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Effect of acetyl content on the sorption isotherm of water by cellulose acetate: comparison with the thermal analysis results

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Abstract

In this study, the sorption isotherms of water vapor by cellulose acetate for various acetyl contents were measured. The BET adsorption theory was modified for the system which has two different kinds of energy levels in the water adsorption sites, i.e. a hydroxyl group and an acetoxyl group, and applied it to the experimental results in order to examine the effect of acetyl content on the sorption isotherm of water using the parameters which represented the total number of adsorption sites, V_m, the interaction energy between water and the adsorption sites, K, and the number of adsorbed layers, n. V_m and K decreased with an increase in acetyl content and n remained constant. The apparent activation energies of the water desoption were also determined using differential thermal analysis. They are nearly constant with an increase in the acetyl content. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Sorption isotherm of water; Cellulose acetate; BET equation; Hydroxyl group; Acetoxyl group; Differential thermal analysis

1. Introduction

The state of the glassy polymer is determined not only by the state variables, pressure (p) and temperature (T), but also requires a third state variable, a so-called ordering parameter (ξ) for full characterization of its state (Haward, 1973; Motamedian, Pusch, Tanioka & Becker, 1998). The sorption isotherm of water by a glassy polymer shows a sigmoid shape (Fukuda, 1997; Fukuda, Kohata, Fukuda & Kawai, 1989; Hinatsu, Mizuhara & Takenaka, 1994; Isasi, Cesteros & Katime, 1994; Nakajima & Gocho, 1978; Nakajima, Hattori & Uno, 1976; Nakajima, Katano & Isobe, 1976; Nakajima, Tamaru & Hattori, 1981) and has to be explained by the theory based on the non-equilibrium thermodynamics (Motamedian et al., 1998). However, this theory cannot cover the whole range of the relative vapor pressure because water-sorbed polymers already turn to the rubbery (equilibrium) state in the region of the high water content. On the other hand Brunauer, Emett and Teller's multi-layer adsorption theory (BET) (Barrer, 1990; Brunauer, Emmett & Teller, 1938; Timmermann, 1989; Young & Crowell, 1962), which is based on the kinetic theory, is one of the models to explain the sorption isotherm in the full range of the relative vapor pressure. According to the assumption of this theory the interaction between the water molecules and the adsorption sites in the polymer has to be considered for the first layer; and the nth layers except for the first layer correspond to the water molecules successively condensed on the first layer.

In previous papers, the BET adsorption equation of the n-th layer was modified for the system which has different kinds of energy levels in the water adsorption sites (Gocho, Tanioka & Nakajima, 1998). Applying the n-th layer BET equation to the sorption isotherm of water by a block copolymer, random copolymer, grafted polymer and blend polymer, the total number of adsorption sites in the polymer, V_m, the interaction energy between water and adsorption sites, K, and the number of adsorbed layers, n, in the modified BET equation were calculated. It was proven that these parameters could well explain the state of the polymers composed of more than two adsorption sites.

In this study, we applied the modified BET equation to the water–cellulose acetate system and discussed the effect of acetyl content on the sorption isotherm of water by V_m, K and n. Finally, the energy parameter K is compared with the apparent activation energy of desorption based on differential

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Table 1
Degree of acetylation, concentration of hydrolyzed agent (NaOH) and reaction time

	CA 32	CA 38	CA 44
Degree of acetylation (% of acetyl group)	32.2	38.4	44.3
Concentration of NaOH (N)	0.75	0.5	Untreated
Reaction time (h)	5	6.5	–

thermal analysis (DTA) measurements in order to examine the physicochemical meaning of *K*.

2. Experimental

2.1. Samples

The cellulose acetate films used in this study, each of which has a different degree of acetylation (abbreviated as CA 32, CA 38 and CA 44), were prepared from commercial cellulose triacetate film (Chiyoda Gravure Printing Co., Ltd.). Twenty grams of cellulose triacetate film was immersed in ethyl ether for 30 min and ethanol for 1 h, and subsequently washed in distilled water. The sample, with removed impurities, was kept in water at 80°C for 3 h before air drying. A 5 g purified sample was hydrolyzed by an NaOH aqueous solution at 70°C in order to prepare the samples which have different degrees of acetylation. The experimental conditions are shown in Table 1 along with the degree of acetylation. The degree of acetylation was determined using the acetyl group microanalysis method based on the saponification and successive titration by NaOH (Fukuda, 1969; Kuln & Roth, 1933).

2.2. Measurements of sorption isotherm (Nakajima & Gocho, 1978)

The samples, completely dried by P_2O_5 in weighing bottles were placed in desiccators for 10 days where the humidity was controlled by various saturated aqueous salt solutions. The weighing bottles with samples were removed from the desiccator for quick weighing. After weighing, the bottles were placed back in the desiccator. After 10 days, they were weighed again. This procedure was repeated every 2 or 3 days until the weight change was within ±0.05%. The measurement temperature was 20 ± 0.2°C. The water content in the polymer (water regain), *V*, was represented by the weight of sorbed water (g) per weight of dried polymer (g) as a function of relative vapor pressure, *x*.

2.3. Measurements of DTA

The DTA method was used in order to determine the apparent activation energy of the water desorption in cellulose acetate film (Kambe, 1973). A disc-shaped sample film was first immersed in distilled water for 24 h and the surface wiped softly with filter paper as early as possible after removing it from the water. This sample was immediately replaced in the cell attached to the Micro DTA apparatus (Shimadzu Co.). The cell was heated at various heating

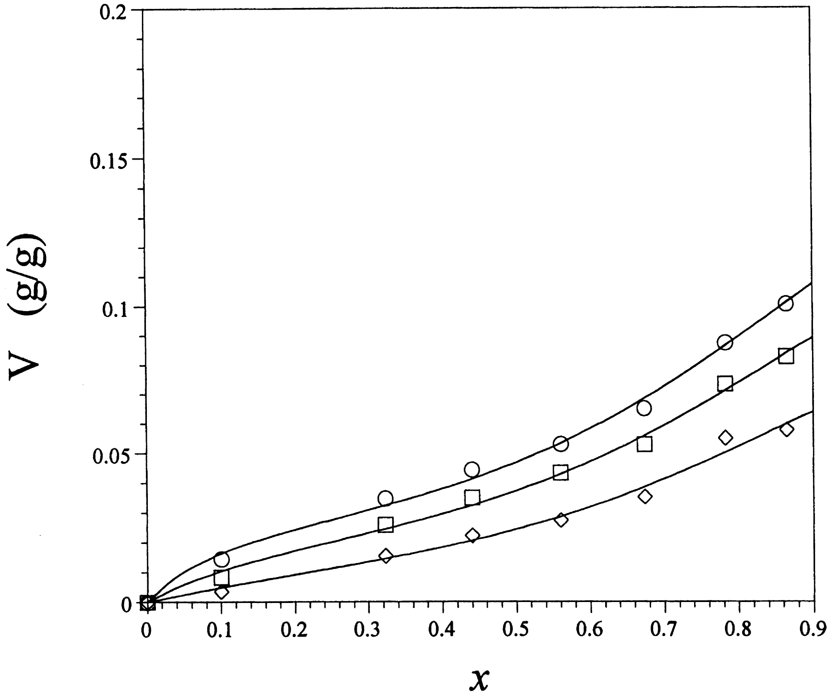

Fig. 1. The amount of water content in the chitosans, *V*, represented by the weight of sorbed water (g) per weight of dried polymer (g) as a function of relative vapor pressure $x = p/p_0$ and application of the modified BET equation, where ○ is CA 32; □ CA 38; and ◇ CA 44.

Table 2
Parameters of modified BET equation in various cellulose acetate films

	CA 32	CA 38	CA 44
V_m	0.025	0.021	0.016
K	13.4	7.50	3.60
n	9	9	9

rates, ϕ, i.e. 2, 5, 7.5, 10, 15 and 20°C/min in air. Al_2O_3 powder was used as a reference material. The temperature difference between the reference and sample was recorded on the DTA recorder chart to determine the peak temperature caused by the water desorption. An activation energy of water desorption, E_d, was determined from the following equation from the slopes of $\ln(\phi/T_m^2) \sim 1/T_m$ plots (Ito, 1972; Kambe & Ozawa, 1992)

$$\frac{d(\ln \phi/T_m^2)}{d(1/T_m)} = -\frac{E_d}{R} \tag{1}$$

where T_m is the peak temperature and R is the gas constant.

3. Results and discussion

In Fig. 1 the sorption isotherms for water vapor by various cellulose acetates at 20°C are shown. These curves show the sigmoid shape which is characteristic of a glassy polymer–organic or water vapor system (Fukuda et al., 1989). The amount of adsorbed water increased with a decrease in acetyl content. If we assume the cellulose acetate has two principal adsorption site groups, i.e. the hydroxyl and acetoxyl groups which have different energy levels (Jeffries, 1960; Polymer Society of Japan, 1968), the BET adsorption theory is modified for the system which has two different kinds of energy levels in the water adsorption sites as shown in a previous paper (Gocho et al., 1998). A polymer material has N_m adsorption sites which can be divided into two different energy levels as (Fukuda et al., 1989; Gocho et al., 1998):

$$\varepsilon_{OH}(N_{mOH}) \quad \text{and} \quad \varepsilon_{AC}(N_{mAC}) \tag{2}$$

where the subscripts OH and AC correspond to the hydroxyl and acetoxyl groups, respectively, N_{mOH} and N_{mAC} are the number of sites which have ε_{OH} and ε_{AC} energy levels, respectively, and

$$N_m = N_{mOH} + N_{mAC}. \tag{3}$$

The total amount of adsorbed water, V (g/g-polymer), with the total amount of the adsorbed water in the first layer V_m (g/g-polymer) is represented as follows:

$$V = \frac{V_m Kx[1 - (n+1)x^n + nx^{n+1}]}{(1-x)[1 + (K-1)x - Kx^{n+1}]} \tag{4}$$

where x corresponds to the relative vapor pressure ($= p/p_0$), and

$$K = f_{mOH}C_{1OH} + f_{mAC}C_{1AC} \tag{5}$$

f_{mOH} and f_{mAC} are the fractions of unadsorbed sites of the hydroxyl and acetoxyl groups relative to the total number of unadsorbed sites, respectively, and C_{1OH} and C_{1AC} are the C parameter in the original BET equation. The following relationship is found between f_{mOH} and f_{mAC}:

$$f_{mOH} + f_{mAC} = 1. \tag{6}$$

Since the differential sorption enthalpy of cotton is about 4 or 5 times larger than that of cellulose triacetate, C_{1OH} is much larger than C_{1AC} (Jeffries, 1960; Polymer Society of Japan, 1968). Applying Eq. (4) to the experimental data, the non-linear regressions were performed in order to determine the parameters V_m, K and n, and the correlation coefficient was within 0.98. The theoretically predicted curves are shown as solid lines in Fig. 1 and the calculated V_m, K and n values are listed in Table 2. The total amount of adsorbed water on the first layer, V_m, decreases with an increase in the acetyl content, which shows that an acetoxyl group is not so effective as an adsorption site compared with a hydroxyl group in the cellulose acetate. The energy parameter, K, also decreased with an increase in acetyl content. According to Eq. (5), the increase in the acetyl content reduces the K value. On the contrary, the n value remains constant for all samples. In Table 3, the apparent activation energies of water desorption E_d, which were determined by DTA, are shown. They are nearly constant with an increase in the acetyl content. This result suggests that E_d is influenced only by the interaction between water molecules. On the other hand, K includes the interaction term between an adsorption site and a water molecule as shown in the definition of the BET equation.

Table 3
Apparent activation energy of water desorption (E_d) for various cellulose acetate films

	CA 32	CA 38	CA 44
E_d (kJ/mol)	54.0	53.5	57.2

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