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Development of a novel moisture sensor based on superabsorbent poly(acrylamide)-montmorillonite composite hydrogels

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The time dependence of water vapour absorption by superabsorbent polymer clay composite (SAPC) hydrogels was studied using thermophysical methods. For the purpose of comparison the average value of the specific interaction enthalpy of liquid water with the SAPC structure was calorimetrically determined for a defined interaction time. Dynamic vapour absorption measurements confirmed that the SAPC material has a sufficiently high absorption capacity and good selectivity for water vapour. A prototype moisture sensor with excellent reproducibility of the output voltage signal was constructed by coating a silicon integrated thermotransducer with a thin SAPC membrane.

1. Introduction

It is well known that some polymer hydrogels will change their chemical, physical and mechanical properties, for example electrical resistance, capacity, size and shape in response to environmental stimuli through the absorption and desorption process of water [1–3]. These changes can be converted into an electric signal which in turn can be used to monitor changes of the surrounding environment. In principle, a sensor can be constructed if the sensing material is properly combined with an integrated circuit. Moisture sensors differ in the way they respond to the environmental stimulus and which measurement methods are being utilized, e.g. measurement of electrical (potential Φ, current I, capacity C, conductivity σ), thermal (heats of adsorption Q_{ad} and reaction Q_{r}), optical, and frequency signals. The most important properties of a material to be used in a sensor are sufficient sensitivity to the environmental stimulus, selectivity for the species to be detected, short response time, and reproducibility of the output signal.

We have synthesized a superabsorbent poly (acrylamide)-montmorillonite composite (SAPC) material by UV-induced polymerization. The SAPC has excellent water absorption capacity; up to a thousand grams of water can be absorbed per gram SAPC. Previously, we have studied selected material properties of SAPC hydrogels [4–6]. In this contribution, the dynamic water moisture absorption of SAPC will be discussed.

2. Experimental

2.1. Chemicals

To synthesize SAPCs, acrylamide (GC grade), acrylic acid (GC grade), sodium vinylsulfonate (CP grade, 30% aqueous solution), sodium styrenesulfonate (GC grade), N,N-methylene bisacrylamide, and potassium persulfate (98%), all from Fluka Chemie AG, Switzerland as well as sodium hydroxide (AR grade, Merck KG, Germany), and bentonite (Süd-Chemie AG, Germany) were used.

The bentonite clay contains 64.9% SiO_2, 19.4% Al_2O_3, 3.3% Fe_2O_3, 1.2% CaO, 2.3% MgO, 1.9% Na_2O, and 0.4% K_2O. The loss on drying at 110°C was 5.3%. The mineralogical phase composition was determined by XRD and yielded the following minerals: montmorillonite 70–85%, quartz 3–4%, feldspar 7–8%, and cristobalite approx. 4%. The bentonite was dried at 120°C for 24 hours to remove the absorbed water before preparation of SAPC. The original particle size of bentonite ranged from +10–28 μm. Comminution was done using an agate ball mill. After grinding the

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bentonite had a particle size distribution of +0.17–0.57 μm. Other chemicals were used as received without further purification.

2.2. Preparation of SAPC samples by UV-induced polymerization

Polymerization of the monomers was carried out using an UV lamp (Solimed, TA150) with an output power of 140 W. First, aqueous solutions were prepared of different monomers with some additives. Subsequently, the solutions were purged with nitrogen gas to remove dissolved oxygen, and irradiated with the UV light at a distance of 100 mm. The irradiation time differed slightly from sample to sample depending on their composition. The structure of the SAPC was characterized by Fourier-transform infrared spectrometry (FTIR), nuclear magnetic resonance spectroscopy (NMR, ^{29}Si, ^{27}Al and ^{13}C) and X-ray diffraction (XRD) [7]. Water absorption capacities of the materials were measured gravimetrically.

3. Results and discussion

3.1. Enthalpy measurements

To confirm the feasibility of using a thermal method to monitor the absorption process, a first experiment was performed to determine the heat generated by the interaction of liquid water with SAPC using a standard reaction calorimeter (LKB 8700, LKB product, Sweden). SAPC samples were sealed in a glass ampoule and installed in a thermally insulated reaction cell placed in a constant temperature bath as shown in Fig. 1. Calibration and enthalpy determinations were performed using standard procedures [8]. To start the measurement, the ampoule was broken by the stirrer to allow the SAPC to make contact with water.

A typical result of the measurement is shown in Fig. 2. It is evident that there are two distinct water absorption mechanisms, the wetting and diffusion/swelling process. The specific enthalpy of the wetting process, estimated from the calorimetric measurements for a water interaction time of 5 minutes, is exothermic at $\Delta H = -(120.7 \pm 3.6)$ J/g as follows from the results shown in Table I. Due to the complexity of the second process, its enthalpy could not be determined unambiguously. The long duration of this process makes the estimation of an enthalpy value from the slope of the calorimetric curve problematic. Bakass *et al.* [9] used a similar calorimetric method to measure water absorption enthalpies, but the meaning of the values obtained is subject to many questions.

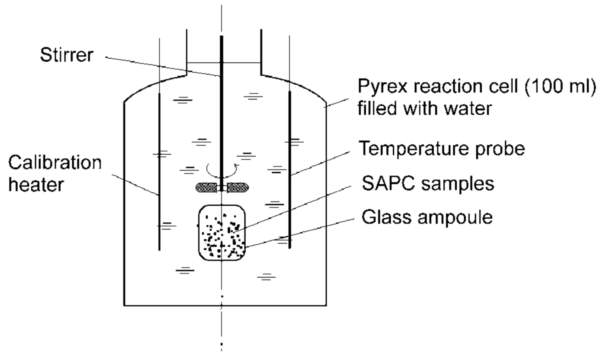

Figure 1 Scheme of the calorimetric cell.

TABLE I Specific interaction enthalpies ΔH of SAPC on contact with water

Sample	Mass of SAPC (mg)	Mass of H_2O (g)	q (J)	$-\Delta H$ (J/g)
SAPC1	32.20	85.200	3.82	118.6
SAPC 4	33.55	85.200	4.19	124.9
SAPC 5	32.63	85.467	3.87	118.6

q: measured heat exchanged, ΔH: specific enthalpy per gram of SAPC.

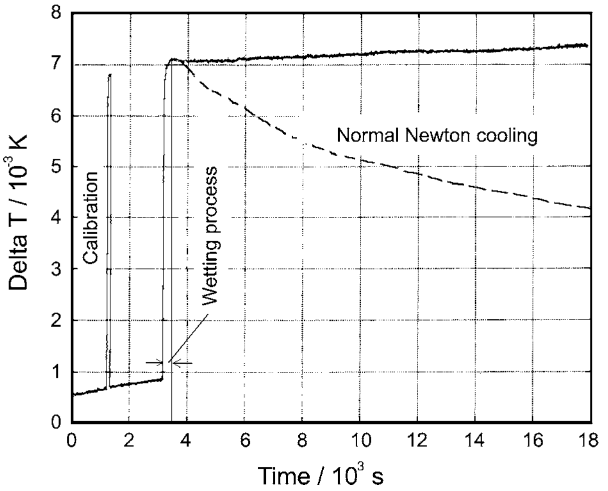

Figure 2 Typical curve of the calorimetric measurements.

3.2. Thermogravimetric measurements

To measure the moisture absorption behaviour, a thermogravimetric analyzer was used (Q-Derivatograph; MOM Budapest, Hungary) operated in an isothermal mode at room temperature. A stream of argon gas containing different moisture concentrations was led over the sample. The moisture contents of the inert gas (relative humidity) were fixed with saturated solutions of LiCl, KCl and $Mg(NO_3)_2$ as well as pure H_2O at 20°C. The mass of the samples was about 100 mg. Fig. 3 shows the nearly linear relationship over a wide range between the moisture content (relative humidity) and the maximum moisture absorption of SAPC.

Further experiments were carried out by varying different experimental parameters such as the type of ionic species in the SAPC as well as the geometrical shapes and the masses of the samples. In these experiments, the SAP samples A, B, E and F were copolymers of acrylamide (AM) and sodium acrylate (AANa), and the SAPC samples C and D were composites of AM/AANa with montmorillonite. Samples A, B, C and D consisted of fine particles with diameters less than 0.125 mm, samples E and F were thin membranes. The masses of the samples A, B, C, D, E and F were, respectively, 106.7 mg, 95.9 mg, 105.7 mg, 102.3 mg, 23 mg and 16 mg.

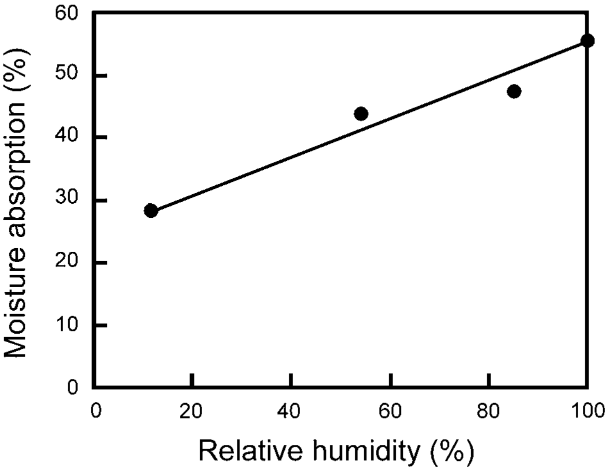

Figure 3 Water moisture absorption capacity of SAPC versus relative humidity (absorption time: 3000 min).

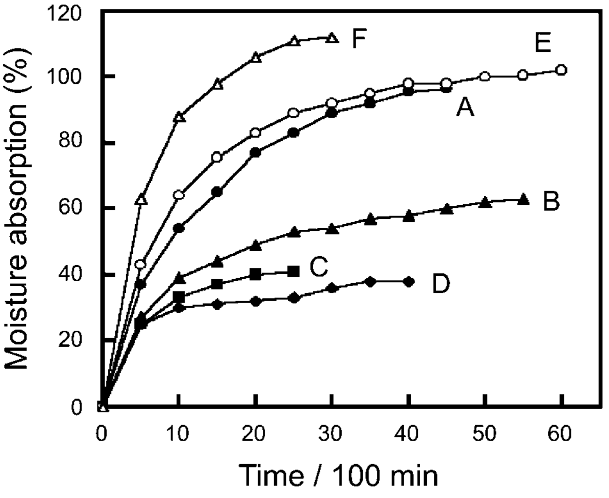

Figure 4 Time dependence of the absorption of moisture by different SAP (A, B, E, F) and SAPC (C, D) samples at 100% relative humidity.

Fig. 4 shows the dynamics of moisture absorption of SAP and SAPC samples with different compositions and geometries at 100% relative humidity. The addition of montmorillonite in the composite samples (C, D) strongly reduces the water absorption capacity in comparison to the pure SAP materials. The membrane samples (E, F) absorbed moisture much faster than the powder samples (A–D). At the beginning, the absorption rate was relatively fast because it occurred at the free surface of the material. Later this process slowed down because of the saturation of the surface with water. However, since saturation takes place only at the surface of the material, the exterior water tends to diffuse into the interior, hence controlling the absorption rate by inward diffusion of water. This process is much slower than the former one, hence samples with a larger mass showed slow absorption rates. Since the powdered samples have large specific surface areas, they should absorb water vapour quickly. The reason that these samples absorbed water vapour slower than expected is due to fact that the powdered samples are highly compacted. In addition, after absorption of some critical amount of water vapour the pore system will be plugged by the swollen hydrogel. This suggests that the moisture absorption rate of SAPC is predominantly controlled by the diffusion rate of water within the SAPC network. Because of the relatively short diffusion paths in the thin membrane samples, the absorption equilibrium can be reached more quickly. From this analysis, it is obvious that very thin membranes are needed to accelerate the absorption process in order to meet the requirements for sensor application.

3.3. Measurement of moisture absorption of SAPC membranes by a thermotransducer

Based on the experimental results described above and from the point of practical application, membrane-type SAPCs were used for additional experiments. To obtain satisfactory control over the required properties, a method was developed to reliably control the thickness and size of the membranes [10]. Series of membranes with reproducible properties were cast with thicknesses between several and 400 micrometers.

A prototype moisture sensor was constructed by integrating an SAPC membrane with a thermotransducer. The schematics of the measurement process and the chip structure of the sensor are shown in Fig. 5 [11, 12]. Measurements of the dynamic water moisture absorption were performed using synthetic air.

Fig. 6 shows the output voltage of a transducer constructed with composite material (SAPC) and pure polymer (SAP) in response to synthetic air containing a water vapour content of 0.34%. First, the absorption process was carried out for about 100 seconds. Then, dry air was led for another 100 seconds over the membrane to remove the absorbed moisture. Obviously, the

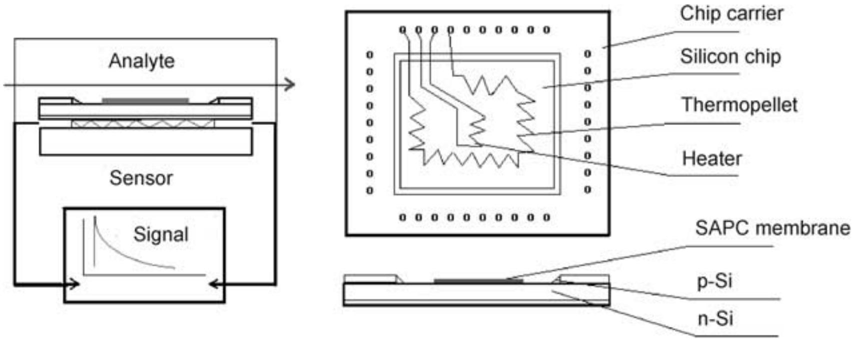

Figure 5 Schematics of the measurement process (left) and the layout of the silicon transducer chip (right).

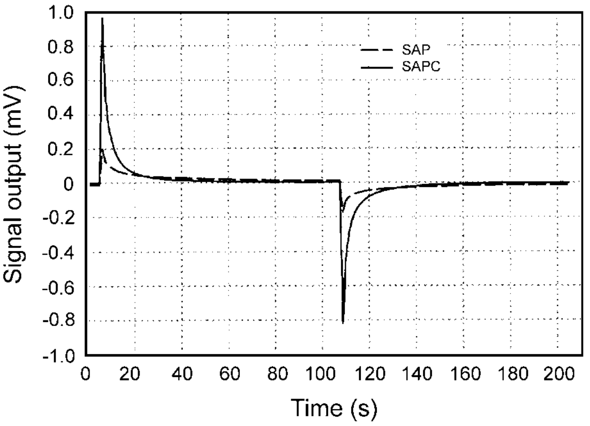

Figure 6 Output voltage signal measured during dynamic moisture absorption obtained by a thermosensor coated with SAPC and SAP membranes of 18 μm thickness. The curves show the average of 10 measurements.

composite material (SAPC) had a much higher output signal than the pure polymer system (SAP). The water moisture absorption of the membrane was much improved compared to those shown in Fig. 4 (E, F) with a thickness exceeding 50 μm. At the start of the process, the absoption rate was very fast and reached its maximum almost instantaneously. After saturation of the surface of the membrane, the water absorption rate decreased since the process was then controlled by inward diffusion of water. Within about 40 seconds the signal output dropped from +0.95 mV to 0 mV.

Since diffusion predominantly determines the shape of the absorption and desorption curves we tried to fit the time dependence of the signal decay by a series of exponential terms assuming the validity of Fick's law [13]. As a result of a non-linear regression fit using ORIGIN software an equation with two exponential terms was obtained that can be expressed by

$$R_{ab} = 1.13\,e^{-t/1.74} + 0.29\,e^{-t/8.80} \qquad (1)$$

where t is the absorption time.

The water vapour desorption process showed the same characteristics. The desorption rate reached its maximum quickly and decreased according to a similar exponential decay model expressed by the equation

$$R_{de} = -3.36\,e^{-t/0.92} - 0.38\,e^{-t/8.65} \qquad (2)$$

It is remarkable that the essential time constants agree rather well for both processes.

Absorption of organic solvent vapours by SAPC was measured for the purpose of comparison. Fig. 7 shows that the signal output sensitivities of the absorption of some organic solvents e.g. dioxane and chloroform to SAPC were 1.14×10^{-4} mVs/ppm and 6.23×10^{-6} mVs/ppm, respectively, one to two orders of magnitude lower than that of water (1.30×10^{-3} mVs/ppm).

To check the reproducibility of the process, the absorption and desorption cycles were repeated more than a 100 times (Fig. 8) without noticeable decay of the maximum (about +1 mV) or minimum (about −0.8 mV) output voltages thus confirming the feasibility to utilize SAPC membrane to construct a functional moisture sensor.

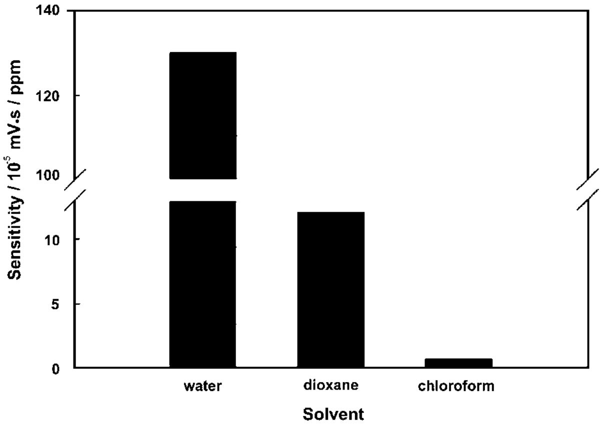

Figure 7 Comparison of signal sensitivities of different absorbates bound to SAPC.

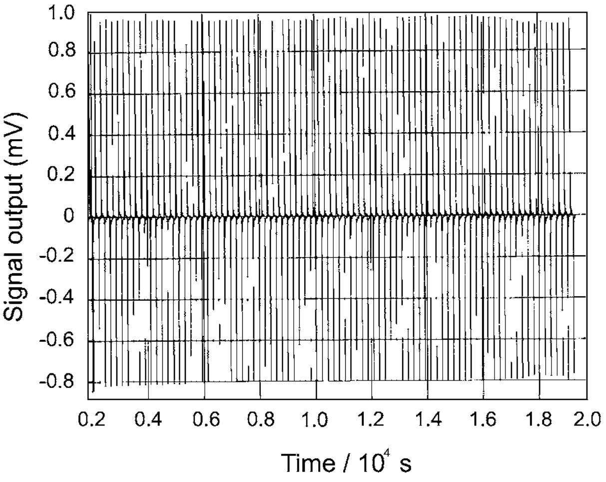

Figure 8 Reproducibility of the output voltage signal of a moisture sensor coated with a 18 μm thick membrane of SAPC.

4. Conclusions

1. Different samples of superabsorbent polymers (SAP) and composites with clays (SAPC) were synthesized and their water vapour absorption behaviour was studied by thermogravimetric and calorimetric methods. All samples show a high absorption capacity for water vapour which can be controlled by the chemical composition. The maximum absorption capacity depends nearly linearly on the relative humidity of the gas phase. Only very thin membranes show the sufficiently fast absorption rate required for sensor application owing to reduced diffusion limitations in their polymer network.

2. Dynamic measurements with thin membranes showed that the SAPC has better water vapour absorption properties than the pure superabsorbent polymer (SAP). Hence the former may be utilized as a moisture sensitive material to construct a moisture sensor.

3. A prototype moisture sensor was constructed by integrating a thin (18 μm) SAPC membrane with a thermotransducer, showing sufficient sensitivity and good selectivity to water moisture, and excellent reproducibility of the voltage signal.

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