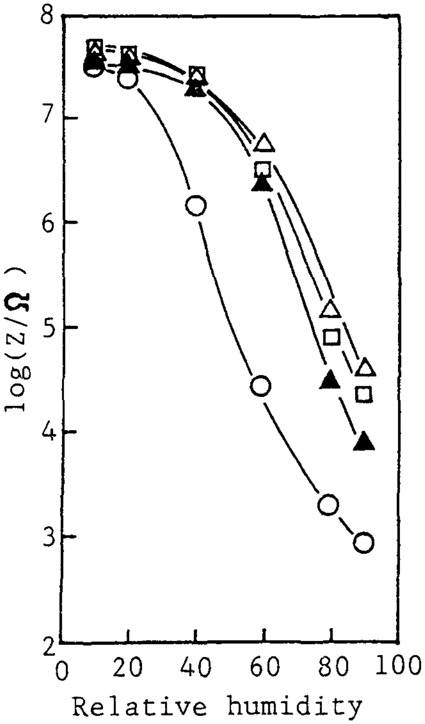

Fig. 3: Impedance dependence on humidity for PTFE-graft-poly AMPS alkali salts. Grafting ratio is 0.315.
(○) acid form,
(△) Li salt,
(□) Na salt,
(▲) K salt.

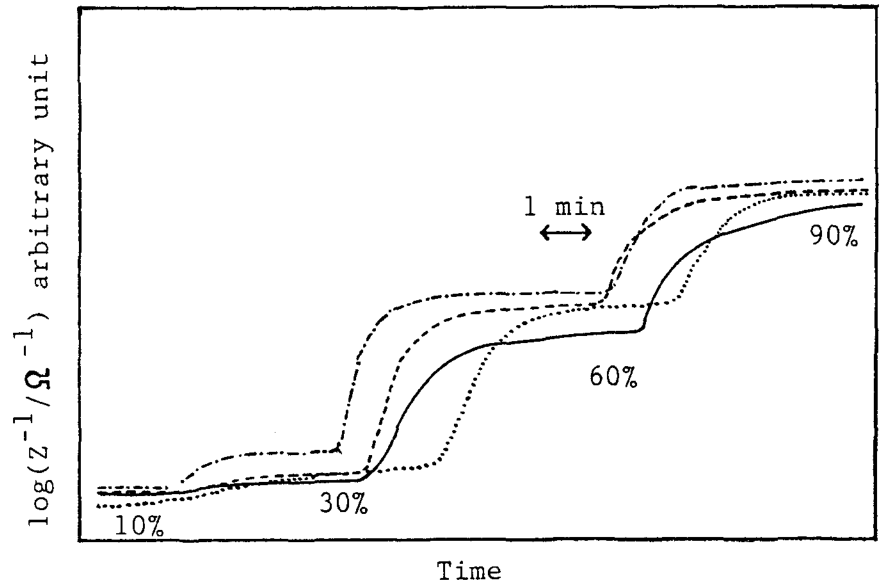

Fig. 4: Response curve for an abrupt increase in humidity. Grafting ratio is 0.315.
(·····) acid form, (——) Li salt, (---) Na salt, (—·—) K salt.

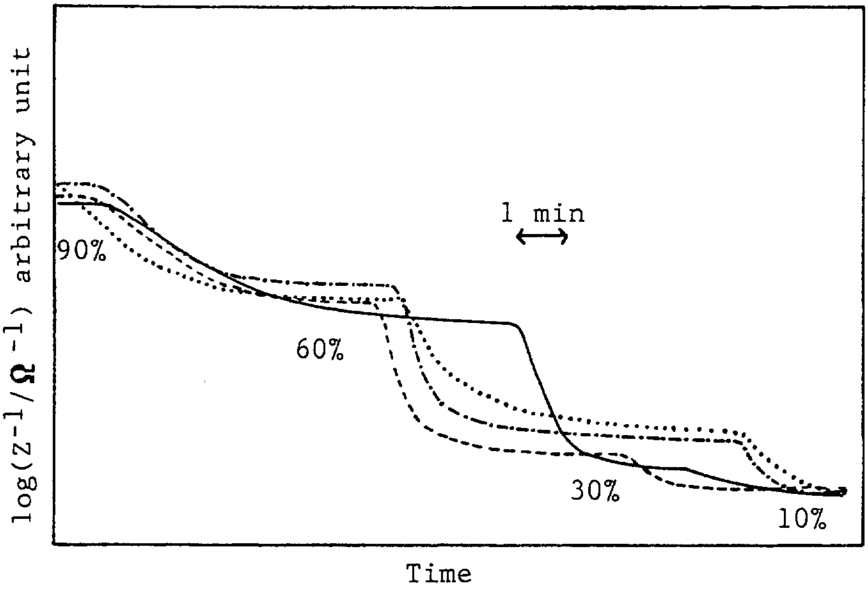

Fig. 5: Response curve for an abrupt decrease in humidity. (······) acid form, (——) Li salt, (– – –) Na salt, (—·—) K salt.

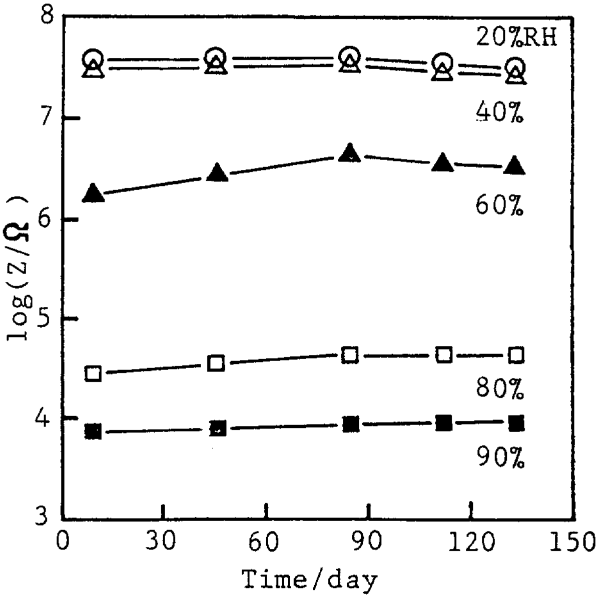

Fig. 6: Long term stability test for PTFE-graft-poly AMPS K salt.

followed by the K salt. Li and Na salts have almost the same response time.

Long-term stability was also measured. The result was plotted in Fig.6. This figure shows that appreciable change in the characteristics of the sensor was not observed even after 120 days.

In conclusion, graft copolymerization of hydrophilic polymers in a microporous polyethylene film is an excellent method to prepare a humidity sensor which is durable in a high humidity atmosphere and has a long term stability and relatively short response time. This sensor is washable with water or solvents if it is contaminated with substances which are soluble in water or other solvents.

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