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Optical Humidity Sensor Using Reichardt's Betain Dye-Polymer Composites

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By using Reichardt's betain dye dispersed in poly(methyl methacrylate) thin film, a bifunctional optical humidity sensor was fabricated. The optical intensity and the wavelength of maximum observed at around 780 nm were sensitive to the humidity. The characteristic of the dye dispersed in polymer was also influenced by the hydrogen bond acidity of the polymer matrix.

The development of optical fibres has given to new technology. A great number of optical fibre sensors have been devised for the measurement of physical parameters like temperature and displacement. There has been an increasing interest in optical sensor to detect gas species in atmosphere such as H_2O, NH_3, NO_2, organic vapour.$^{1-5)}$ Humidity is a most important factor to evaluate the atmosphere. Many kinds of humidity sensors (capacitive, resistive, mechanical, galvanic, or optical type) have been proposed as well known. Chemical sensors based on optical fibre offer several advantages, i.e., the sensors are electrically safe, their signals are not influenced by electrical disturbances, and the separation of sensing element and actuators is easy. Most of optical humidity sensor is composed of polymer thin film with dye in which the intensity of the absorption or fluorescence peak is a function of the humidity. These sensors must be operated in the shorter wavelength range below 600 nm. It is desired that the sensor can be operated in a longer wavelength range to prevent the photochemical degradation of the sensor materials on exposure to light. It is well known that the absorption peak of Reichardt's dye dissolved in non-polar solvent such as hexane, toluene, benzene is observed at around 850 nm and the coexisting of polar solvent such as water, alcohol, acetone induces the blue shift. Recently, Paley et al.$^{6)}$ have reported that the wavelength of absorption peak of Reichardt's dye dispersed in polymer is sensitive to the acidity of the polymer and the water content. It seems that the Reichardt's dye-polymer composites are useful materials to fabricate a chemical sensor having selectivity to detect ambient gases. The wavelength of absorption peak is a function of hydrogen bond acidity or polarity of sorbed molecule and the optical intensity is a function of the concentration of that in which the sensor acts as a bifunctional detector. Furthermore, the selectivity of vapour sorption may be controlled by the polymer species.

We propose in this Letter a new type of humidity sensor composed of Reichardt's dye doped polymer thin film which can be operated in the longer wavelength range (700 nm - 800 nm) and at room temperature.

Reichardt's betain(2,6-diphenyl-4-(2,4,6-triphenylpyridino)phenolate, poly(methyl methacrylate)(PMMA), poly(ethylene oxide)(PEO) and poly-(vinylpyrrolidone)(PVP) were used. For thin film preparation, Reichardt's dye was dissolved in acetone-water mixture with PEO (dye:PEO=20:5 in weight), in acetone with PMMA (dye:PMMA=0.55:5 in weight) and in methanol with PVP (dye:PVP=0.55:5 in weight). The films were prepared on the alumina substrate and the quartz oscillator by coating. After setted the element in the chamber, the Y-type quartz fibre was fixed just in front of the film. Light from D_2/I_2 lamp 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 analyzed by using a spectro multi-channel photodetector in the region of 400 - 1100 nm. The water sorption isotherm was measured by using a quartz oscillator as a microbalance for the composite film formed on the element. All of the measurements were proceeded at 30 °C. The humidity in the chamber was controlled by mixing of dry air and humid air prepared by allowing dry air to bubble through a water phase at 30 °C. The steady-state in the humidity was obtained within 20 s in the humidification and desiccation processes.

In Fig. 1, the reflection spectra in 45 %RH (relative humidity) atmosphere for the composite films are shown. The reflection spectrum of the alumina substrate was used as the reference. The position of the absorptin band of Reichardt's dye in polymer was influenced by the polymer matrix. The wavelength of the peak observed in 45 %RH air was 600 nm, 630 nm and 600 nm for PMMA, PEO and PVP composite, respectively. It is clear that the peaks appeared in a shorter wavelength region than that of the dye dissolved in non-polar solvent. For the composite with PMMA, the absorption peak observed at 720 nm in a dry air was shifted to 600 nm by the humidification to 80 %RH, while the absorption peak of Reichardt's dye dissolved in water appeares at 453 nm. It seems that the reason for the absorption peak of the polymer composites appeared at the longer wavelength range in a humid atmosphere is that the hydrogen bond acidity of the sorbed water is less than that of the liquid water.

The water sorption isotherm for the PMMA composite was measured by the quartz oscillating microbalance method. At 60 %RH, 22 mg/g of water

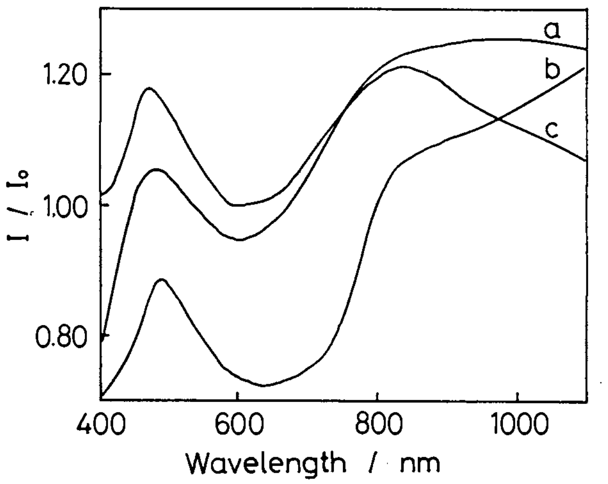

Fig. 1. Spectra of Reichardt's dye-polymer composites in 45%RH atmosphere. (a) PMMA, (b) PEO, (c) PVP.

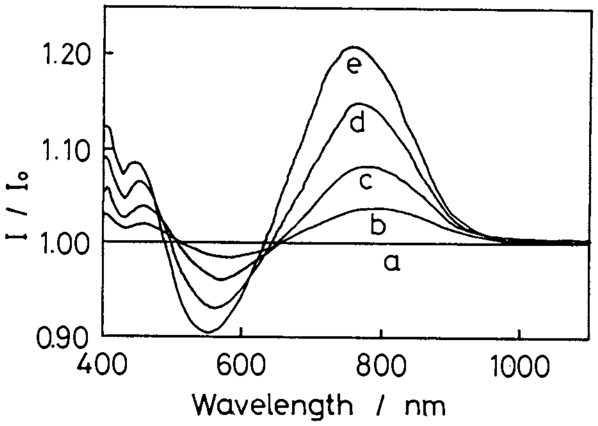

Fig. 3. Humidity dependence of spectrum for the PMMA composite. (a) 0, (b) 5, (c) 13, (d) 38, (e) 71 in %RH.

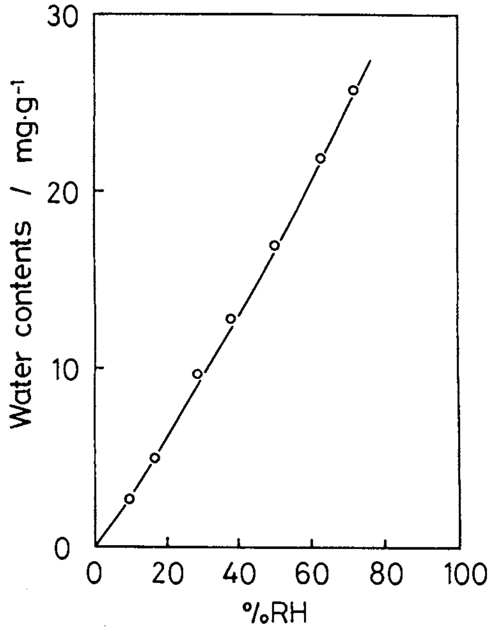

Fig. 2. Water sorption isotherm of the PMMA composite.

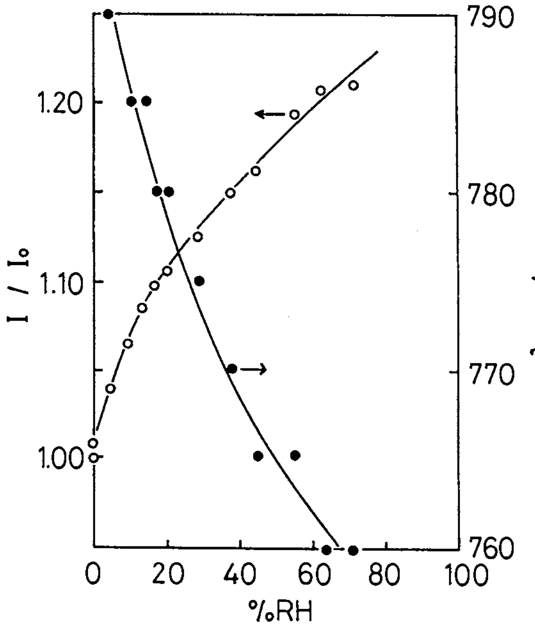

Fig. 4. Humidity dependence of optical intensity and wavelength at maximum appeared around 780 nm for the PMMA composite.

was sorbed on the composite and the water content was monotonically increased by the humidification (Fig.2). As reported previously,$^{7)}$ it seems that water molecules sorbed in PMMA exist in the form of non-liquid phases since the estimated dielectric constant of the sorbed water is about 25 for 30 mg/g. The results of the sorption isotherm substantiates our consideration mentioned above. As the water sorption ability of the composite can be controlled by using a suitable polymer as a matrix, the wavelength of the absorption peak can be also controlled. In Fig.3, the spectrum changes observed in the reflection mode as a function of the humidity are shown for PMMA composite. In these cases, the spectrum observed in dry air for the composite was used as the reference. The optical intensity observed at around 780 nm increased with the humidity, while the optical intensity at around 550 nm decreased . Furthermore, the wavelength of the both peaks (λ_{MAX}) became shorter. The reflection peak at around 780 nm is more sensitive to the humidity than that at around 550 nm. The results observed at around 780 nm were replotted in Fig.4. Since both the optical intensity and the wavelength of the composite film varied monotonically within the broad humidity range, the present composite film can be used as a bifunctional humidity sensor. Similar results were confirmed for PEO composite in which the wavelength of the peak in the reflection mode was shifted from 790 nm to 760 nm with increasing relative humidity while the water sorption ability was about 2-fold higher than that of PMMA composite. For the PVP composite, the wavelength of the peak was about 800 nm and the optical intensity was less sensitive to the humidity. These results suggest that the optical behavior of the present composite system was also influenced by the hydrogen bond acidity of the polymer matrix.

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