JOURNAL OF MATERIALS SCIENCE 29 (1994) 883–886

Optical properties of fluorescent dye-doped-polymer thin film and its application to an optochemical sensor for quantification of atmospheric humidity

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The humidity sensor used utilized a fluorescent dye entrapped within a poly(ethylene oxide) or poly(acrylic acid) matrix. The fluorescence intensity increased strongly and linearly with increasing humidity. The wavelength of the fluorescence maximum was 525 nm for the composite with poly(acrylic acid) over the whole range of the humidity. For the poly(ethylene oxide) composite, the fluorescence maximum in the lower humidity region was about 550 nm and it shifted to lower wavelengths with an increase in humidity. In both cases, the intensity of the fluorescence increased linearly with humidity. The 90% response and recovery time for humidity changes was less than 20 s for the poly(ethylene oxide) composite, while a longer time was observed for the poly(acrylic acid) composite.

1. Introduction

In recent years, optochemical sensors have attracted attention because of their remote-analysis capability, high sensitivity and compactness. There has been an increasing interest in optical sensors to detect gas species such as humidity, ammonia, nitrogen dioxide and organic vapours in the atmosphere [1–9]. Most of the optochemical sensors are composed of a dye-dispersed polymer in which the optical intensity of the absorption or fluorescence peak depends on the chemical species and the concentration. In general, the width of absorption band is considerably broader than that of fluorescence. It is expected that optochemical sensors based on the fluorescence changes with ambient conditions are more preferable than those based on the absorption changes, since the former having a sharp sensitive band is applicable to a multichannel optochemical sensor for determinations of the many species contained in an ambient atmosphere. Methyl calcein has a high fluorescence quantum yield, and an absorption band appeared in the wavelength range 400–600 nm (the visible region). The fluorescence is observed in an acidic solution and it is deactivated in a strong basic solution. It is expected that the optical characteristic of methyl calcein entrapped within a polymer matrix is also influenced by the acidity of the matrix and by sorption of ambient gases. In particular, methyl calcein is a stable functional dye and it decomposes at 300 °C, so that it is a preferable material for a gas sensor requiring long-term stability and good reversibility.

In this work, the optical properties have been examined as functions of humidity and ammonia concentrations for methylcalcein dispersed polymer films as a fluorescence type of optochemical sensor for determination of humidity in ambient air.

2. Experimental procedure

Methyl calcein (fluorescein-di(methylene-*N*-methylglycine), disodium salt), poly(acrylic acid) (PAA, molecular weight (MW), 1 250 000) and poly(ethylene oxide) (PEO, MW 5 000 000) were used. Methyl calcein ($0.5\ \mathrm{mg\,ml^{-1}}$ for PEO, $0.182\ \mathrm{mg\,ml^{-1}}$ for PAA) and polymer ($5\ \mathrm{mg\,ml^{-1}}$ for PEO, $1.82\ \mathrm{mg\,ml^{-1}}$ for PAA) were dissolved in water. Films were formed on alumina substrates by coating with the solution and then drying. After seating the element in the chamber, the Y-type glass fibre was fixed just in front of the film. Selected light (non-monochromated light) from a D_2/I_2 lamp (400–800 nm) was guided into the fibre and directed to the film; the reflected and modulated light was collected by the same optical fibre. The collected light was analysed using a spectro multichannel photodetector (MCPD-1000, Otsuka electronics) in the region 400–800 nm. In addition, fluorescence spectra were also measured using a spectrofluoro-photometer (RF-5000, Shimazu) in the region 300–800 nm. In these cases, monochromated light was used. The water contents of the films were measured by using a quartz oscillating element as a microbalance. The amount of sorbed water was estimated from the oscillating-frequency changes of the element coated with film. All the measurements were done at 30 °C. The humidity in the chamber was controlled by mixing standard air and humid air (prepared by allowing standard air to bubble through a water phase at 30 °C). The concentration of ammonia was controlled by mixing 0.5% ammonia in air and standard air (O_2 = 21%, N_2 = 79%, CO < 1 p.p.m. (parts per million), CO_2 < 2 p.p.m., HCl < 1 p.p.m. and H_2O < 10 p.p.m.).

3. Results and discussion

3.1. Optical properties of methyl calcein in solution and entrapped within the polymer matrix

Firstly, the wavelength dependence of the excitation light on the fluorescence was examined for a methyl-calcein solution in which monochromated light was used for the excitation. The solution was yellowish and fluorescence was observed. The colour of the PEO-composite film in an ambient atmosphere was reddish orange. The PAA-composite film had a similar colour to the solution, and fluorescence was also observed. The λ_{EX} (excitation maximum wavelength) and λ_{EM} (emission maximum wavelength) were estimated to be 494 nm and 512 nm for the solution, respectively; the wavelength of λ_{EM} was uninfluenced by the wavelength of the excitation light. For the composites in an ambient atmosphere, λ_{EX} and λ_{EM} were estimated to be 502 nm and 529 nm for the PAA composite and 554 nm and 554 nm for the PEO composite, respectively. The wavelength of the fluorescence was influenced by the polymer matrix. The changes of the reflection spectrum with moisture were examined by using a multichannel spectrometer and non-monochromated light in the region 400–800 nm. The results are shown in Figs 1 and 2 for the PEO and PAA composites, respectively. In both cases, the spectrum observed for the composite in dry air was used as a reference. For the PEO composite, the optical intensity at about 545 nm was increased with increasing humidity, and the wavelength of the maximum was shifted from 550 to 540 nm. This signal was caused by the fluorescence light from methyl calcein as mentioned before. When the humidity increased to 60% relative humidity (RH) or more, the intensity of the baseline also increased with the humidity. The shifts of the baseline are attributed to the increase in net backscattering of the light. The enhancements of the fluorescence were also confirmed for the PAA composite and the wavelength of the fluorescence peak, 524 nm, remained constant for different humidity levels. Furthermore, the baseline of the spectrum also remained constant. The sensitivity to humidity changes for the PEO composite was higher than the PAA composite. At this stage, the reason for this difference cannot be clarified, since the intensity of the fluorescence emission depends on the lifetime of the excited state, the excitation coefficient etc. In Fig. 3, the response and recovery behaviour are shown for the composites. For the PEO composite, the 90% response and recovery time was less than 20 s and the time in the response when the humidity changed from 0% to 50% RH was less than in the recovery when the humidity was cut off. A longer time was observed for the PAA composite. The difference of the responsibility corresponds to that of the water-sorption kinetics. It should be noticed that the wavelength of the fluorescence peak for the PAA composite remained constant while the wavelength for the PEO composite was 550 nm in dry air and it shifted towards lower wavelength with an increase in the humidity. For the PEO composite, it is confirmed that there are small shifts of the absorption maximum towards lower wavelengths; this is related to the small shifts of the fluorescence maximum towards lower wavelengths. It has been reported that the humidification of the alkali salts (potassium- or sodium-salt types) of fluorescein linked covalently to polymers induces the shifts of the absorption peak by the hydrolysis of the alkali salts [10]. It is presumed that a part of a lactone ring is

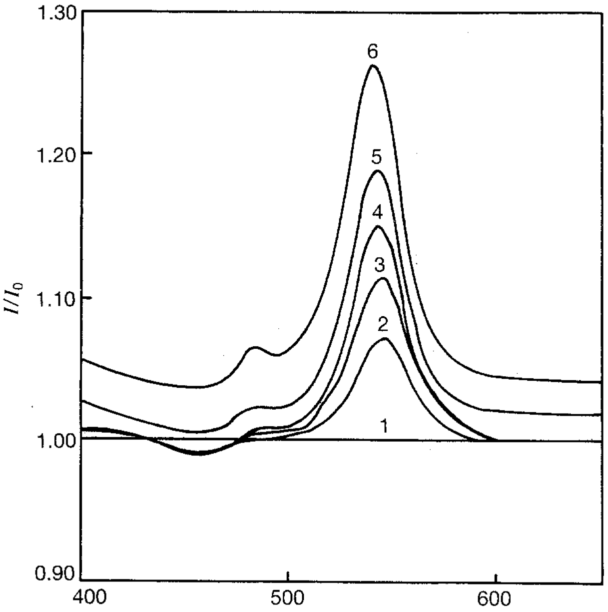

Figure 1 Spectrum changes of the PEO composite with percentage relative humidities of: (1) 0, (2) 29, (3) 44, (4) 63, (5) 71, and (6) 83%.

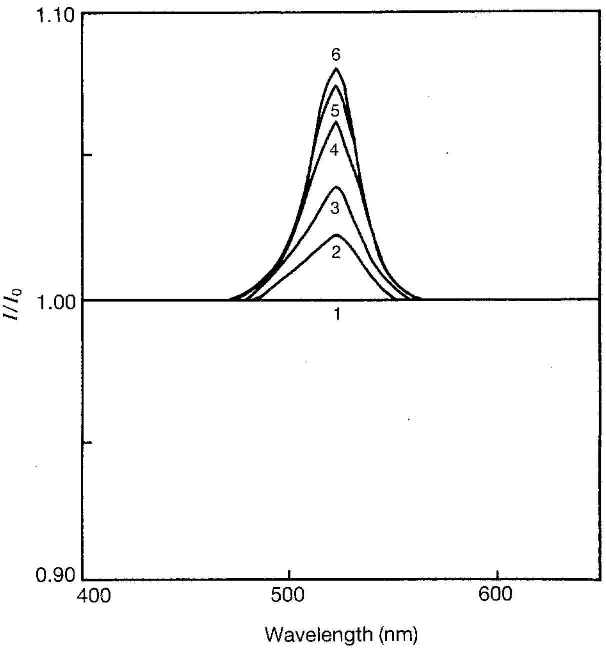

Figure 2 Spectrum changes of the PAA composite with percentage relative humidities of: (1) 0, (2) 29, (3) 38, (4) 50, (5) 63, and (6) 83%.

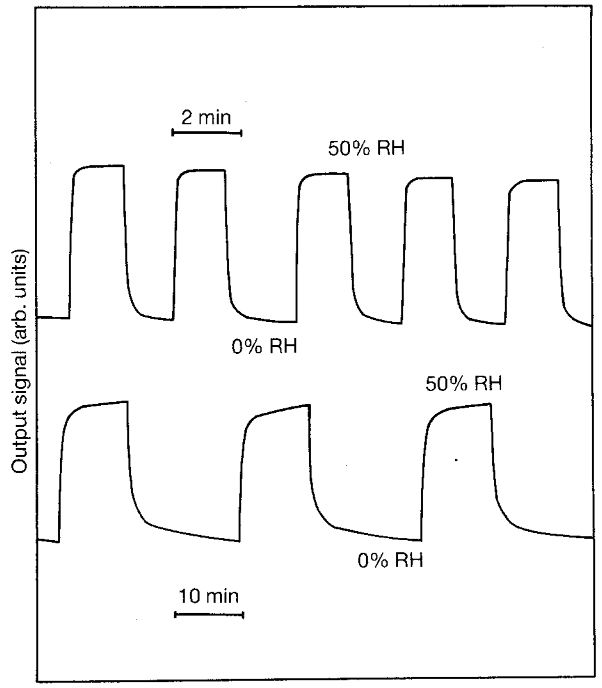

Figure 3 Response curves for the changes of humidity between 0% and 50% RH: (a) PEO composite, and (b) PAA composite.

opened and that this exists as –COONa. If hydrolysis of the alkali salt is the origin of these shifts, using a more acidic polymer matrix may depress the concentration of the sodium salts and this results in the disappearance of the shifts with humidity. The use of a perfluorinated ion exchanger, such as Nafion, having strong acidic protons was considered instead of PEO, but a good solution with both methyl calcein and Nafion could not be obtained. So, the film of methyl calcein entrapped within a PAA matrix was examined. For the composite film, it is expected that shifts of the wavelength maximum of fluorescence are depressed. As shown in Fig. 2, this expectation is clearly confirmed. Furthermore, it is suggested that the enhancements of water gain induce the enhancements in the acidity of the composite accompanying the shifts of the fluorescence maximum towards lower wavelengths. As is known, the fluorescence emission intensity depends upon two factors. One is the rate and extent of non-radiative transitions, including solvent relaxation. The other factor that affects the fluorescence intensity is the excitation efficiency. If the excitation efficiency is enhanced, fluorescence increases proportionally because more excited molecules are produced. Usually, the presence of a solvent will shorten a fluorescence lifetime and weaken the intensity. We believe that the enhancement of the absorbance of the entrapped dye is caused by the water sorption, and consequently higher-excited-state dyes are produced. This is apparently the reason that the fluorescence intensity increases with humidity.

As is known, methyl calcein has a high fluorescence quantum yield and this fluorescence is observed in acidic solutions and it is quenched in strong basic solutions. For the solid state, similar changes are also expected. In Fig. 4, the spectrum changes for the PAA composite, when the concentration of ammonia is increased at 50% RH, are shown. The intensity of the fluorescence sharply decreased with the ammonia concentration, with small shifts towards higher wavelengths. Similar spectrum changes were also confirmed in dry air, although the effect was considerably less. The decrease in the optical intensity of fluorescence with ammonia was also observed for the PEO composite, although the wavelength of the fluorescence peak almost remained constant at 540 nm (see Fig. 5). As shown, the optical intensity of the fluorescence is also very sensitive to ammonia, but the recovery time after cutting off the ammonia is very slow at 30 °C. The formation of an ammonium salt is considered to be the origin of this behaviour. When the operation temperature is raised a good reversibility may be confirmed, since the polymer and dye used are thermally stable materials and the ammonium salt is not so stable.

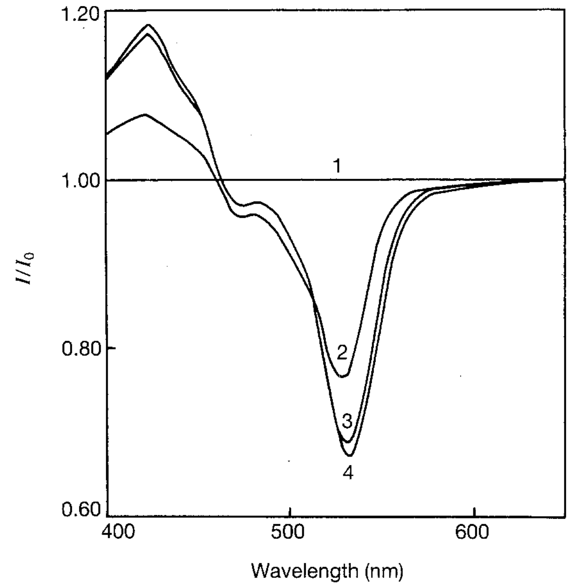

Figure 4 Spectrum changes of the PAA composite in 50% RH with the following ammonia concentrations: (1) 0, (2) 250, (3) 500, and (4) 1000 p.p.m.

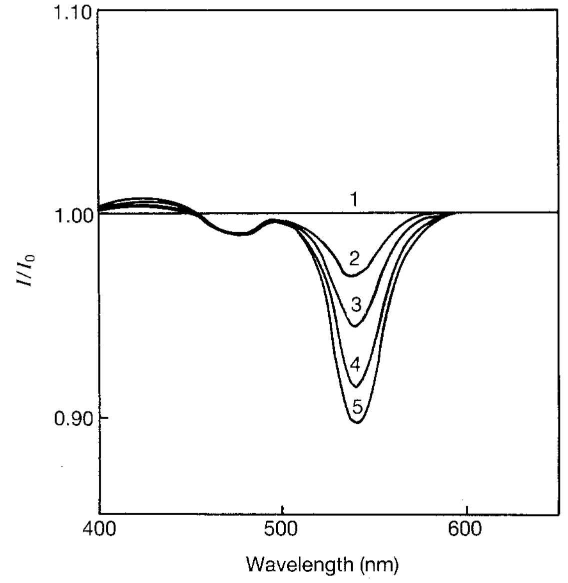

Figure 5 Spectrum changes of the PEO composite in 50% RH for the following ammonia concentrations: (1) 0, (2) 250, (3) 500, (4) 1500, and (5) 2500 p.p.m.

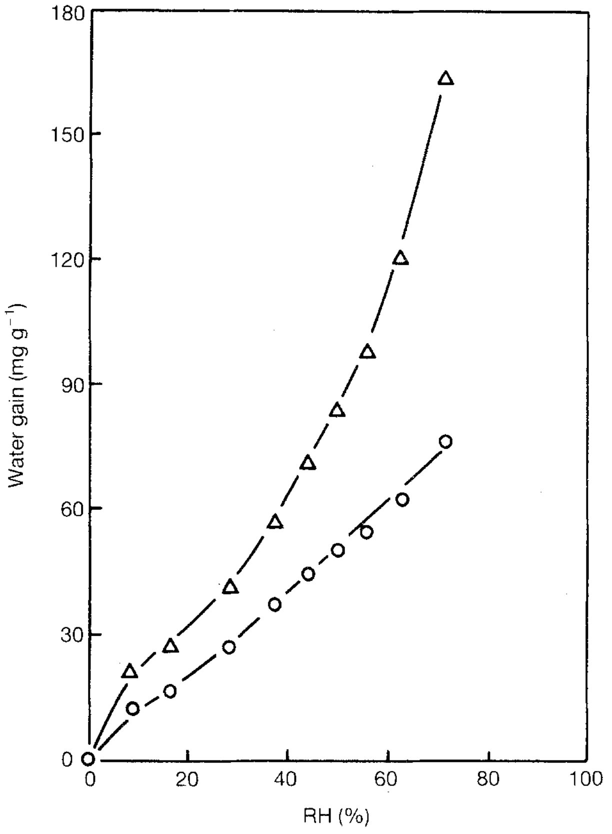

Figure 6 The humidity dependence of the water gain for the composites: (△) PAA composite, and (○) PEO composite.

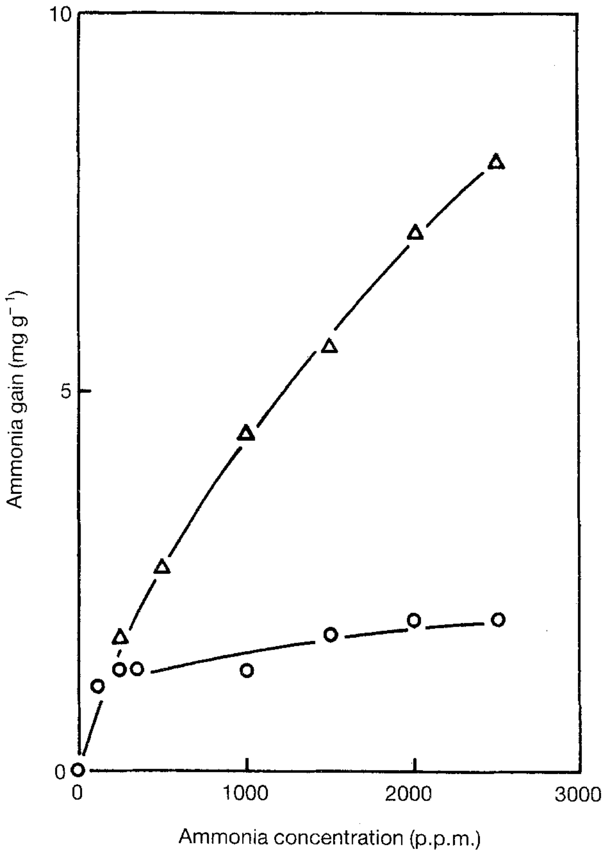

Figure 7 The concentration dependences of the ammonia gain for the PEO composite: (△) 50% RH, and (○) 0% RH.

3.2. Gas-sorption abilities of dye-dispersed films

For methylcalcein dispersed PEO film, the water gain also linearly increased with the humidity as shown in Fig. 6 and this was mostly the same as in the PEO alone; in addition, no distinct deviations of the water gain measured in humidification and in desiccation processes were detected. For the PAA composite, the water gain increased monotonically with the humidity, and the water sorption ability was considerably higher than for the PEO composite, as shown in Fig. 6. It was confirmed that the sorption rate of the PEO composite was considerably faster than that of the PAA composite. For ammonia in dry air, the gain increased sharply up to 200 p.p.m. of ammonia and then more moderately at higher concentrations for the PEO composite (Fig. 7). The measurements of ammonia gains proceeded with an increase in the ammonia concentration, since the desorption of the sorbed ammonia was very slow. This is caused by the chemical interaction between the dye and the ammonia molecules. The sorbed ammonia concentration at 2500 p.p.m. NH_3 in dry air corresponds to 0.8 molecules of ammonia per dye molecule. Humidification induced the enhancements of the ammonia gain. At 50% RH, the ammonia gain was considerably higher than in dry air, as is shown in Fig. 7. The number of the sorbed ammonia molecules at 2500 p.p.m. was estimated to be about three molecules per dye molecule. It seems that two phenolic, –OH, and an opened lactone, –COOH groups, interact with ammonia and form the salt, while the structure is not clarified. As mentioned above, after cutting off ammonia at 30 °C, the optical intensity could not be recovered to the initial value which was confirmed in ammonia-free air.

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Received 21 July 1993
and accepted 16 August 1993