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Competitive Adsorption of Water and CO₂ on Acetylene-Terminated Polyimide Resins for a Humidity Sensor

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Received January 23, 1995 ; Accepted May 8, 1995

1. INTRODUCTION

Since polyimides possess high workability, excellent thermal and chemical stability, low hygroscopicity, low solubility to common organic solvents, etc., they are used for adhesives, coatings, and film applications for electronic devices. Among these polyimides, acetylene-terminated polyimide resins have preferable characteristics for the above application. The starting materials of acetylene-terminated polyimide are polyimide oligomers which are soluble in some organic solvents and polymerization proceeds without by-products. Furthermore, each polyimide oligomer is cross-linked by a heat treatment and leads to the formation of a rigid and less hydrophilic film without microvoids. We have already presented the results of a study on the water sorption behavior of the film and their application for capacitive-type humidity sensors practically used¹⁾.

On the other hand, it is well known that polyimides offer attractive characteristics of gas barrier and membrane separation properties. Many researchers have been studying the gas adsorption and transport properties of polyimide films²⁻⁶⁾. CO₂ is one of the gases to which much attention is being devoted, since some polyimides show high CO₂ permeability and selectivity. In this study, we examined the CO₂ adsorption behavior in the acetylene-terminated polyimide resins. Further, since there was a fear of

influence of the coexisting CO₂ gas on the humidity sensor characteristics, the competitive adsorption behavior of water and CO₂ gases in this polyimide was also studied and discussed.

2 EXPERIMENTAL

The commercially available acetylene-terminated polyisoimide (API-10) oligomer (Kanebo NSC CO. Ltd.) and its polymer were used in this study. The molecular structure and the abbreviation have been described elsewhere¹⁾. The oligomer powder was dissolved in 2-methoxyethyl ether. The solution was coated on a quartz crystal oscillating element (4 MHz) which had a silver electrode. In order to obtain the oligomer film, the solvent was evaporated at 60 °C under reduced pressure. The polymer film was prepared by heating this obtained oligomer film at 180 °C for 2 h in N₂ flow (50 ml/min).

The element with polyimide film was placed in a thermostated measuring chamber. Various concentrations of CO₂ cylinders, which were diluted with N₂, and a high purity N₂ cylinder were obtained from a commercial supplier. The humidity was varied by controlling the mixing ratio of a dry gas and a water saturated gas, which was prepared by bubbling the gas through water. All the adsorption experiments were performed under atmospheric pressure at 30 °C. The amount of sorbed gases was estimated from the variation in the oscillating frequency of the crystal as described elsewhere⁷⁾.

3 RESULTS AND DISCUSSION

3.1 Adsorption of water

The water adsorption ability of API-10 oligomer and polymer was measured as a function of relative vapor pressure (p/p_0)_w. The adsorption isotherms obtained at 30 °C are shown in Fig. 1. The amount of adsorbed water, W_w , which was defined as milligrams of water sorbed in one gram of dry

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Key Words: competitive adsorption, humidity sensor, CO₂, polyimide

polymer, was plotted on the ordinate. It is observed that there is a distinction between the water adsorption behavior of the oligomer and that of the polymer. The isotherm for the oligomer is linear at low $(p/p_0)_w$ and curved upward more than that predicted by Henry's law at high $(p/p_0)_w$. This curve is similar to Type III according to Brunauer's classification⁸⁾ and is sometimes called a Flory-Huggins type isotherm⁹⁻¹¹⁾. The isotherm is observed when the attractive forces between adsorbed gas and adsorbent are smaller than the attractive forces between adsorbed gases. Inherent in the Flory-Huggins statistics is the idea that there will be some clustering of the solutes at a higher concentration. On the other hand, the isotherm shown for the polymer is concave toward the abscissa. This is essentially Langmuir-type equation for unimolecular adsorption¹²⁾.

$W_w = W_w^s ((K_w(p/p_0)_w / (1 + K_w(p/p_0)_w)))$ (1)
where W_w^s is a saturation constant and K_w is a constant at a given temperature. The linear relationship between $1/W_w$ and $(p/p_0)_w$ was obtained and the constants were calculated from Langmuir's formula. The obtained results are shown in Table 1. The difference in these adsorption behaviors between oligomer and polymer can be explained by the difference of their morphology. Polyimide is a glassy polymer and the adsorption of gases in glassy polymer is successfully described by the dual-mode sorption model. The dual-mode sorption is based on the principle of two sites; [1] site for the dissolution according to Henry's law and [2] site for the adsorbed

Fig. 1 Water adsorption isotherms measured at 30 °C; (●) oligomer, (▲) polymer.

Table 1. Constants in Langmuir adsorption equation.

	$W_w^s / \text{mg g}^{-1}$	$W_c^s / \text{mg g}^{-1}$	K_w	K_c
oligomer		6.0		2.4
polymer	78.1	10.4	0.81	2.6

molecules according to Langmuir's law in the frozen microvoids in the glassy polymer. The present polyimide is a cross-linked rigid polymer as well as a glassy polymer and the frozen microvoids are further divided into small fixed interstices by the cross-linking reaction. The small fixed interstice is termed a hole in this paper. Consequently, swelling of the polymer is not expected and the holes in the polymer seem to play an important role in the adsorption behavior. In such a case, the formation of the cluster of sorbed water molecules seems to be prevented by the space limitation. However, the oligomer is mobile enough to create free volume after filling interstices. Swelling of the oligomer is likely to occur by adsorbing water which results in a cluster formation at a large amount of adsorbed water. The water molecule is highly condensable due to its highly polar and amphiprotic structure. This explanation is consistent with the obtained Flory-Huggins type isotherm.

3.2 Adsorption of CO₂

The amount of adsorbed CO₂, W_c , was determined as a function of pressure p_c . The result is shown in Fig. 2. The W_c of the polymer is almost twice as much as that of the oligomer. It is well-known that the adsorption of CO₂ in a glassy polymer, including polyimide films, is successfully described by the dual-mode sorption model, especially at high CO₂ pressure^{3,4)}. While both isotherms were similar in form to the model, a good linear relationship between W_c and $1/p_c$ (Langmuir type isotherm) was obtained. The calculated Langmuir's constants are also shown in Table 1. The obtained isotherm suggests that the present adsorption behavior is explained by the simple adsorption on the surface of the holes. In order to explain the difference of CO₂ adsorption ability between the polymer and the oligomer, the distribution of holes with various volume should be considered. As mentioned in the previous section, the formation of a cross-linking structure makes the

Fig. 2 CO_2 adsorption isotherms measured at 30 °C; (●) oligomer, (▲) polymer.

polymer rigid and produces new holes. Furthermore, the formation of cluster of CO_2 , which was observed in the case of water adsorption in the oligomer, is not expected. Therefore the polymer adsorbs more CO_2 compared to the oligomer.

The amount of adsorbed CO_2 was considerably small compared with that of water. The estimated moles of adsorbed CO_2 per gram of oligomer and polymer were about 1.0×10^{-4} mol / g and 1.8×10^{-4} mol / g at $p_c = 1.0$ atm, respectively. Water was adsorbed an order of magnitude more than CO_2 at $(p/p_0)_w = 0.76$. The Langmuir's saturation constants obtained for the polymer were converted into moles of solutes, yielding 4.3×10^{-3} mol water / g (M_w^s) and 2.4×10^{-4} mol CO_2 / g (M_c^s), respectively. The CO_2 molecule possesses a linear structure having two double bond linkages ($\text{C}=\text{O}$). The electronic cloud is built through the π -electrons of both double bonds and can interact with the π -systems in the polymer by polar interaction. The present polyimide doesn't have a highly polar group for CO_2 adsorption as well as H_2O , so that the adsorption site of CO_2 is considered to be almost the same as that of the H_2O molecule. The difference in adsorption ability between H_2O and CO_2 seems to be attributed to a complex of many factors, *i.e.*, the difference in measuring relative vapor pressure range for each gases at 30 °C and the difference in cohesive forces between adsorbed gases. Furthermore, the difference in molecular size of H_2O and CO_2 may affect the

adsorption behavior on the present polyimide with small holes. Effective cross section of adsorbed CO_2 (0.216 nm^2) is almost twice as large as that of H_2O (0.125 nm^2). The difference in molar volume of H_2O and CO_2 in the glass polymer seems to be also large. The molar volume of CO_2 in rubbery polymer was reported to be around $40 \text{ cm}^3 / \text{mol}$, which was the same as in liquid (46 ± 3), while it was $20 \text{ cm}^3 / \text{mol}$ in glassy polymer^{12,13}. This was explained by the fact that the glassy polymers were not mobile enough to create free volume after a hole had been occupied. While the molar volume of H_2O in glassy polymer could not be found in the literature, one half molar volume of CO_2 is estimated for H_2O from the van der Waals volume ($10.3 \text{ cm}^3 / \text{mol}$ for H_2O and 19.7 for CO_2). These factors lead to the idea of the different number of effective adsorption sites for CO_2 among all adsorption sites for H_2O . The distribution of holes with various sizes is expected, while larger holes which cause capillary condensation are hardly present. The holes are linked three-dimensionally in the bulk of the polyimide and the surface is complex in shape. The smaller the size of the solute becomes, the smaller the hole in which the solute can enter. It is impossible that CO_2 molecule enters the hole, which is smaller in size than CO_2 molecule. In that case, CO_2 can occupy only a part of the total adsorption sites. Moreover, a single CO_2 molecule may occupy plural sites, especially in the hole which is slightly larger than CO_2 molecule. The sites are closely spaced together in such holes and CO_2 molecules cannot occupy all those sites due to the space limitation. These phenomenon seems to result in the difference in the sorption ability for H_2O and CO_2 .

3.3 Competitive adsorption of H_2O and CO_2

The adsorption experiments were also performed in the coexistence of H_2O and CO_2 . Only the results for the API-10 polymer is shown as a function of pressure of CO_2 at a certain relative water vapor pressure in Fig. 3, since a similar behavior was observed for the oligomer. The ordinate is the experimentally obtained total adsorption amount of the mixed gases, W_{total} . The value of W_{total} was clearly influenced by the partial pressure of water and CO_2 gases in the atmosphere. In a low $(p/p_0)_w$ region, the variation of W_{total} with p_c was resembled with those of W_c . This is because the small amount

Fig. 3 Relation between W_{total} and p_c at several relative vapor pressures at 30 °C; (○) $(p/p_0)_w = 0$, (●) 0.20, (△) 0.33, (▲) 0.50, (□) 0.65 and (■) 0.76.

of adsorbed water. On the other hand, the variation of W_{total} becomes smaller at higher $(p/p_0)_w$ and W_{total} decreased at higher p_c at $(p/p_0)_w = 0.76$.

The simple mechanism for explaining the competitive adsorption is set up by assuming the Langmuir-type adsorption at the same adsorption sites. It is obvious that this assumption is not the case, when the interaction between the solute can not be ignored. However, we did it to analyze this competitive adsorption in this polyimide, since the individual adsorption of water and CO_2 in the polymer was well described by Langmuir's law. With the help of a few simplifying assumptions, it is possible to deal with an isotherm derivation for competitive adsorption. A simple extension of Langmuir's theory of adsorption to the case of present gas mixtures lead to following equation.

First we should notice that the Langmuir's saturation constant of water is quite different from that of CO_2 as shown in Table 1. The constants obtained for the polymer are converted into moles of solutes, yielding $M_w^s = 4.3 \times 10^{-3}$ mol H_2O / g and $M_c^s = 2.4 \times 10^{-4}$ mol CO_2 / g, respectively. The ratio $\alpha (=M_c^s / M_w^s)$ is equal to 5.3×10^{-2} . Based on the possible adsorption form for H_2O and CO_2 discussed in section 3.2, three assumptions were made for competitive adsorption as follows; (1) the total adsorption site is equal to M_w^s , (2) n adsorption sites are needed for adsorption of one CO_2 molecule,

and (3) there are two kinds of sites (site A and site B) and only a site B is effective for CO_2 adsorption (competitive adsorption occurs only on site B). In this case, the fraction of site B against the total site is equal to $n\alpha$. In other words, under the conditions of competitive adsorption the number of site A is equal to $M_w^s - n\alpha M_w^s$ and that of site B is $n\alpha M_w^s$. The number of the site free from gas is $M_w^s - n\alpha M_w^s - M'$ for site A and $n\alpha M_w^s - M_w'' - nM_c$ for site B, where M_w' and M_w'' are the number of adsorbed H_2O molecules on site A and site B and M_c is the number of moles of adsorbed CO_2 , respectively. If the adsorption energy of both site A and site B is the same for H_2O , M_w' and M_w'' will be equal to $(1-n\alpha)M_w$ and $n\alpha M_w$, respectively. Therefore, we can obtain the number of total sites free from gas is $M_w^s - M_w - nM_c$. The rate of adsorption of H_2O , r_w' , is equal to $k_w(p/p_0)_w(M_w^s - M_w - nM_c)$, where k_w is a constant at a given temperature. The rate of desorption, r_w' can be expressed by the equation $r_w' = k_w' M_w$. At equilibrium, r_w is equal to r_w' and leads to

$$k_w(p/p_0)_w(M_w^s - M_w - nM_c) = k_w' M_w \quad (2)$$

Substitution of K_w for k_w/k_w' gives

$$M_w = K_w(p/p_0)_w(M_w^s - M_w - nM_c) \quad (3)$$

Similarly the rate of adsorption of CO_2 , r_c , is equal to $k_c p_c[(M_w^s - M_w)n\alpha - nM_c]$, since the number of site B free from gas is $n\alpha M_w^s - n\alpha M_w - nM_c$. The rate of desorption is $r_c' = k_c' nM_c$. At equilibrium, the following equation is obtained;

$$nM_c = K_c p_c[(M_w^s - M_w)n\alpha - nM_c] \quad (4)$$

where $K_c = k_c / k_c'$.

From eqs. (3) and (4),

$$M_w = K_w(p/p_0)_w X M_w^s / (1 + K_w(p/p_0)_w X + K_c p_c) \quad (5)$$

and for M_c

$$M_c = \alpha K_c p_c M_w^s / (1 + K_w(p/p_0)_w X + K_c p_c) \quad (6)$$

where $X = (1 + (1-n\alpha)K_c p_c)$. Finally we can obtain the individual amount of adsorbed gases as follows;

$$W_w = M_w \times N_w = N_w K_w(p/p_0)_w X M_w^s / (1 + K_w(p/p_0)_w X + K_c p_c) \quad (7)$$

and

$$W_c = M_c \times N_c = N_c \alpha K_c p_c M_w^s / (1 + K_w(p/p_0)_w X + K_c p_c) \quad (8)$$

where N_w and N_c represent the molecular weight of H_2O and CO_2 , respectively. Equations (7) and (8) involve constants determined for separate gases as shown in Table 1. In the case that each gas occupies

the same site equally ($\alpha = 1$), n essentially results in unity. From these equations and the constants, the amount of adsorbed gases was calculated.

Figure 4 compares the W_{total} with a model prediction by using the above equation. The n , which is the number of adsorption sites consumed by the adsorption of one CO_2 molecule, depended on the pressure of the gas. In the case of $n = 3$, it was proved that Equations (7) and (8) are fairly satisfactory for mixtures of H_2O and CO_2 below $(p/p_0)_w = 0.50$, but are inadequate when applied to mixtures at high vapor pressure. However, these failures were improved by using $n = 5$. The coverage of H_2O molecule is approximately 0.3 in the region of which n varies. The coverage of CO_2 molecule is considerably lower than that of H_2O . Therefore, the interaction between H_2O and CO_2 molecules seems to be hardly considered as a reason of the variation of n . The estimated n value is an experimentally obtained mean value based on the present adsorption model and it is difficult to explain its physical meaning clearly from a microscopic point of view. At any rate, it was confirmed that the competitive adsorption behavior on the complex surface was well described theoretically by the present simple treatment.

Fig. 4 Relation between W_{total} and p_c at several relative water vapor pressures at 30 °C; symbol and $(p/p_0)_w$ are referred to Fig. 3, —) calculated data by using $n = 3$, and - - -) calculated data by using $n = 5$.

3.4 Effect of coexisting CO_2 on the humidity sensitivity.

Since it is confirmed that this prediction holds, the estimated amount of adsorbed gases either H_2O or CO_2 are plotted against p_c as shown in Fig. 5. It is observed that the W_c decreases slightly with increasing $(p/p_0)_w$. The W_w is hardly affected by the coexistence of CO_2 in the low $(p/p_0)_w$ while the influence becomes larger with increasing $(p/p_0)_w$ and W_w decreases slightly with increasing p_c . This effect occurs, of course, when the humidity is detected from the change of electrical capacitance. The electrical capacitance is directly related to the amount of adsorbed water in the polymer. However, it is well-known that the concentration of CO_2 is about 0.03 % in air. The fluctuation of CO_2 concentration seems to be also small except for exhaust gases. Consequently, it is concluded that the effect of CO_2 on the sensitivity of the present polyimide sensor is quite small, when we use it in the ordinary environment.

Fig. 5 Relation between calculated W_w , W_c and p_c at several relative water vapor pressures at 30 °C; (○) $(p/p_0)_w = 0$, (△) 0.20, (□) 0.33, (▽) 0.50, (◇) 0.65 and (▷) 0.76: closed symbols, W_w , open symbols, W_c .

The values are evaluated by using $n = 3$ at $(p/p_0)_w = 0, 0.20, 0.33$ and 0.50 and $n = 6$ at $(p/p_0)_w = 0.65$ and 0.76 .

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