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Humidity sensor using microporous film of polyethylene-graft-poly-(2-hydroxy-3-methacryloxypropyl trimethyl-ammonium chloride)

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An hydrophilic monomer, 2-hydroxy-3-methacryloxypropyl trimethylammonium chloride, was graft-polymerized in a microporous polyethylene film using three different initiation methods, that is, with benzyl peroxide, pre-U.V. irradiation and mutual photo-initiation. Humidity dependence of the impedance was measured for the grafted microporous polyethylene films. Among the three graft polymers, the one prepared by pre photo-irradiation seems to have the most homogeneously grafted layer. The impedance increases as the grafting percentage increases except in the low grafting percentage region. The response time for the abrupt change of humidity becomes longer as the grafting percentage increases. The activation energy for conductivity has a maximum at 40% relative humidity in the plot of activation energy against humidity.

1. Introduction

In recent years, there has been an increasing demand for electrical humidity sensors applicable to consumer products, air conditioning systems, and medical and industrial equipments.

Since Dunmore [1] has first investigated an electrical detection method for humidity using LiCl, many kinds of humidity sensitive polymeric materials were developed [2–12]. Solid polyelectrolytes can be used as humidity sensors since their electrical conductivity increases when they absorb water. However, polyelectrolytes are generally soluble in water and therefore conventional humidity sensors made from polyelectrolytes are disadvantageous against water and dew drops. Hijikigawa *et al.* [2] have reported a water resistant thin film humidity sensor made from polystyrene sulphonate by crosslinking with N,N′-methylene bisacrylamide. A water resistant humidity sensor was also developed by crosslinking polyvinylpyridine with dibromobutane by us [12]. We have also succeeded in making a water resistant humidity sensor by the heterogeneous grafting of hydrophilic branches on a hydrophobic backbone (polytetrafluoroethylene) by γ-irradiation [11]. This paper deals with the grafting of 2-hydroxy-3-methacryloxypropyl trimethylammonium chloride (HMPTAC) monomer on porous polyethylene film in aqueous medium by U.V. irradiation or catalytic initiation. Gold electrodes were vacuum deposited on the resulting graft copolymers and their characteristics as humidity sensors were studied. Surface type and sandwich type sensors were made and their properties were compared. Sandwich type sensors were advantageous in view of protecting the sensors from the dust, cigarette smoke and other impurities.

2. Experimental procedures

2.1. Materials

The microporous polyethylene film was Hipore 2000 (Asahi Kasei Kogyo Co., Ltd, Yuraku-cho, Tokyo). The thickness and porosity is 100 μm and 70%, respectively. The average and maximum pore diameter of this film is 0.15 μm and 0.4 μm, respectively. HMPTAC monomer was supplied by Shinyei Co., Ltd. and was used without further purification. Benzoyl peroxide (Wako Chemicals Co., Ltd, Dosho-machi, Osaka, Japan) was recrystallized with methanol from a chloroform solution. Benzophenone (Wako Chemicals Co., Ltd) was used without further purification.

2.2. Catalytic graft polymerization

Hipore PE film was immersed overnight in an acetone solution containing 0.5 wt % of benzoyl peroxide, and then dried under reduced pressure at room temperature. The films were put in the pyrex tubes along with 20% aqueous solution of HMPTAC. The tubes were degassed by freeze-thaw cycles. The reactions were carried out at 85 $\pm$ 0.1° C in a thermostat bath. At various reaction times, the reaction tubes were taken out and the samples were washed with methanol and acetone to remove the homopolymer and the unreacted initiator respectively. The samples were dried and weighed. The grafting percentage is expressed by $(W_m - W_0)/W_0 \times 100$, where W_m and W_0 is the weight of the grafted film and the initial weight of the film, respectively.

2.3. Graft polymerization by mutual photo-irradiation

Hipore PE film was immersed overnight in methanol

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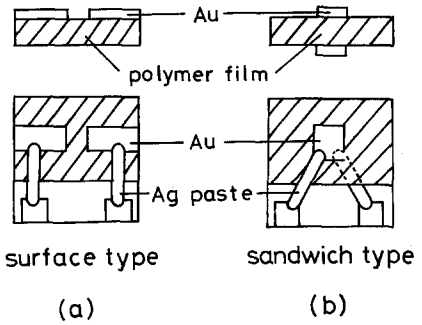

Figure 1 Structure of the sensor. (a) Surface type, (b) Sandwich type.

solution containing 10 wt % of benzophenone and then dried under reduced pressure at room temperature. The amount of impregnated benzophenone on the film was 30–40%. The film was put into the reaction tubes along with 20% aqueous solution of HMPTAC. The tube was degassed and irradiated with an 500 W high pressure mercury lamp. The irradiated samples were washed with methanol to remove benzophenone and homopolymer.

2.4. Graft polymerization by pre-irradiation with ultra-violet light

Hipore PE film was irradiated in air with a 500 W high pressure mercury lamp at room temperature for 10 h. The film was rotated during irradiation. Then, the film was put in a glass tube along with a 20% methanol solution of HMPTAC, degassed and sealed. The ampule was heated at 70° C for a given period, then the film was washed with methanol.

2.5. Measurements

Surface type sensors were made by vacuum depositing the gold electrodes on the surface of the grafted PE film. The distance between electrodes was 40 μm. The film was fixed on a glass substrate and the leading wires were connected with silver paste. The structure of the sensor is illustrated in Fig. 1a. Sandwich type sensors were made by vacuum depositing the gold electrodes (4 × 4 mm) on both sides of grafted PE

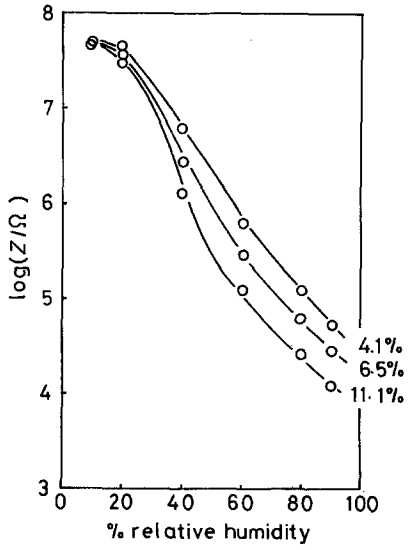

Figure 2 Plot of logarithm of impedance as a function of humidity for the surface type sensor. The grafting percentage of the films are 4.1, 6.5 and 11.1.

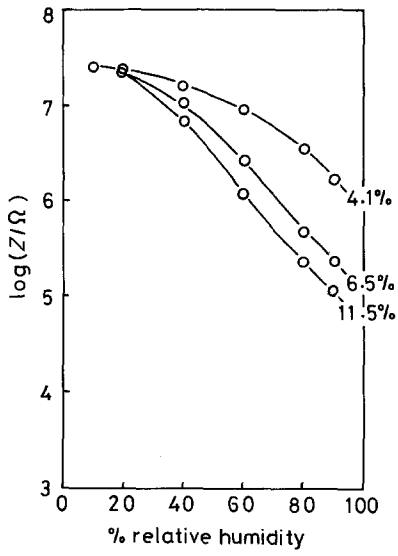

Figure 3 Plot of logarithm of impedance as a function of humidity for the sandwich type sensor. The grafted films are the same as in Figure 2.

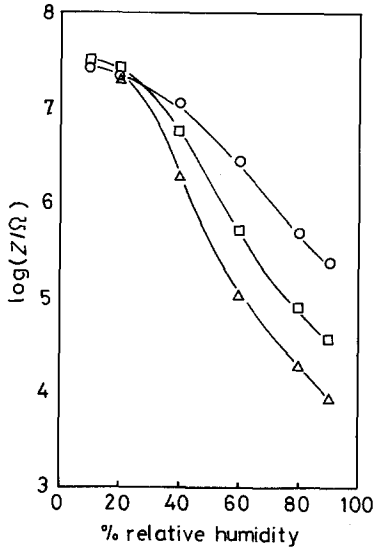

Figure 4 Comparison of the impedance of the films prepared by the three different methods. (○) Catalytic initiation, (△) pre-irradiation with U.V. light, (□) mutual photo-irradiation.

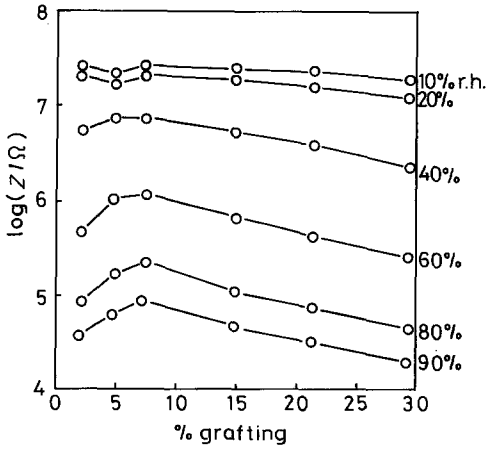

Figure 5 Plot of impedance at various humidities against the grafting percentage. The films were grafted by mutual photo-irradiation.

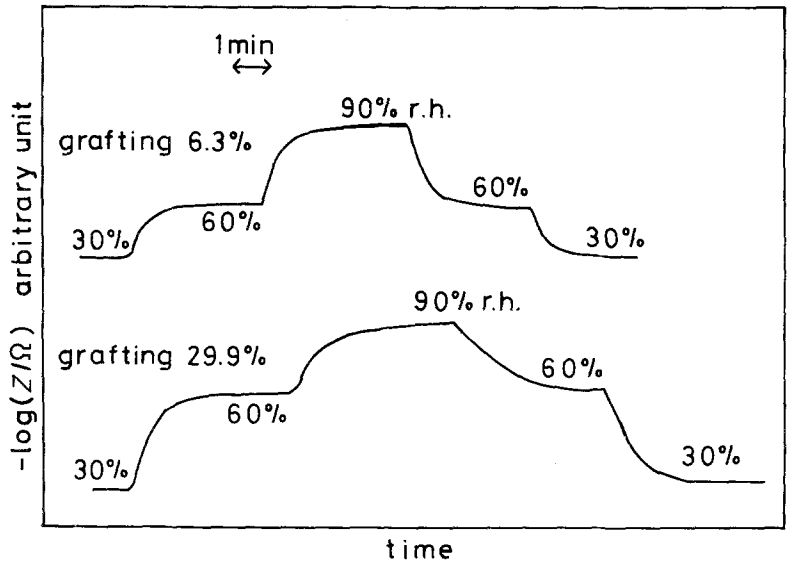

Figure 6 Response curve for abrupt change of humidity. The films were grafted by mutual photo-irradiation.

film (Fig. 1b). The device was fixed in a vessel in which the humidity and temperature were controlled (Shinyei, Kyomachi, Kobe, Japan, SRH-1R). The impedance of the sensor was measured with an LCZ meter (Yokogawa Hewlett Packard, Takaido-higashi, Suginami, Tokyo, 4276A and 4277A).

3. Results and discussion

Three kinds of grafted films were prepared by catalytic polymerization. Their grafting percentages were 4.1, 6.5 and 11.1. Both surface type and sandwich type sensors were fabricated with these films. The impedance was measured at various humidities and the results are plotted in Figs 2 and 3. In both types of sensor, the impedance decreased as the relative humidity increased. The impedance also depends on the grafting percentage. The higher the grafting percentage, the lower the impedance.

Impedance of the sandwich type sensor also depends on the method of graft polymerization. In Fig. 4, the impedance was plotted for the three films which have almost the same grafting percentage but prepared by the different methods. The film prepared by pre-irradiation has the lowest impedance, while the film prepared by catalytic polymerization has the highest impedance. This difference of impedance comes from the difference of degree of inhomogeneity in the grafted film. Usually the grafted layer proceeds from both surfaces toward the inside of the film. When the grafted layer is completed at the middle of the film, the impedance will become very low. Consequently, the impedance seems to be a measure of homogeneity of the grafted layer inside the film.

The humidity dependence of impedance was measured for the films prepared by the mutual graft polymerization in various irradiation times. The impedance was plotted against the grafting percentage. As shown in Fig. 5, the impedance decreased as the grafting percentage increased except in the low grafting percentage region.

The grafting percentage also affects the response time. As shown in Fig. 6, when the humidity was abruptly changed, the film having a 29.9% grafting percentage showed a longer response time than that of 6.3%. The films having higher grafting percentages have a denser and deeper distribution of the hydrophilic sites inside the film, so that it will take a longer time for water molecules to be sorbed and desorbed in the film.

Impedance was measured at frequencies in the range of 100 to 1 MHz and temperatures (30 to 45° C). The complex impedance was plotted, as in Fig. 7. The value of parallel resistance R_p was determined by extrapolating the semicircle to the real axis. An equivalent circuit of the parallel combination of the resistance R_p and the capacitance C_p was assumed for the present system. From the Arrhenius plots of R_p, the activation energy for R_p was determined. The

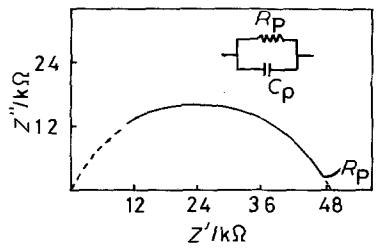

Figure 7 An example of complex impedance plot.

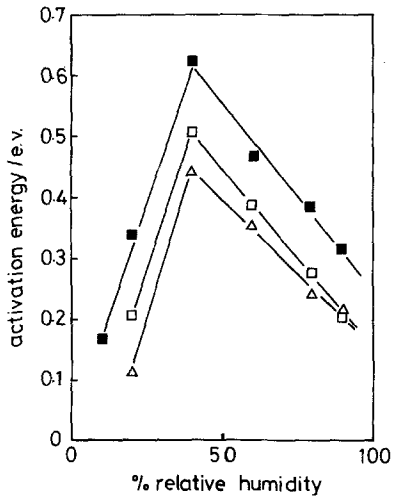

Figure 8 Plot of activation energy for R_p against relative humidity. (■) grafting percentage is 29.2% by mutual photo-irradiation, (□) 6.3% by mutual photo-irradiation, (△) 6.6% by pre-irradiation.

obtained activation energy was plotted against the relative humidity in Fig. 8. There is a maximum around 40% relative humidity. At a lower humidity region, the carrier ion Cl^- obtains more hydrating water molecules as the humidity increases, so that the mobility decreased with an increase in humidity. This may be the cause of the increment of activation energy below 40% relative humidity. Above 40%, the amount of sorbed water is sufficient to promote the transfer of hydrated Cl^- ion. In addition, the protons from the water also can become the carrier at high humidity.

In conclusion, the microporous polyethylene film can be grafted with 2-hydroxy-3-methacryloxypropyl trimethylammonium chloride, which has a hydrophilic quaternary ammonium group. The grafted film can be fabricated to form a humidity sensor. The electrical properties as a humidity sensor depend on the method of graft polymerization.

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