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Mechanism of Moisture Sensing in Organic Polymer

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Absorbing process of water molecules into polyvinyl alcohol or polymethyl methacrylate is examined. In a low humidity range, BET equation is applicable to the mass of adsorbed water vapor. It is found that the condensation of absorbed water molecules causes the occurrence of hysteresis in humidity cycles. Moreover, it is presumed that the adequate use of organic polymer containing carbonyl groups as the adsorption sites of water molecules enables us to fabricate "a relative humidity sensor".

1. Introduction

The humidity sensitizers used in the humidity sensors are classified roughly as follows:

- 1) Ceramics^(1,2)
 - 2) Organic polymer^(3,4).

In the case of the sensors using ceramics, they work relatively stable even in a high temperature range and durable against the vapor of organic solvent. However, they show relatively large hysteresis in adsorption-desorption isotherms, and need a temperature-compensating circuit for measuring relative humidity.

In the case of organic polymer, some sensors show quick response against step humidity changing, and show hysteresis scarcely. The humidity characteristics, however, changes irreversibly if the sensor is kept in a high temperature and humidity atmosphere. To settle these problems, we must reveal the mechanism of moisture sensing⁽⁵⁻⁸⁾.

We paid our attention to a point that a state of hydrophilic groups contained in organic compounds is preciser than that of ceramics. Then we have investigated the moisture sensing mechanism by using organic polymers, which contain different hydrophilic groups.

2. Experimentals

For the humidity sensitizer, polyvinyl alcohol(PVA; special grade by ALDRICH Inc.) and polymethyl methacrylate (PMMA; special grade by ALDRICH

Inc.) are selected. The structural formulae of the polymers are shown in Fig.1. PVA and PMMA possess hydroxyl groups and carbonyl groups, respectively, which work as the adsorption sites of water molecules.

The solution of the sensitizer is spread with a spinner on a quartz crystal which is the microbalance measuring head. Then the films are dried in air at 120°C. Mass variation of the polymer films (M_{water}) due to absorption and desorption of water vapor is measured by using the microbalance (EVM-32B by Nichi-den ANELVA Inc.).

A thermo-hygrostat used in the experiments is a divided flow type humidity generator of SRH-IR135ADR by SHINEI KAISHA.

The measurements are carried out in the relative humidity (RH) range from 0% to 70% at 30 °C.

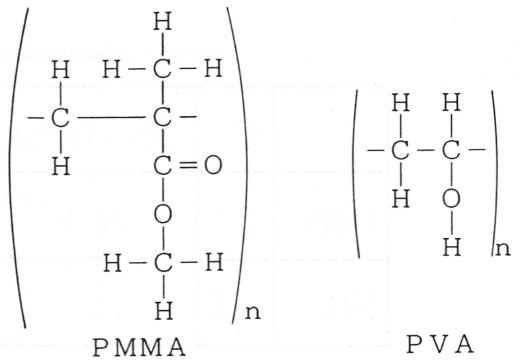


Fig.1 Structure formulae of PMMA and PVA.

3. Results and discussions

RH-M_{water} characteristics are shown in Fig.2. M_{water} of PVA is larger than that of PMMA on the whole humidity range. It is observed that the hysteresis on PMMA is very small, on the other hand, on PVA is relatively large.

The BET adsorption isotherm equation for water vapor is given by

$$M_{\text{water}}/M_1 = f(RH, C) \quad (1)$$

and

$$C = \exp(E_1 - E_L)/RT \quad (2)$$

where M₁: mass of adsorbed monolayer
 E₁: heat of adsorption for 1st layer
 E_L: heat of adsorption for Lth layer (L>2)
 C : BET constant
 R : gas constant.

BET plots of RH-M_{water} characteristics are shown in Fig.3. It is found that BET equation is applicable to PVA and PMMA in the RH range below 10% and 20%, respectively.

Over the RH of 10%, BET plot of PVA shifts it's position to lower side of theoretical line. It means that absorbed water molecules condense at the inner part of the film. The hysteresis of RH-M_{water} characteristics can be explained by capillary phenomenon.

In the case of PMMA, the BET plot over the RH of 20% shifts it's position to upper side. It is considered that the shift is caused by steric hindrance.

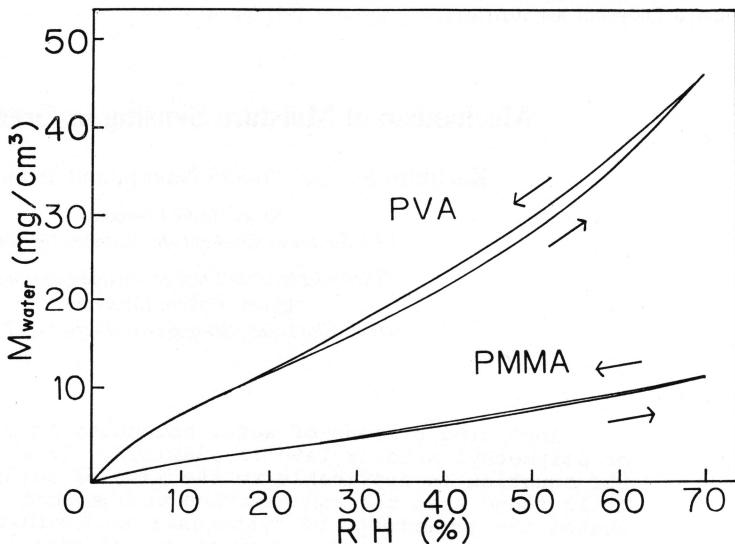


Fig.2 RH-M_{water} characteristics.

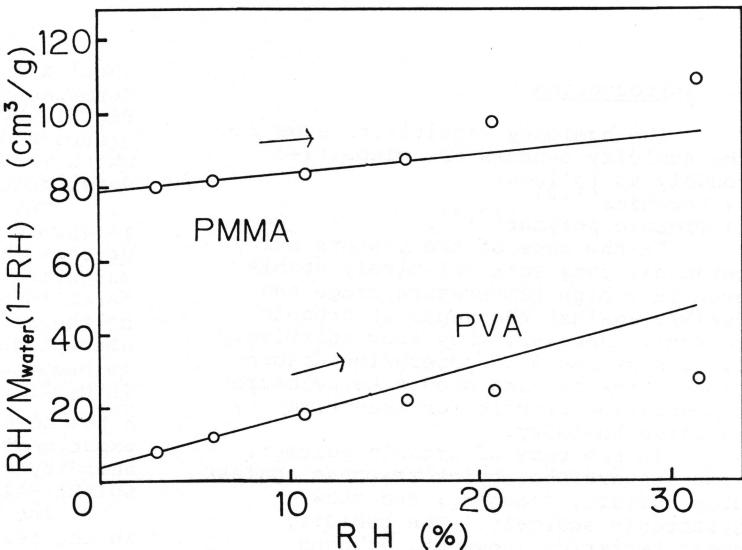
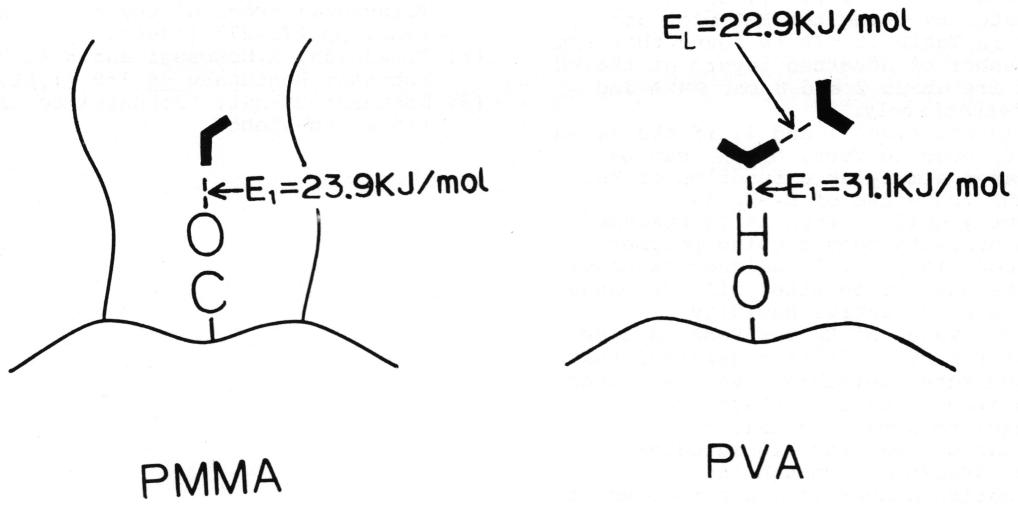


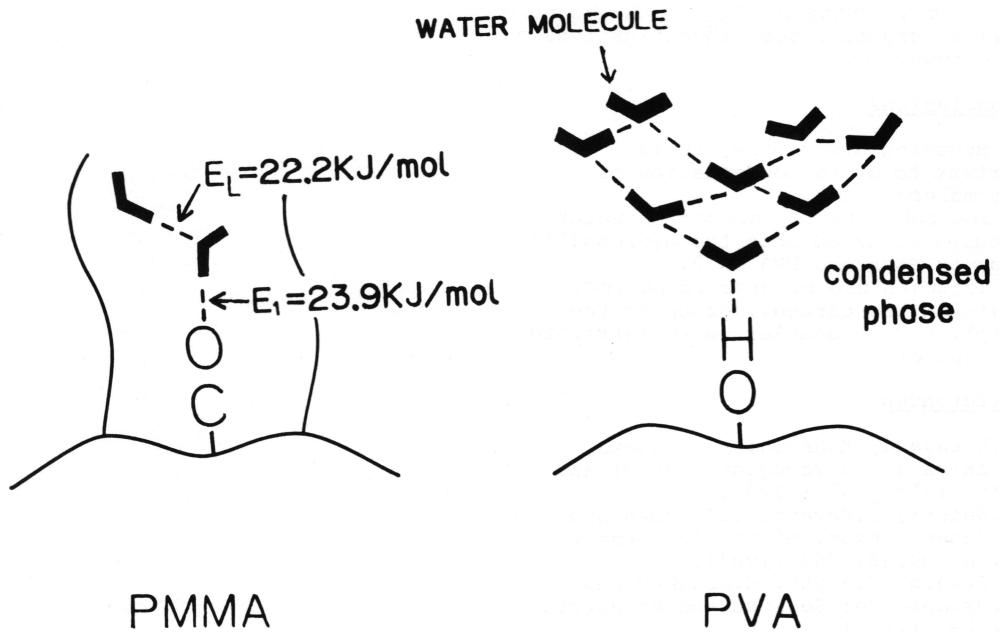
Fig.3 BET plot of RH-M_{water}.

Table 1 Adsorption factors for PMMA and PVA.

	C	E ₁ (KJ/mol)	E _L (KJ/mol)	M (mg/cm ³)
PMMA	1.9	23.9 ⁽⁹⁾	22.2	~5.6
PVA	26	31.1 ⁽⁹⁾	22.9	~4



(a) low humidity region



(b) high humidity region

Fig.4 Water absorbing model for PMMA and PVA.

The values of C , E_1 , E_L and M_1 calculated by using the BET plot are listed in Table 1. It is found that the mean number of adsorbed layers at the RH of 70% are about 2 and 8 for PMMA and PVA, respectively.

In equations 1 and 2, if the value of $E_1 - E_L$ goes to zero, M_{water} can be formulated simply as a function of RH. For PMMA the value of $E_1 - E_L$ is relatively small. Then it is presumed that a humidity sensor using polymers which contain the well designed carbonyl group as adsorption sites will respond directly to "relative humidity".

The value of E_L for PMMA is close to that for PVA. It is considered that adsorbed water molecules over 1st layer are in almost the same state. E_L obtained are about the half of vaporization heat for liquid water at 30°C of 44KJ/mol. Though the coordination number of a water molecule which is in the liquid state is 4, the coordination number of adsorbed water molecules is estimated to be 2. The similar consideration does not applicable to the humidity region where condensation occurs. Water absorbing models for PMMA and PVA are shown in Fig.4.

The conversion of M_{water} change to electrical signals, more investigations will be required.

4. Conclusions

- 1 Reducing hysteresis, it is important to avoid condensation of water molecules.
- 2 The coordination number of water molecules adsorbed onto the hydrophilic groups in PMMA and PVA is 2.
- 3 Adequate use of organic polymer containing the carbonyl group as the adsorption site enables us to fabricate an RH sensor.

5. References

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