A humidity sensor using graft copolymer with polyelectrolyte branches

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2-Hydroxy-3-methacryloxypropyl trimethylammonium chloride was grafted on to the pore wall of microporous polyethylene film by a γ-ray pre-irradiation method. A humidity sensor was prepared by depositing gold electrodes on both surfaces of the grafted film. Complex impedance measurements were carried out at various humidities. From the complex impedance analysis, the values of parallel resistance and parallel capacitance were estimated. The parallel resistance decreased as the humidity increased, while the parallel capacitance remained constant. The parallel resistance also decreased as the grafting ratio increased. The value of parallel resistance depends on the amount of sorbed water in the film. The sensor is stable for a long time in ordinary atmospheric conditions. It is even stable in water for more than 2 h. The sensor prepared by γ-ray pre-irradiation at 9.0×10^4 R h^{-1} for 4 h was heat-resistant up to 130°C.

(Keywords: humidity sensor; graft film; pre-irradiation; microporous polyethylene film; 2-hydroxy-3-methacryloxypropyl trimethylammonium chloride; impedance)

INTRODUCTION

In recent years, there has been an increasing interest in humidity sensors in various fields such as air-conditioning systems, medical and industrial equipment, etc.

Since Dunmore's initial invention of an electrical humidity sensor using LiCl dispersed in poly(vinyl acetate)[1], many kinds of humidity-sensitive polymeric materials have been developed[2–13]. Polyelectrolytes can be promising materials for humidity detection because their electrical conductivity varies when they sorb moisture. However, as polyelectrolytes are soluble in water, they cannot be used at high humidities because they may swell or deform irreversibly and a reversible change of conductivity cannot be expected. In order to overcome this shortcoming, Hijikigawa *et al.*[2] have proposed the crosslinking of poly(styrene sulphonate) with *N,N'*-methylenebisacrylamide. On the other hand, we have prepared a humidity sensor by simultaneously crosslinking and quaternizing poly(vinylpyridine) with α,ω-dichloro- or α,ω-dibromoalkanes[12,13]. Graft copolymerization is another excellent method of preparing water-insoluble materials for humidity sensors. In a previous report[11], poly(styrene sulphonate) was grafted on to the surface of a poly(tetrafluoroethylene) film. Quaternized poly(vinylpyridine) was also grafted on to the surface of a poly(tetrafluoroethylene) film[12]. Both of the grafted films were completely insoluble in water and absorbed a small amount of moisture which lowered the surface electrical resistivity. The disadvantage of these graft films is that it takes a certain amount of time for the water vapour to penetrate into or out of the grafted layer, and, as a result, the response time for the detection of humidity change is long.

In order to make the response faster, a microporous polyethylene film was used as a trunk polymer. The surface of the pore wall was grafted with 2-hydroxy-methacryloxypropyl trimethylammonium chloride (HMPTAC) by a γ-ray post-polymerization method. The characteristics as a humidity sensor were also investigated.

EXPERIMENTAL

The microporous polyethylene (PE) film was Hipore 2000 (Asahi Chemical Industry Co. Ltd). The thickness and porosity are 100 μm and 70%, respectively. The average and maximum pore diameters of this film are 0.15 and 0.4 μm, respectively. A 50% aqueous solution of HMPTAC monomer (Nippon Oil and Fats Co. Ltd) was used without further purification.

The microporous PE film was irradiated in air with γ-rays at an intensity of 9.0×10^4 R h^{-1}. The irradiation time was between 1 and 4 h. The irradiated PE film and the solution of HMPTAC diluted with the same volume of methanol were degassed by freeze–thaw cycles in a Pyrex tube. The sealed tube was heated to 85°C in a thermostatted bath. After various reaction times, the grafted films were thoroughly rinsed with methanol to remove the homopolymer and unreacted monomer. The films were dried and weighed. The grafting ratio is expressed by:

$$[(W - W_0)/W_0] \times 100$$

where W and W_0 are the weight of the grafted film and the initial weight of the film, respectively.

A sandwich-type humidity sensor was made by vacuum deposition of gold electrodes (4 × 4 mm) on both sides of the grafted PE film. In order to compare the properties of the grafted film with those of the HMPTAC homopolymer, a thin film of HMPTAC homopolymer was cast on a ceramic substrate having interdigitated gold electrodes. The sensors were fixed in a vessel in

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which the humidity and the temperature were controlled (Shinyei SRH-1R). The humidity was varied by controlling the mixing ratio of dry air and wet air. The a.c. impedance of the sensor at various humidities was measured with an LCZ meter (Yokogawa Hewlett–Packard 4276A and 4277A) in the frequency range of 100 Hz to 1 MHz. The sorption isotherm was obtained gravimetrically.

RESULTS AND DISCUSSION

The a.c. impedance was measured at different frequencies and various humidities for the graft films. The results are plotted in *Figure 1*. As the humidity increased, the impedance Z decreased exponentially. A pronounced sensitivity to humidity was observed at the lower frequencies. Complex impedance measurements were also carried out with the graft films of various grafting ratios.

From the complex impedance plot shown in *Figure 2*, the value of the parallel resistance R_p was determined by extrapolating the semicircle to the real axis. This was based on the assumption of an equivalent circuit comprising the parallel combination of resistance R_p and capacitance C_p. The value of C_p was estimated from the relation:

$$2\pi f^* C_p R_p = 1$$

where f^* is the frequency at which the imaginary part Z'' of the complex impedance takes its maximum value. It was found that the values of the parallel capacitance C_p are almost constant for all films over the whole humidity range. As a result, it was found that the change in impedance with humidity is due to change in the parallel resistance.

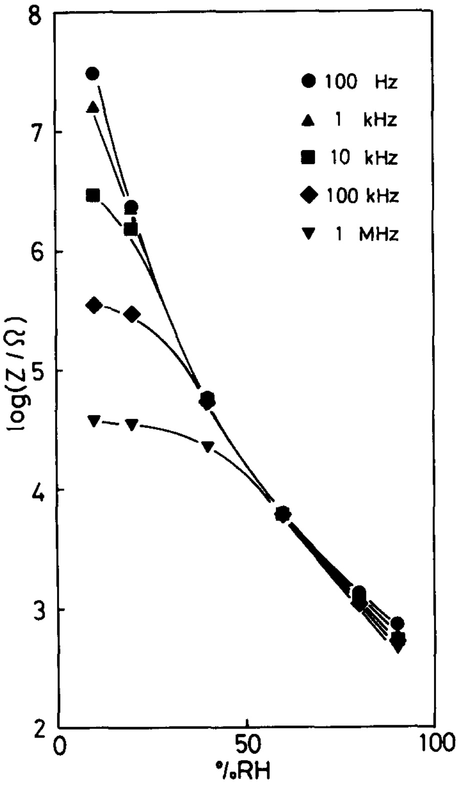

Figure 1 Plot of the logarithm of impedance against the relative humidity measured at various frequencies

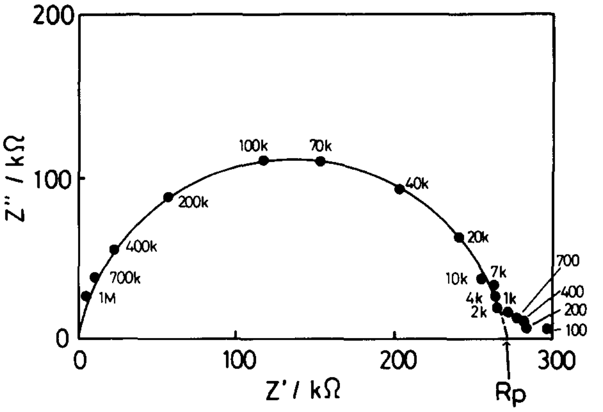

Figure 2 An example of the complex impedance plot for a film of 11% grafting ratio measured at 40% relative humidity at 30°C. The number at each point denotes the frequency

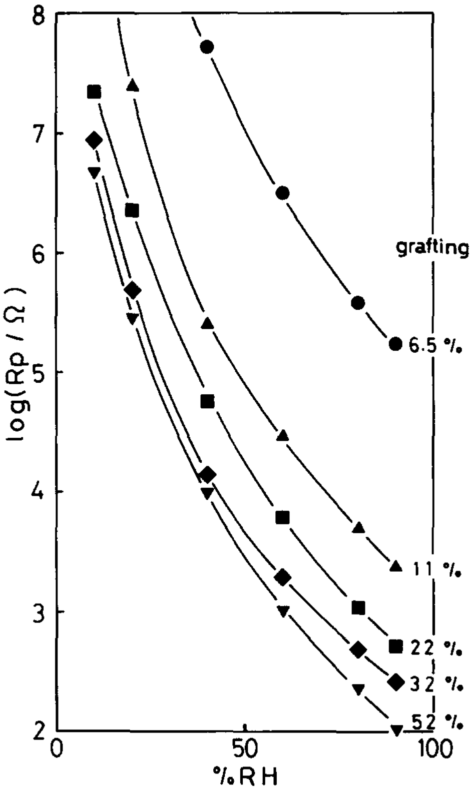

Figure 3 Plot of the logarithm of R_p against the relative humidity for films of various grafting ratio

In *Figure 3*, R_p is plotted against the relative humidity for samples of various grafting ratios. The humidity dependence of R_p was pronounced for films of higher grafting ratios. In *Figure 4*, R_p is replotted against the grafting ratio at various humidities. A pronounced sensitivity to humidity appeared at a grafting ratio between 6 and 11%. In order to elucidate the cause of the decrease in R_p with humidity, a sorption isotherm was obtained for films of various grafting ratio. The sorption curves are plotted in *Figure 5*. As can be expected, more water was sorbed in the highly grafted films than in the films of low grafting ratio.

From the sorption isotherm measurements, the amount of water sorbed in a small piece of grafted film between the deposited gold electrodes ($0.4 \times 0.4 \times 0.01$ cm^3)

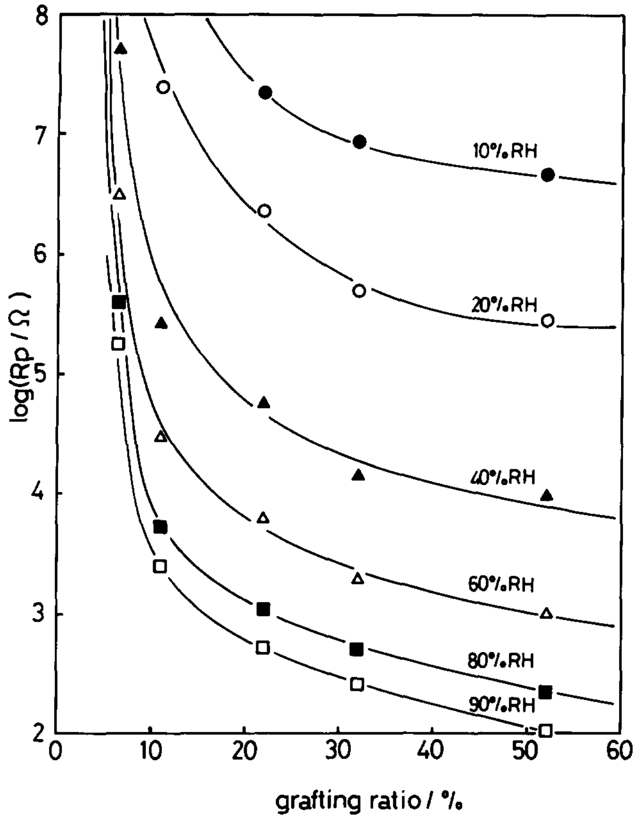

Figure 4 Plot of the logarithm of R_p against the grafting ratio

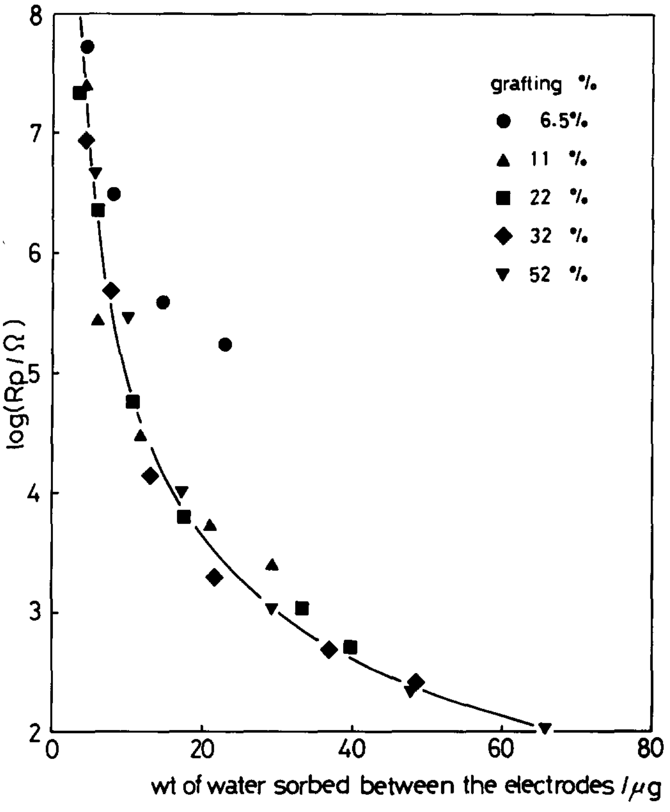

Figure 6 Plot of the logarithm of R_p against the amount of sorbed water between the electrodes

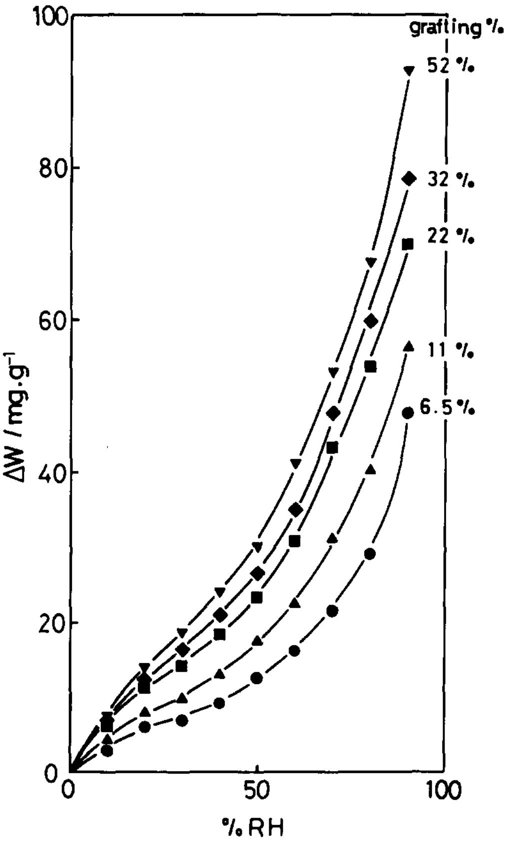

Figure 5 Plot of the sorbed water per gram of film against the relative humidity

was estimated for films of various grafting ratio and humidity. In *Figure 6*, the value of R_p is plotted against the amount of water sorbed between the electrodes. All the plots, except for that for very low grafting ratio, lie on the same line irrespective of the grafting ratio. *Figure 6* indicates that the resistance R_p is determined by the amount of sorbed water.

Three aspects of the stability of the present humidity sensor were tested, that is stability through long-term usage, durability when immersed in water and stability on heating.

The impedance as a function of humidity was measured at certain intervals during long-term storage for as long as 150 days in an ambient atmosphere. The results show that the sensor is quite stable when stored in an ordinary atmosphere.

After the sensors were kept in water for a given time and then dried in air, the impedance was measured at each humidity. These procedures were repeated several times during 16 h. The same test was carried out with a HMPTAC homopolymer film coated on an alumina substrate having interdigitated gold electrodes. It was found that the grafted film sensor is stable even when placed in water for more than 2 h, while the homopolymer film sensor on the alumina substrate is not.

The sensor was heated for 1 h at a given temperature and cooled to room temperature. Then the impedance was measured as a function of humidity. The above procedures were repeated, raising the heating temperature in each run. The grafted film sensor prepared by the pre-irradiation method with a total dose of 9.0×10^4 R could be used only up to 80°C, while the film sensor prepared with a dose of 3.6×10^5 R was usable up to

130°C. The HMPTAC homopolymer film sensor itself is stable up to 180°C. It is well known that when polyethylene is crosslinked by γ-ray irradiation, the melting point rises. The difference in heat stability between the two film sensors described above is due to the difference in the degree of crosslinking of the trunk polymer (PE) when they were pre-irradiated with γ-ray.

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