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Optical humidity sensing characteristics of composite thin films of hydrolysed nafion-dye with a terminal *N*-phenyl group

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By using composite films of hydrolysed nafion and dyes having cyanine or triphenyl structures and with a terminal *N*-phenyl group, an optical humidity sensor has been fabricated. In the reflection mode, the optical intensity of the absorption peaks which depend on the used dyes decreases with relative humidity. The raising and recovery times are less than 1 min. In dry air, the alkyl amine group reacted with SO_3H of hydrolysed nafion and formed a proton additive. Sorption of water molecules induces the deprotonation of the quaternized ammonium group.

1. Introduction

The development of optical fibres has led to a new technology. A great number of optical fibre sensors has been devised for the measurement of physical parameters such as temperature and position. Recently, an optical fibre system has become of interest in a technique to detect gas species in the atmosphere [1–5]. Chemical sensors based on optical fibres offer several advantages, i.e. the sensors are electrically safe and the signals do not fluctuate due to electrical disturbances. For the film with dyes, optical characteristics such as absorption or emission bands can be controlled using special materials and selective influence by the polarity and acidity (basicity) of the objective gas molecules. In addition, it is easy to fabricate a multi-component detecting sensor with some different dyes each having different absorption or emission peaks. In this case, each sensing material can be formed on each element of a combined fibre and detection may proceed by using a multichannel spectrum analyser. Recently, we have proposed that a hydrolysed nafion thin film with dyes is applicable to an optical humidity sensor [6, 7]. By using dyes with terminal *N*-phenyl groups (auxochrome) and diphenyl carbonium ions or cyanine groups (chromophore), humidity can be detected as a change in the optical intensity in visible light. Illumination with ultraviolet light is inferior for the optical sensor with dyes, because most dyes are chemically unstable when exposed to ultraviolet light.

In this paper, the effects of heat pretreatment on optical properties as a function of humidity have been examined for a composite film of hydrolysed nafion with dyes used as a new optical humidity sensor operable in the visible light range.

2. Experimental procedure

Hydrolysed nafion perfluorinated ion-exchange powder (equivalent weight 1100 g) dissolved in a mixture of lower aliphatic alcohols and 10% water (5 wt % solution) was obtained. Thin films of hydrolysed nafion about 5 μm thick were prepared on alumina substrates and on a quartz oscillating element with gold electrodes by dipping and/or spin coating. Composite films with dyes were prepared from a water–alcohol solution of hydrolysed nafion and dye. Crystal violet (C.I. Basic Violet 3,42555), malachite green (C.I. Basic Green 4,42000), ethyl violet (C.I. Basic Violet 4,42600), aizen cathilon pink FGH (C.I. Basic Red 13,5-1950), aizen cathilon red 6BH (C.I. Basic Violet 7,5-1972), aizen cathilon brilliant red 4GH (C.I. Basic Red 14,5-1951) and aizen cathilon yellow 3GLH (C.I.

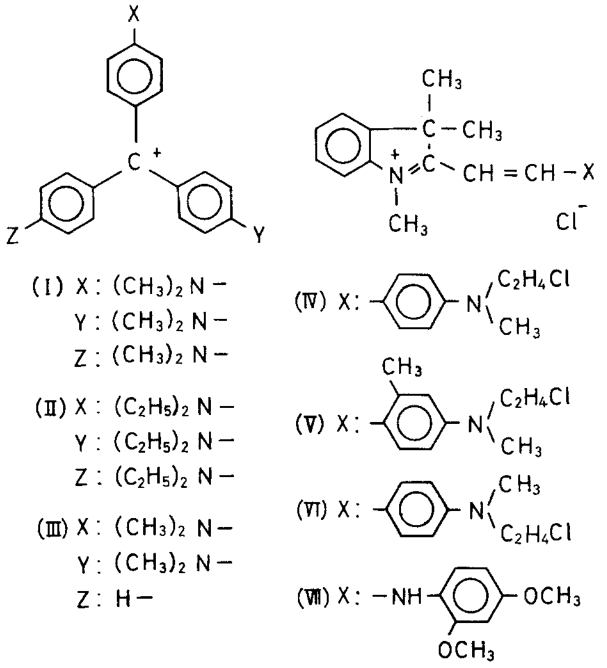

Figure 1 Molecular structures of the dyes. (I) crystal violet, (II) ethyl violet, (III) malachite green, (IV) aizen cathilon pink FGH, (V) aizen cathilon red 6BH, (VI) aizen cathilon brilliant red 4GH, (VII) aizen cathilon yellow 3GLH.

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Basic Yellow 11,5-1918) were used. The molecular structures are illustrated in Fig. 1. Only in yellow 3GLH, is the terminal *N*-phenyl group absent. The films were annealed at certain temperatures in air for 1 h. The humidity in the measuring chamber was controlled by mixing synthesized air and humid air prepared by bubbling air through the water. The water sorption isotherms were measured using a quartz oscillating element with gold electrodes. In this case, the mass of the thin film and sorbed water can be detected as changes in oscillating frequency. The optical characteristics were measured using a multichannel photodetector (Otsuka Electronics, model 1100). A Y-type quartz fibre was fixed just in front of the sensor. Light from a D_2/I_2 lamp was aimed at the fibre and directed to the sensor, and the reflected and modulated light was collected by the same optical fibre. All of the measurements were carried out at 30 °C. The film structure and morphology were examined by standard X-ray diffraction and scanning electron microscopy.

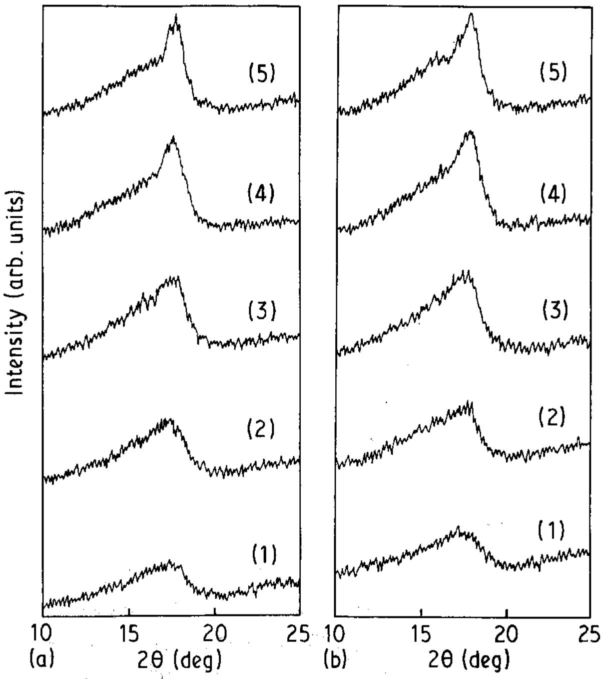

Figure 2 XRD patterns for annealed hydrolysed nafion film in air (a) before and (b) after exposure to humid air for 3 days. Annealing temperature: (1) room temperature (2) 60 °C, (3) 100 °C, (4) 150 °C, (5) 200 °C.

3. Results and discussion

3.1. Annealing effects on water sorption ability of hydrolysed nafion thin film with and without dyes

First, the structure changes of the hydrolysed nafion film singly by the heat pretreatments were examined by wide-angle X-ray diffraction. For the as-prepared film, a diffraction peak was observed at 17.5 in 2θ as shown in Fig. 2a and b. Annealing up to 120 °C did not induce any apparent changes in the diffraction pattern. The height of this peak was increased and the width was narrowed by treatment at 150 °C or more. The peak height and width were uninfluenced by exposure to humid air for 3 days at room temperature. It seems that the crystallinity of the film is enhanced by heat pretreatment at 150 °C or more and is uninfluenced by exposure to humid air. The morphology in nafion has been studied using a wide- and small-angle X-ray diffractometer and it was noted that the crystallinity decreased somewhat upon hydrolysis while the hydrolysed polymer was still partly crystalline [8]. The used hydrolysed nafion film prepared from solution assumed an amorphous phase and crystallization proceeded with heat treatment. Grot [8] has reported that the liquid obtained is not a true solution and that the hydrolysed nafion forms micelles surrounded by ionic groups. In addition, if the solvent is evaporated hot or if the cast film is heated to 100–120 °C, the dispersed fluorocarbon phase will, to some extent, fuse together and the film will become insoluble. Furthermore, it is believed that heating at 120 °C induces the formation of micelles surrounded by a hydrophobic phase. The film becomes insoluble in water when annealed at 100 °C or more, while no distinct changes in the morphology were observed using a scanning electron microscope. Furthermore, the amount of residual water was determined by thermogravimetry. In this case, the measurements were conducted in dry air. The desorption of water was achieved by heating to 220 °C and the decomposition was started at 290 °C during which the heating rate was 5 °C min^{-1}. From the results of differential scanning calorimetry, it was observed that the first desorption of water was achieved at about 100 °C and the second at about 200 °C. In Table I, the total weight loss caused by the water desorption in dry air is summarized for the films before and after exposure to

TABLE I Water loss in dry air on annealing up to 200 °C of nafion and composite

Annealing temperature (°C)	Water loss (wt %)			
	Nafion	Nafion[a]	CV composite	MG composite
Room temperature	3.72	3.38(4.49)	2.91	2.83
60	3.30	2.09(4.57)	3.31	2.03
100		3.76		
120	2.77	3.10(3.19)	2.78	1.93
150	2.58	2.38(2.72)	2.05	2.47
200	1.43	2.04(2.69)		

[a] After exposure to humid air for 3 days.

humid air for 3 days. For the film before exposure to humid air, the amount of the desorbed water in the region of room temperature to 100 °C decreased monotonically with increasing annealing temperature, while that in the region 100–200 °C was scarcely influenced (1–1.6 wt %). The exposure to humid air induced increments of the sorbed water in dry air. The amount of residual water in dry air after exposure to humid air for 3 days for the annealed film at 120 °C or more, was less than that for the as-prepared film. The observed decrements in sorption ability with heat treatment may be correlated to the crystallinity of film. The heat treatment also affects the water sorption ability. In Fig. 3, the water sorption isotherms are shown. In each case, the measurements were carried out from 0–80% RH (relative humidity) and reversed. The results observed in the desorption process have been omitted for simplicity, because there were no serious differences between the results measured under humidification and desiccation processes. For the film held at room temperature, the water-sorption behaviour may be represented by the Brunauer–Emmett–Teller (BET) type formula. In addition, an about six additional water molecules per one polar group (–SO_3H) of hydrolysed nafion were sorbed at 80% RH and two or three water molecules per one polar group were already sorbed in the dry atmosphere at room temperature, as noted in Table I. The heat pretreatments of the film induced a decrease in the water content, while no apparent hysteresis in the sorption isotherms was observed. Steady values were achieved within 5 min after setting the humidity in the chamber. The heat treatment at 100 °C or more results in a decrease in the sorption ability. The sorption isotherm observed for the film annealed at 120 °C for 1 h was nearly consistent with that for the film annealed for 12 h at the same temperature. Hydrolysed nafion is an excellent polyelectrolyte and is stable at 120 °C or more in air, and so the decrements in water sorption ability are not caused by decomposition of the polymer. In particular, for the annealed films, no peeling from the substrate was observed, while the as-coated film was easily dissolved in water. The influence of immersion in water on the water sorption isotherm for the film annealed at 120 °C was examined, and the solubility of the film was observed to be extremely depressed. Immersion in water for more than 10 min at room temperature induced an increase in hydrophilicity but this enhancement of hydrophilicity was completely removed by the reheat treatment at 120 °C. Fig. 4 shows the water sorption isotherms of the composite with 0.022 wt % crystal violet. The doping of crystal violet induced a decrease in the water sorption ability while the BET type isotherms were also observed. Even for the composite films, the water sorption ability was depressed by the heat pretreatment. Furthermore, the doping of dyes did not contribute to the origin of hysteresis in the water sorption isotherm. Because the solubility of the dyes was greatly depressed by the formation of the composite, the doped dye was stabilized by the formation of a new salt with the polar group of hydrolysed nafion. The results of the composite with 0.022 wt % malachite green are also indicated in Fig. 5. The sorption ability of water is depressed by the doping of malachite green, and the heat treatments decrease the sorption ability.

3.2. Optical characteristics of the composite

It is well-known that crystal violet and malachite

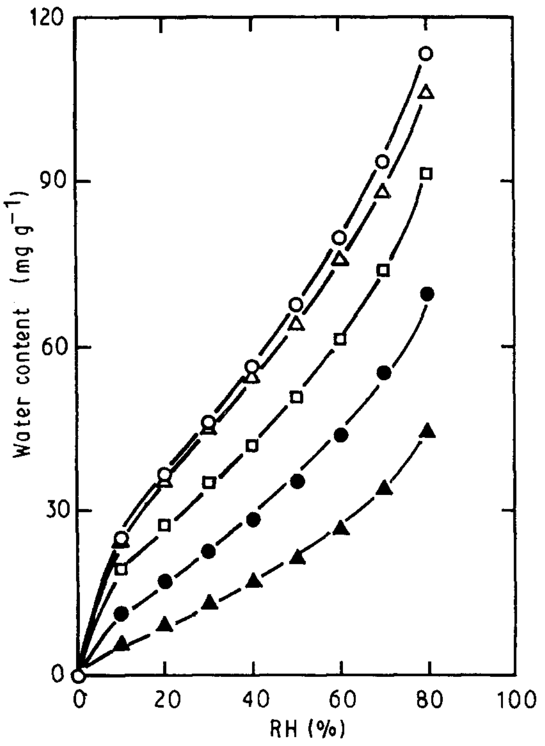

Figure 3 Water-sorption isotherms for the annealed hydrolysed nafion film. Annealing temperature: (○) room temperature, (△) 60 °C, (□) 120 °C, (●) 150 °C, (▲) 200 °C.

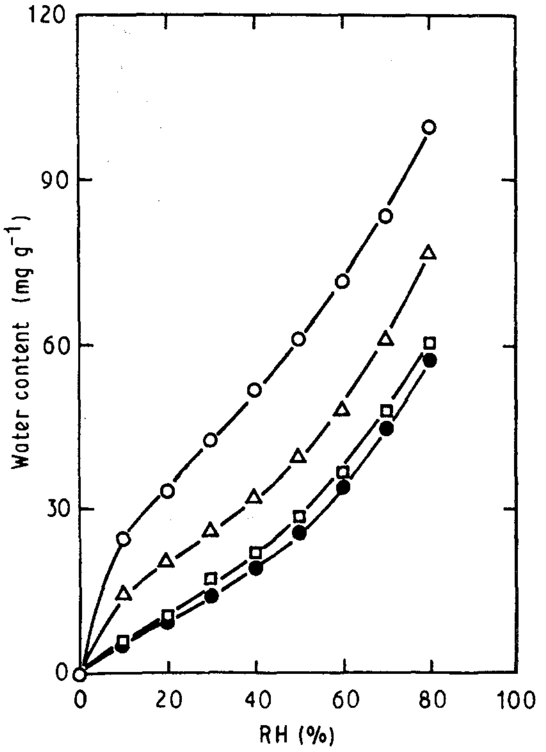

Figure 4 Water-sorption isotherms for the annealed composite with crystal violet. Annealing temperature: (○) room temperature, (△) 60 °C, (□) 120 °C, (●) 150 °C.

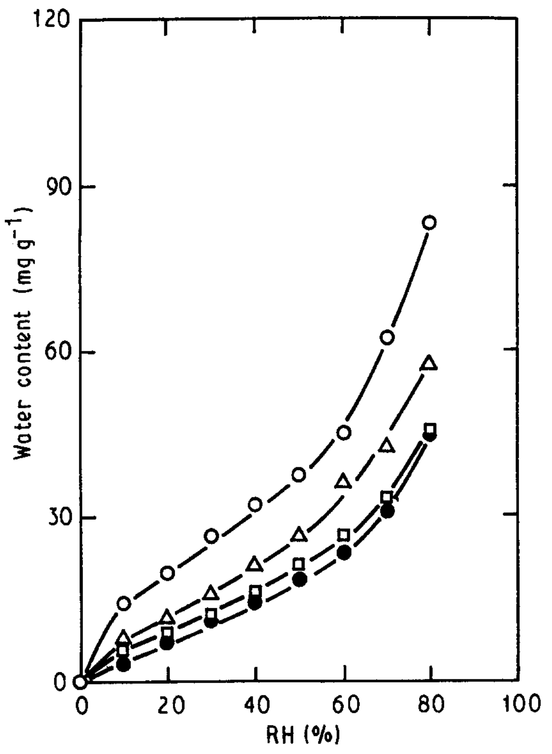

Figure 5 Water sorption isotherms for the annealed composite with malachite green. Annealing temperature: (○) room temperature, (△) 60 °C, (□) 120 °C, (●) 150 °C.

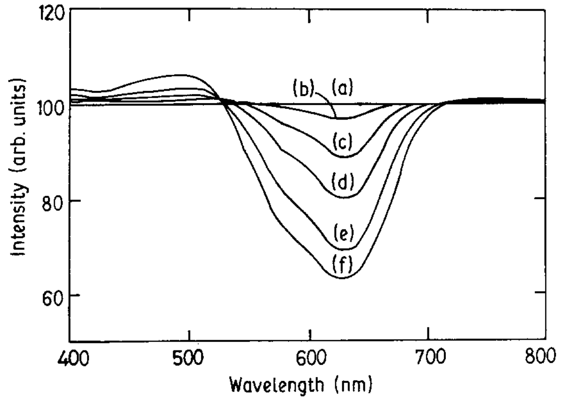

Figure 6 Humidity dependence of the spectra for the composite with crystal violet. (a) 0%, (b) 17%, (c) 29%, (d) 38%, (e) 56%, (f) 71% RH.

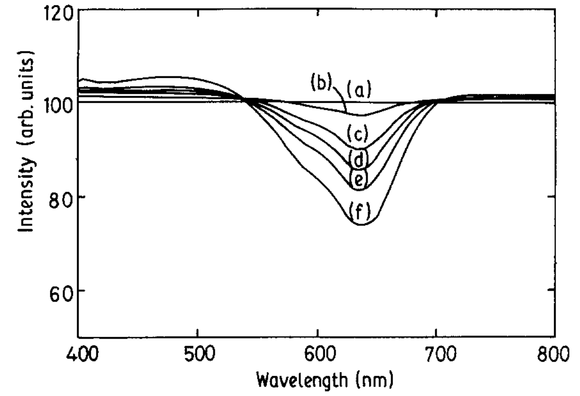

Figure 7 Humidity dependence of the spectra for the composite with ethyl violet. (a) 0%, (b) 29%, (c) 38%, (d) 56%, (e) 63%, (f) 83% RH.

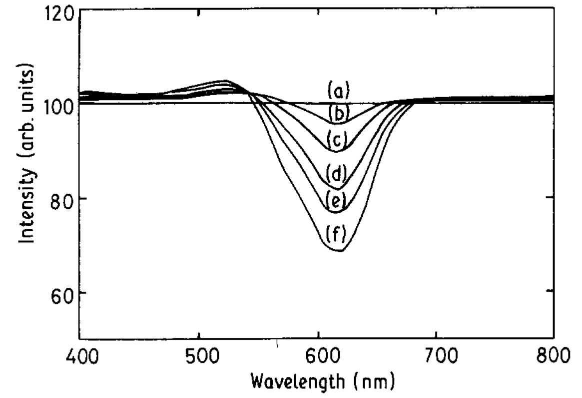

Figure 8 Humidity dependence of the spectra for the composite with malachite green. (a) 0%, (b) 29%, (c) 38%, (d) 56%, (e) 63%, (f) 83% RH.

green undergo solvatochromism in which the colour is very sensitive to the acidity of protons. For the composite film, the dye was entrapped as a result of the formation of a new ionic salt and the solubility of the dye in water was extremely depressed as mentioned. Crystal violet and malachite green are intensely coloured violet and green in neutral water, respectively, and in the entrapped dyes on hydrolysed nafion; both dyes are slightly yellowish in dry air. It is expected that the acid strength of the solid acid is weakened by the sorption of water molecules and this change induces a colour change in the dyes caused by the change in the molecular structure. In a dry atmosphere, the protons of sulphonic acid form a salt with two of the terminal *N*-phenyl groups of crystal violet (yellowish), and the sorbed water induces a change of the quaternized ammonium to alkyl amine, i.e. deprotonation. In this case, the degree of the deprotonation is accelerated with increasing water content. A similar reaction is also expected with the composite with malachite green. The spectra in the reflection mode of the composites were examined as a function of the relative humidity. The signals were measured as the ratio of the reflected intensity to that in dry air. A reflection minimum was observed at 630 nm with a shoulder at 585 nm for crystal violet, at 535 nm with a shoulder at 590 nm for ethyl violet and at 610 nm for malachite green as shown in Figs 6–8. For crystal violet entrapped on hydrolysed nafion, the colour was changed by the sorption of water molecules from violet to green with increased humidity, and good reversibility for the humidity changes was observed. The reflectance at 630 nm decreased with increasing humidity and the reverse tendency was confirmed at 470 nm, although the former signal was more sensitive than that of the latter. In addition, a isosbestic point was observed at 525 nm for crystal violet, at 540 nm for ethyl violet and at 540 nm for malachite green.

These observed results convinced us that the reaction caused by sorption of water is in equilibration for the composite with triphenyl dyes. The differences (hysteresis) in the intensity observed in the humidification and desiccation processes are very small. The sensitivity to humidity decreased with an increase in the heat pretreatment temperature for the composite

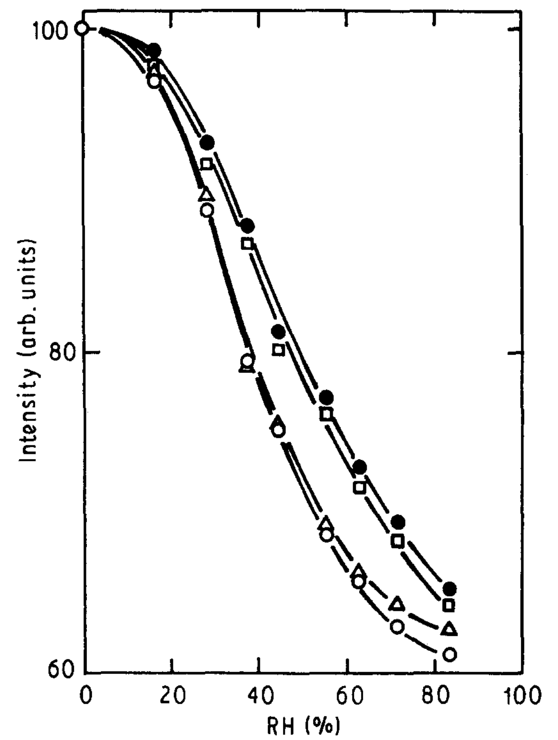

Figure 9 Humidity dependence of the intensity at 630 nm for the composite with crystal violet. Annealing temperature: (○) room temperature, (△) 60 °C, (□) 120 °C, (●) 150 °C.

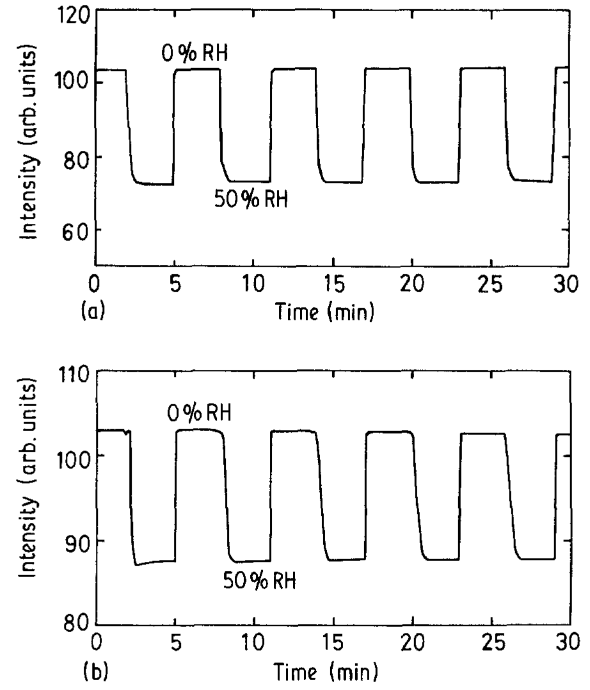

Figure 11 Response to the changes of humidity from 0–50% RH and inversed for the composites with (a) crystal violet or (b) malachite green.

films used, as shown in Figs 9 and 10. While we failed to determine a quantitative correlation between the optical intensity and the water content, the optical intensity may be correlated to the water content, and the water sorption ability is influenced by phase transitions of hydrolysed nafion such as crystallization and fusion. For a more detailed discussion, it is necessary to measure simultaneously the optical characteristics and the absolute value of the water content using the same composite film formed on a quartz oscillating element. Furthermore, the response times to humidity changes from 0–50% RH and the inverse, were examined. The raising and recovery times are within 1 min and 10 s, respectively, and are reversible as shown in Fig. 11 for the composites with crystal violet or malachite green. The sensitivity to humidity was decreased by the heat pretreatment as mentioned. For the composite with ethyl violet, especially, the sensitivity was completely lost with heating at 100 °C or more, or by holding for 1 day in a laboratory atmosphere, while the other composites maintained the sensitivity after the same treatments. The long term stability for the composite with crystal violet or malachite green was superior to that of the composite with ethyl violet, and the stability was also affected by the ambient conditions. The de-activated composites with crystal violet or malachite green indicated the colour of the dye alone, but the colour of the de-activated composite with ethyl violet was completely different from the original one, i.e. colourless.

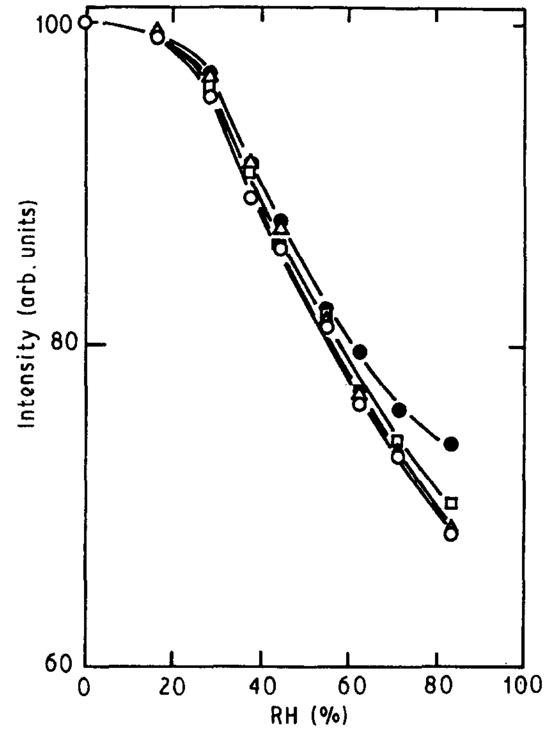

Figure 10 Humidity dependence of the intensity at 617 nm for the composite with malachite green. Annealing temperature: (○) room temperature, (△) 60 °C, (□) 120 °C, (●) 150 °C.

For the composite films with cyanine dyes, the optical intensity at 540, 550 and 530 nm for pink FGH, red 6BH and brilliant red 4GH, respectively, decreased with increasing humidity, while that at 500 nm for yellow 3GLH increases slightly. The spectra for the composites with pink FGH or brilliant red 4GH are shown in Figs 12 and 13 as a function of humidity. Yellow 3LH is a dye with a cyanine structure but without a terminal *N*-phenyl group as the auxochrome. The other three cyanine dyes have an alkyl amine group which easily forms a proton additive for the composite in dry air. While an isobestic

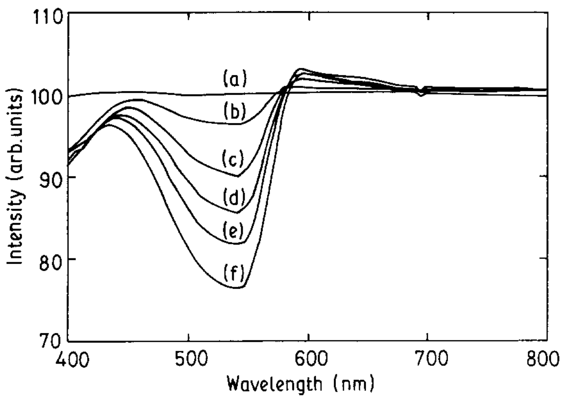

Figure 12 Humidity dependence of the spectra for the composite with pink FGH annealed at 60 °C. (a) 0%, (b) 17%, (c) 38%, (d) 56%, (e) 63%, (f) 71% RH.

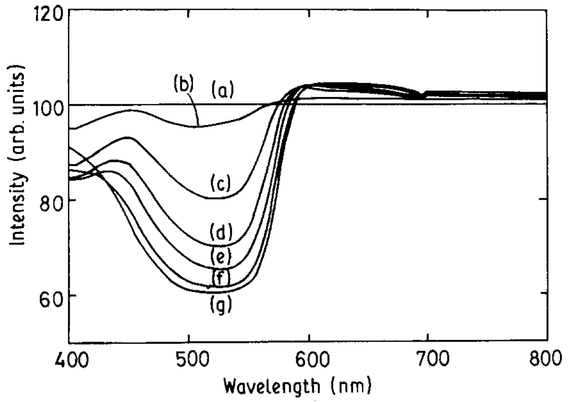

Figure 13 Humidity dependence of the spectra for the composite with brilliant red 4GH annealed at 60 °C. (a) 0%, (b) 17%, (c) 29%, (d) 38%, (e) 44%, (f) 63%, (g) 83% RH.

point was noted in the observed spectra for the composite with triphenyl dyes, no well-defined isosbestic points were observed for the composites with cyanine dyes.

For all the composite films examined, a deterioration of the humidity sensitivity with time was observed in which the degree of deterioration was dependent on the dye structure. The coloration in the long test period may be caused by the isolation of the dye, i.e. the formation of alkyl amine from the quarternized form (proton additive) because the spectrum of the deteriorated composite film was almost the same as that of the dye alone, except for the composite with ethyl violet as mentioned. The long-term stability of the sensitivity was improved by using a thicker hydrolysed nafion membrane 117 of about 0.2 mm thickness, instead of the film prepared from nafion solution, although the response behaviour was inferior and some detectable hysteresis was observed. Improvements in the long-term stability with superior response behaviour are now being investigated.

The optical intensities of the absorption peaks were not changed by humidity for the composites with poly(ethylene oxide) or poly(methacrylic acid) and the cyanine or triphenyl dyes because the acidity of the polymers was considerably less than that of hydrolysed nafion. Furthermore, it was observed that the composite films of poly(ethylene oxide) with triphenyl dyes or cyanine dyes with a terminal *N*-phenyl group could be used as optical chemical sensing materials to detect some basic gases such as NH_3 and acidic gases such as HCl and HNO_3. In these cases, the sensitivity was strongly accelerated by the existence of water molecules (humidity) and was influenced by the acidity or basicity of the gas molecules.

4. Conclusion

By using hydrolysed nafion films with triphenyl or cyanine dyes with terminal *N*-phenyl groups, an optical humidity sensor was fabricated. In the reflection mode, the optical intensity of the absorption peaks which depend on the dye structure with alkyl amine groups decreased with the relative humidity. The raising and recovery times are less than 1 min. The sensitivity is influenced by the heat pretreatment. Heat treatment induced a decrement in the water-sorption ability which may be caused by crystallization and/or inversion of the micelles surrounded by ionic groups to that surrounded by the fluorocarbon chain. For all dyes used with poly(ethylene oxide) or poly(methacrylic acid), the optical intensities of the absorption peaks were not influenced by humidity, because the acidity of the polymers was considerably less than that of hydrolysed nafion, although these composites could be used as chemical sensors to detect a stench or toxic gases such as NH_3, HCl, or HNO_3.

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