Outgassing characteristics of a polycarbonate core material for vacuum insulation panels

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ABSTRACT

Performance deterioration with time is one of the most important issues in a vacuum insulation panel (VIP), which is mostly due to the inner gas pressure rise. Outgassing from the interior of core materials is the major gas source when the core material is a polymer. Outgassing characteristics of a polycarbonate as the VIP's core material are examined theoretically and experimentally. To measure the outgassing rate, specific outgassing tests are carried out using a pressure rise method. Diffusive outgassing mechanism is discussed based on the Fick's law. As the result, the total amount of dissolved gas and the diffusion coefficients of various gases in the polycarbonate are obtained by using the measured outgassing rate. Temperature dependence of the diffusion coefficient of nitrogen is also examined. It is shown that the outgassing rate of polymer core materials can be significantly reduced to a negligible level by a baking pre-treatment in vacuum and/or by a metal coating on the polymer surface.

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1. Introduction

Vacuum insulation panels (VIPs) as a high-performance thermal insulator have been widely developed to reduce not only energy consumption but also CO2 emissions. The VIP has various applications such as buildings, refrigerators and cryogenic devices. Although insulation performance of VIPs usually degrades with time, the initial thermal resistance of VIPs for refrigerator application is about 5 times as high as that of conventional insulation materials at the same thickness. A VIP consists of a core material to withstand the external atmospheric pressure, an almost gas-tight envelope to maintain the inside vacuum and a getter or desiccant to adsorb various gas flowing into the panel. The core material has to be porous to easily evacuate and to have a minimum solid conduction effect. For this reason, bulk type materials in the form of powders, foams and fibers are frequently used as the core material [1]. In addition to these bulk type core materials, an artificial structure like multi-layered staggered beams (Fig. 1) can be applied [2]. It was shown that the initial thermal resistance of the staggered beam VIP is similar to that of the VIP with glass fiber arranged perpendicular to the heat flow direction.

The effective thermal conductivity \( k_{\text{eff}} \) (center-of-panel \( k \) value, excluding the edge conduction effect) is the most important measure of initial and long-term performance of a VIP. It can be determined by summation of the solid conductivity \( k_s \), the gaseous conductivity \( k_g \) and the radiative conductivity \( k_r \) as

\[
k_{\text{eff}} = k_s + k_g + k_r.
\]

Among these, \( k_g \) is responsible for the long-term deterioration. It increases with pressure and pore size of the core. Because the gas pressure in VIPs increases with time due to leaks and inner outgassing, the performance deterioration is an inevitable consequence to some degree. Especially in case of the VIP with the multi-layered staggered beam core, slight pressure increase can increase \( k_g \) significantly due to the relatively large pore size [3]. Pressure rise should be suppressed, thus.

The increase of pressure in VIPs, initially at a high vacuum, is attributed to gas permeation through the envelope surface and sealing edge, and outgassing from the core material. Gas permeation through heat-sealed flanges is the most important factor responsible for the pressure increase when inorganic materials such as glass fiber or silica powder are used for the VIP's core. However, for the case of polymer core materials, outgassing from them has been suspected of the major gas source. The author's group has been working on such structures, including the aforementioned multi-layered staggered beam core made of polycarbonate. For this background, outgassing from the core material is investigated in this research.

There have been a few studies on the outgassing contribution in VIPs. For instance, outgassing in the VIP consisting of glass or ceramic spacer and stainless steel foil envelope is experimentally...
measured by Nemanic and Setina [4]. Outgassing of rigid open-celled polyurethane foam is investigated by Yang et al. [5]. However, a comprehensive interpretation of the diffusive outgassing mechanism for the VIP with the polymer structured core, as the staggered beam VIP is such an example with high outgassing potential, has not been reported yet.

The objective of this paper is thus to understand gas transport mechanisms in a vacuum for the VIP’s core material and to evaluate it experimentally. Polycarbonate is used as the test specimen in this study, although the reported results are widely applicable to other materials too. A new technique measuring diffusion coefficients depending on gas species and temperature of the bulk type material is proposed. Based on the experimental results, a few methods for reduction of the outgassing contribution are proposed.

2. Gas emission from the core material

When a material is exposed to vacuum, the gas release (or, ‘outgassing’) occurs due to vaporization of the material, gas desorption from the surface of the material and/or diffusion from inside the bulk material (Fig. 2).

Vaporization occurs in all materials. The vapor pressure is defined as the partial pressure of the vapor over the surface in an equilibrium state, and it can be expressed by the following Clausius–Clapeyron equation [6]:

\[ \ln P_s = A - \frac{B}{T} \]

where \( P_s \) is the saturation pressure, \( A \) and \( B \) are the constant. Based on the above equation, vapor pressure of various polymer materials is investigated by Jensen [7]. Vapor pressures of all the considered plastic materials in room temperature are in the range of 10\(^{-7}\) to 10\(^{-5}\) Pa. For example, polyethylene shows vapor pressure of 4.0 \times 10^{-6} \text{ Pa}. Due to lack of data, the vapor pressure of a polycarbonate is roughly estimated to be in the range of 10\(^{-7}\) to 10\(^{-5}\) Pa based on Jensen’s result. Because the vacuum level in VIPs is generally about 10\(^{-1}\) to 10 Pa, the vaporization effect can be safely ignored.

Gases or vapors adsorbed on the surface while in atmosphere are slowly released by desorption phenomena. Gas molecules can be trapped or bound on the surface by physisorption and chemisorption. Physisorption occurs when molecules are bound to the surface by van der Waals force with energy less than 10 kcal/mol and chemisorbed molecules are trapped at energies greater than 10 kcal/mol [8]. Weakly physisorbed gases such as nitrogen, oxygen and rare gases can be removed at the surface in a short pumping time, while chemisorbed gases such as most organic species, water and carbon dioxide can be removed by applying an external heat. Desorption mechanism can be interpreted theoretically using a thermodynamic or a kinetic approach. Desorption rate when the surface is covered with multiple adsorbed layers is given by the following zero order desorption model [9]:

\[ \frac{dN(t)}{dt} = a \exp\left(-\frac{E_v}{R_u T}\right) \]

where \( N \) is the total number of adsorbed molecules, \( E_v \) is the latent heat of vaporization, \( R_u \) is the universal gas constant and \( a \) is a constant. This equation can be applied to the case of the surface saturated with multiple layers of water vapor. However, the rate of desorption for the surface coverage of a monolayer or less can be expressed by the following first order desorption model [10]:

\[ \frac{dN(t)}{dt} = a_N \exp\left(-\frac{E_v}{R_u T}\right) \]

where \( a_N \) is the decay exponent.

### Nomenclature

- \( A \): surface area, m\(^2\)
- \( C \): gas concentration, Pa L/cm\(^3\)
- \( C_0 \): initial gas concentration, Pa L/cm\(^3\)
- \( d \): thickness, m
- \( D \): diffusion coefficient, cm\(^2\)/s
- \( D_0 \): diffusivity at ‘infinite’ temperature, cm\(^2\)/s
- \( E_a \): activation energy of desorption, J/mole
- \( E_v \): latent heat of vaporization, J/mole
- \( k \): thermal conductivity, W/m\(\cdot\)K
- \( N \): number of molecules
- \( P \): pressure, Pa
- \( q \): specific outgassing rate, Pa L/s\(\cdot\)cm\(^2\)
- \( Q \): gas flow, Pa L/s
- \( R_u \): universal gas constant, J/mol\(\cdot\)K
- \( t \): time, s
- \( T \): temperature, K
- \( V \): volume, m\(^3\)

### Greek symbols

- \( \alpha \): decay exponent
- \( \tau_0 \): nominal period of vibration

### Subscripts

- \( a \): apparatus
- \( c \): coating
- \( eff \): effective
- \( out \): outgassing
- \( p \): polymer
- \( s \): sample
\[
\frac{dN(t)}{dt} = \frac{N(t)}{t_0} \exp \left( \frac{-E_d}{R_u T} \right),
\]

where \(t_0\) is the nominal period of vibration of an adsorbed molecule and \(E_d\) is the activation energy of desorption. Desorption phenomena in real vacuum systems shows different characteristics with the above theoretical models due to complicated molecular behaviors such as readsorption and sticking phenomena. Empirically, it is known that the outgassing rate governed by the surface desorption is inversely proportional to time [8].

Finally, gas diffusion from the interior of a material occurs with a concentration gradient. The rich concentration of initially dissolved gas inside the material pushes it to the surface, where it is released from the surface after undergoing a desorption process. Usually, the diffusive outgassing from the bulk materials is the major residual gas source in a leak-tight vacuum system. Since the diffusion process is often very slow compared to the surface desorption, gas transport from the bulk material is a controlling factor for the outgassing rate of the materials in VIPs considering a long-term application. So, the diffusive outgassing is mainly discussed in this paper.

### 3. Outgassing measurement

Although the outgassing characteristic has been studied in numerous researches, it is difficult to exactly predict the outgassing behavior due to the combined nature of several outgassing mechanisms, microscopically irregular surface and unclear material property, etc. Therefore, the outgassing study should be accompanied by an experiment with the materials of interest. Outgassing rate can be represented by the following empirical equation [11]:

\[
q_{out}(t) = \frac{q_{1h}}{t^{\alpha}}
\]

where \(q_{out}\) and \(q_{1h}\) are the outgassing rates at \(t\) hours and 1 h respectively after the start of evacuation and \(\alpha\) is the decay exponent which ranges from about 0.2 to 1.2. The decay exponent gives a hint about the types of outgassing mechanism. For example, outgassing governed by the surface desorption gives \(\alpha \approx 1\) and diffusive outgassing yields \(\alpha \approx 0.5\) (this shall be treated in detail later) [12].

There are a few outgassing measurement methods such as the pressure rise method, the throughput method and the total mass loss method [13]. Considering the sealed-off structure of VIPs, the pressure rise method measuring the pressure increase rate of an isolated volume is selected in this study.

Before describing the experimental system in detail, the theoretical background is explained first. When a vacuum chamber containing the specific material is rapidly evacuated and left isolated with the valves completely shut down, the chamber pressure will begin to rise due to outgassing. After measuring this pressure increase rate, the total gas flow \(Q_{out}\) (Pa L/s) by outgassing can be expressed by the following equation:

\[
Q_{out} = V \frac{dp}{dt} \quad (6)
\]

where \(V\) is the void volume in the chamber. Because the outgassing also occurs on the apparatus including the chamber, gauge and valves, these background effect should be considered together. Total gas flow due to outgassing can be expressed as

\[
Q_{out} = A_s q_s + A_a q_a \quad (7)
\]

where \(A\) is the surface area, \(q\) is the specific outgassing rate (Pa L/s cm²) and subscripts \(s\) and \(a\) denote the sample and apparatus, respectively. Combining these two equations, the specific outgassing rate of the sample is rewritten as

\[
q_s = V \frac{dp}{dt} \frac{A_s}{A_v} - A_a q_a \quad (8)
\]

The second term accounting for the background effect should be minimized to get a reliable result. This effect will be discussed later with the experimental result.

The experimental apparatus consists of a bakeable stainless steel chamber equipped with a vacuum pirani gauge (PG105, Stanford Research Systems, Inc.), valves, thermocouple leadthrough and gas admittance system as shown in Fig. 3. Since the pressure indicated by a pirani gauge depends on the type of gas, the gas correction factors provided by the manufacturer are used to obtain the “actual pressure” readings for several gases. All components are connected with copper gasket flanges to eliminate gas permeation from outside. The double valve system is applied to minimize the permeation effect through an O-ring in the valve. The specific gas can be admitted into the test apparatus to consider gas dependence of outgassing rate. A heating tape surrounds the outer surface of the chamber to ‘bake’ the apparatus. A K-type thermocouple connected to the temperature controller measures the surface temperature of the sample in the chamber. The test apparatus is baked and thus degassed several times for 24 h at 250 °C to minimize the outgassing from the chamber wall and gauge. All experiments are carried out in a constant temperature & humidity room at 23 °C and R.H. 50%.

The detailed experimental procedures are as follows. Firstly, the valves connected to the test chamber are shut down to isolate with the pump system. A 3 cm × 10 cm × 0.05 cm sized plate made of polycarbonate resin (CALIBRE™ 303-10, LG DOW Polycarbonate Ltd.) is inserted into the chamber and sealed-off with the copper...
gasket flange. The venting time during the above process is fixed at 5 min. And then, the chamber is evacuated for 1 min to a base pressure of $10^{-2}$ Pa. After the valves are closed to completely isolate the chamber, the pressure increase is measured over time.

To evaluate the background outgassing effect, outgassing rates are measured with and without the sample in the chamber. Fig. 4 shows the outgassing rate for the two cases. The measured outgassing rate of the empty chamber at 1000 s is $2.1 \times 10^{-7}$ Pa L/s cm$^2$, and that with the sample is $3.3 \times 10^{-4}$ Pa L/s cm$^2$. The second term in the right hand side of the Eq. (8) representing the background outgassing effect accounts for only 0.5% of the first term. Thus, hereafter, we will assume that the background outgassing effect can be ignored.

4. Diffusive outgassing

4.1. Theory – Fick’s law

For a better understanding of the diffusive outgassing process, gas diffusion through solids is theoretically studied first. One-dimensional gas diffusion in solids can be described by the Fick’s law as the following [14]:

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t}$$

(9)

where $D$ (cm$^2$/s) is the diffusion coefficient and $C$ (Pa L/cm$^3$) is the concentration of gas. Note that diffusion coefficient depends on the gas species and the temperature.

Let’s consider, for example, a slab of uniform cross-section and thickness $d$. It is assumed that the dissolved gas concentration is uniform initially. At the surface of the solid, gas is released to the evacuated chamber. With the initial concentration $C_0$, the initial and boundary conditions are:

$$C = C_0 \text{ for } 0 \leq x \leq d \text{ at } t = 0$$

(10)

and

$$C = 0 \text{ for } x = 0 \text{ and } x = d \text{ at } t > 0.$$  

(11)

in Eq. (11), it is assumed that the vacuum level is so high that the surface adsorption is negligible to make the surface concentration zero. In the initial stage, the slab behaves like a semi-infinite medium. Over a short time period, the solution can be obtained by introducing a similarity variable $\eta = x/(4Dt)^{1/2}$ in the following error function [15]:

$$C(x,t) = C_0 \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right).$$  

(12)

The outgassing rate $q_{\text{out}}$ (Pa L/s cm$^2$) can be expressed as

$$q_{\text{out}} = -D \frac{\partial C}{\partial x}{|}_{x=0}.$$  

(13)

Using Eqs. (12) and (13), the outgassing rate over a short time period is given as

$$q_{\text{out, short}} = C_0 \left( \frac{D}{\pi t} \right)^{1/2}.$$  

(14)

Note that outgassing rate is proportional to $t^{-1/2}$ in the initial stage of outgassing ($t < t_c = d^2/16D$). This transition time $t_c$ is defined as the time of Fourier number for mass transfer $Dt/d^2 = 1/16$ when the dimensionless concentration $C_0/C_0 = 0.995$.

After the initial stage of degassing, the effect of finite wall thickness shows up. The solution of Eq. (9) for the finite wall thickness can be obtained by using separation of variable as [15]:

$$C(x,t) = C_0 4 \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin (2n+1) \frac{x}{d} \exp \left( -\frac{(2n+1)^2 \pi^2}{4D} t \right).$$  

(15)

only the first exponential term is significant for long time, so this equation can be approximated by the following equation:

$$C(x,t) = C_0 \frac{\pi x}{d} \exp \left( -\frac{\pi^2}{4D} t \right).$$  

(16)

so, the outgassing rate of the finite system can be expressed by using the Eq. (13) as follows:

$$q_{\text{out, long}} = \frac{4C_0D}{d^2} \exp \left( -\frac{\pi^2}{4D} t \right).$$  

(17)

This solution can be applied for the case of later outgassing period ($t > d^2/16D$). Note that, outgassing rate decreases slowly as $t^{-1/2}$ at the initial stage, and after a long time, it decreases as exp$(-Dt)$. This behavior agrees well with the outgassing test result for nitrogen as shown in Fig. 5. In examining Eqs. (14) and (17), it is found very important to correctly assign $D$. This, in turn, can be best-fit from the curve of Fig. 5.

4.2. Measurement of $D$ and $C_0$

According to Eqs. (14) and (17), gas diffusion coefficient in solids can be deduced if we know the outgassing rate depending on time and initial gas concentration. Gas diffusion coefficient in polymer membranes is generally measured by the steady state permeation experiment referred as a time lag method [16]. The time lag technique is based on the principle of time lag $d^2/6D$ which is required to achieve the steady state permeation through a membrane into a closed chamber. In this study, a new technique for determining the diffusion coefficient of bulk type polymer materials using the short-term outgassing rate over $t \leq d^2/16D$, which is defined as Eq. (14), is proposed and validated.

It is important to note that the diffusion coefficient depends on the types of gas, so outgassing rate should be separately measured for each dissolved gas in the sample. Hence, the composition of gas species dissolved in the polycarbonate is investigated firstly. Usually, a quadrupole mass spectrometer (QMS), referred to as a residual gas analyzer (RGA), is used to analyze the residual gas in vacuum system. The test is performed using a thermal desorption...
spectroscopy at Korea Research Institute of Standards and Science. Fig. 6 shows the mass spectrum of the released gas from the polycarbonate sample at 80 °C. It mainly consists of H2O, OH+, N2, O+, H2, CO2 and O2.

Note that water vapor gives the primary peaks at mass number of 16, 17 and 18 due to the species O+, OH+ and H2O. In addition to these gases, decomposition products like CnHx can be the outgassing species[17,18]. However, it is difficult to quantitatively identify the CnHx species due to overlapping peaks in the mass spectrum. This remains to be further research. Thus, the outgassing rate and diffusion coefficient are measured for four gases such as water vapor, nitrogen, carbon dioxide and oxygen in this study.

To measure the outgassing rate of each gas species, the following experimental procedures are carried out. Firstly, the sample is baked for 12 h at 80 °C in the outgassing test apparatus (base pressure is about 10⁻⁶ Pa) to totally deplete the dissolved gas in it. After the chamber is evacuated, a specific gas is admitted to the closed chamber at 1 atm pressure in order to dissolve the gas into the sample. This dissolving process is performed in the condition of 12 h at 80 °C and another 12 h at 23 °C. The baking condition is employed to accelerate the dissolving procedure. After finishing the degassing and dissolving process, chamber evacuation (for 1 min) and pressure rise measurement are carried out in sequence.

Since carbon dioxide and water vapor are likely to adsorb chemically on the surface of the test chamber, the above procedures for these gases are conducted in an additional vacuum chamber to eliminate the background outgassing effect as shown in Fig. 7. The samples are separately prepared in another vacuum chamber. By doing so, adsorption of CO2 and H2O to the outgassing test chamber is avoided. Also, special care is needed to dissolve H2O to the sample. To supply the water vapor only into the chamber, distilled water is injected using a syringe connected to a vacuum needle valve. As the liquid water flows into the vacuum chamber, it evaporates immediately because the chamber pressure is lower than the saturation pressure of the water. Water vapor admission is continued until the saturation state (e.g., $P_s = 3.169$ kPa @ 25 °C) is reached. After dissolving the gas into the sample, the sample is enveloped with the metal-laminated film in the chamber to prevent the surface adsorption or desorption during the movement to the outgassing test apparatus.

Another important parameter for determining the diffusion coefficient is the initial gas concentration $C_0$ in the sample. Two methods of measuring the initial gas concentration are considered. The first one measures the mass loss before and after the complete depletion of the dissolved gases in the material. However, to implement this method, exact gas composition of the evolved gases from the sample should be known. The second method measures the terminal pressure $P_{terminal}$ in a constant volume chamber after the complete depletion of gas in the sample. This method is used here. Then $C_0$ is calculated as

$$C_0 = \frac{P_{terminal} \cdot V_{chamber}}{V_{sample}} \quad (18)$$

Fig. 5. Outgassing rate of the polycarbonate for nitrogen.

Fig. 6. Mass spectrum of the gases evolved from the polycarbonate.

Fig. 7. Apparatus for dissolving water vapor and carbon dioxide into the sample.

Fig. 8. Pressure rise in the test chamber for the polycarbonate sample.
Table 1

<table>
<thead>
<tr>
<th>Gas</th>
<th>Outgassing rate at 1000 s (Pa L/s cm²)</th>
<th>Decay exponent α</th>
<th>Initial gas concentration C₀ (Pa L/cm³)</th>
<th>Measured D at 1000 s (cm²/s)</th>
<th>Reference D-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>5.2 × 10⁻⁵</td>
<td>0.6</td>
<td>22.4</td>
<td>1.7 × 10⁻⁸</td>
<td>8.1 × 10⁻⁸ [17]</td>
</tr>
<tr>
<td>O₂</td>
<td>1.0 × 10⁻⁴</td>
<td>0.6</td>
<td>27.1</td>
<td>4.3 × 10⁻⁸</td>
<td>2.9 × 10⁻⁸ [17]</td>
</tr>
<tr>
<td>CO₂</td>
<td>4.9 × 10⁻⁶</td>
<td>0.9</td>
<td>296.9</td>
<td>8.7 × 10⁻⁹</td>
<td>4.6 × 10⁻⁸ [17]</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.5 × 10⁻³</td>
<td>0.8</td>
<td>191.6</td>
<td>1.9 × 10⁻⁷</td>
<td>2.1 × 10⁻⁸ [18]</td>
</tr>
<tr>
<td>Dry air</td>
<td>7.1 × 10⁻⁵</td>
<td>0.6</td>
<td>21.4</td>
<td>3.4 × 10⁻⁸</td>
<td>5.4 × 10⁻⁹ [19]</td>
</tr>
<tr>
<td>Humid air (R.H. 50%)</td>
<td>4.2 × 10⁻⁴</td>
<td>0.7</td>
<td>67.0</td>
<td>1.2 × 10⁻⁷</td>
<td>-</td>
</tr>
</tbody>
</table>

Outgassing rate and diffusion coefficient for various gases based on a model that ignores adsorption (For values, taking adsorption into account, see text).

**Fig. 8** shows an example of pressure change rate indicating the terminal state after a day. The terminal pressure is determined when the pressure change rate during 1 h is within 0.01%. The measured initial gas concentrations for various gases are shown in Table 1. The measured value (27.1 Pa·L/cm³) for oxygen is in good agreement with the value (25.4 Pa·L/cm³) reported in reference [19].

Outgassing rate and diffusion coefficient of the polycarbonate sample for nitrogen gas at 23 °C are shown in **Fig. 9**. The decay exponent α from Eq. (5) is obtained as 0.58 from the linear fitting of outgassing rate data. This result is in fair agreement with Eq. (14) which gives α = 0.5. The diffusion coefficients range from 1.7 × 10⁻⁸ cm²/s to 3.4 × 10⁻⁸ cm²/s. To avoid the experimental uncertainty by the desorption effect at the beginning of the test, the diffusion coefficient at 1000 s is taken. At this time, the nitrogen diffusion coefficient is obtained as 1.7 × 10⁻⁸ cm²/s (Fig. 9). The oxygen outgassing rate and diffusion coefficient are shown in **Fig. 10**. The D-value is 4.3 × 10⁻⁸ cm²/s at 1000 s. The nitrogen diffusion coefficient is about 2.5 times smaller than that of oxygen. Data taken from other investigators [20–22] are also shown in Table 1. Since samples of polymer differ in diffusion coefficients even when they have the same chemical composition, data are scattered through the literature. Though scattered, the measured data are in the range of the reported data. **Figs. 11 and 12** show similar data for carbon dioxide and water vapor, respectively. Note that decay exponents for CO₂ and H₂O are higher than these of N₂ and O₂. This seems to be due to desorption caused by chemisorbed tendency of CO₂ and H₂O gases as described earlier. In other words, these species adhere to the surface even in vacuums to maintain the near-surface gas concentration above zero and it makes $q_{out,short}$ more inversely proportional to time. A more careful examination of surface desorption is, thus, appropriate here, especially for CO₂ and H₂O.

### 4.3. Consideration of surface desorption

So far we have assumed that outgassing occurs solely by the diffusion from the bulk material. According to Eq. (4), desorption rate of physisorbed gases such as nitrogen and oxygen decreases exponentially with time. Also, measured decay exponents are closed to 0.5 which is obtained from the diffusive outgassing equation. Thus, desorption effect on the outgassing rate at 1000 s later seems to be very small. However, in case of the water and carbon dioxide, the surface desorption effect should be considered due to their chemisorption characteristic.

To briefly evaluate the surface desorption effect on outgassing, a simple experiment is carried out. Assume that the total amount of gas dissolved in the solid and the total amount of initially adsorbed gas on the surface are $m_1$ and $m_2$, respectively. Since the total amount of dissolved gas is proportional to the volume of the solid, $m_1$ of the 3 cm × 10 cm × 0.1 cm size plate sample will be twice as much as that of the 3 cm × 10 cm × 0.05 cm sized-sample. As noted earlier, the total amount of gas molecules can be expressed with the terminal pressure and chamber volume. The results of test gases such as nitrogen, oxygen, water vapor and carbon dioxide are shown in **Table 2**. For nitrogen, measured terminal pressures of the 0.1 cm-thickness sample and the 0.05 cm-thickness sample are 83.3 Pa and 147.3 Pa, respectively. Using relations of $m_1 + m_2 \sim 83.3$ and $2m_1 + m_2 \sim 147.3$, it is known that the total amount of initially adsorbed molecules on the surface accounts for 30.2% of the...
dissolved gas in the solid. This means that the measured initial gas concentration is overestimated, and it results in decrease of the diffusion coefficient. For the case of water vapor and carbon dioxide, the desorption contribution is much larger than that of nitrogen and oxygen making the earlier measurement of $D_0$ dubious. As noted earlier, these gas species tend to be adsorbed in multiple layers on the surface and desorption rate is expressed by zero order desorption model as Eq. (3). Accordingly, outgassing rate and initial gas concentration seems to be greatly influenced. Because a complete theory of both desorption and diffusion has not been drawn yet, an exact estimation of the desorption effect is difficult. A further research on that is necessary.

5. Outgassing reduction

As mentioned earlier, outgassing rate decreases exponentially with time after long times. As shown in Fig. 5, the outgassing rate for nitrogen is lowered from $2.2 \times 10^{-4}$ Pa·L/s·cm² to $4.9 \times 10^{-7}$ Pa·L/s·cm² after 24 h. Although the outgassing rate decreases rapidly with time, the evacuation time cannot be taken indefinitely. Therefore, baking process in vacuum is recommended to accelerate the degassing process in the materials. The temperature dependence of the diffusion coefficient is expressed by the following Arrhenius-type equation [16]:

$$D = D_0 e^{-E_d/k_BT},$$

where $E_d$ is the activation energy for diffusion and $D_0$ is the diffusivity at ‘infinite’ temperature. This equation tells that temperature increase results in an increase in the diffusion coefficient and reduction of the time necessary to degas the material. The parameters $E_d$ and $D_0$ can be obtained from the slope of ln$D$ vs $1/T$. A series of outgassing experiments is conducted at three different temperatures for nitrogen. From the result shown in Fig. 13, $E_d = 42.0$ kJ/mol and $D_0 = 4.3 \times 10^{-11}$ cm²/s are obtained. Based on the above result, the proper baking condition can be determined. Note that the maximum baking temperature is around 100 °C considering the service temperature of the polycarbonate. Assuming that the dissolved gas in the polycarbonate core (thickness 1 mm) is only nitrogen and the baking temperature is 80 °C, the calculated outgassing rate after 6 h baking in vacuum is $1.4 \times 10^{-10}$ Pa·L/s·cm². This value is as low as the level of hydrogen outgassing rate from a stainless steel [23].

As another method of reducing the outgassing rate, metal coating on the polymer surface after baking process can be considered. It is also aimed to minimize gas dissolution during the manufacturing process. Since gases are generally unable to penetrate the metal layer, very thin metal coating layer is enough to eliminate the outgassing. However, as mentioned earlier, gas permeation through the metal coating layer also occurs through pinholes or defects [24]. It is difficult to exactly determine the equivalent diffusion coefficient through the metal coating layer (through pinholes and defects, mainly) because the pinhole density and size are distributed randomly. For the sake of simplicity, diffusion coefficient of the coating layer in overall can be derived from experimentally obtained equivalent diffusion coefficients of the coated polymer and bare polymer as follows [25],

$$L_{\text{total}} = L_p + L_c,$$

where $L$ is the thickness and subscripts $p$ and $c$ denote the polymer and coating layer, respectively. As the sample, a polycarbonate plate coated at both sides with an aluminum coating (50 nm thickness) and bare polycarbonate plate are used. Bare sample was exposed to air for a sufficient time to adsorb gas, while Al-coated one was.

Table 2

<table>
<thead>
<tr>
<th>Gas</th>
<th>Terminal pressure (Pa)</th>
<th>$m_1$ (Pa)</th>
<th>$m_2$ (Pa)</th>
<th>$m_2/m_1$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d = 0.05$ cm</td>
<td>$d = 0.1$ cm</td>
<td>$d = 0.1$ cm</td>
<td>$d = 0.1$ cm</td>
</tr>
<tr>
<td>N₂</td>
<td>83</td>
<td>147</td>
<td>64</td>
<td>19</td>
</tr>
<tr>
<td>O₂</td>
<td>101</td>
<td>186</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>CO₂</td>
<td>561</td>
<td>824</td>
<td>263</td>
<td>298</td>
</tr>
<tr>
<td>H₂O</td>
<td>588</td>
<td>849</td>
<td>261</td>
<td>326</td>
</tr>
</tbody>
</table>

![Fig. 11. Outgassing rate and diffusion coefficient for carbon dioxide.](image1)

![Fig. 12. Outgassing rate and diffusion coefficient for water vapor.](image2)

![Fig. 13. Diffusion coefficient of nitrogen depending on temperature.](image3)
shown that the measured outgassing rate is measured using the pressure rise method. It is shown that the equivalent diffusion coefficient of the Al coating layer \( D_c \) is calculated as \( 1.6 \times 10^{-13} \text{ cm}^2/\text{s} \). Although the metal coating on the polymer surface significantly reduces the outgassing rate, it also would hinder the gas outdiffusion into the vacuum during baking process as well. So, the baking pre-treatment in vacuum must be performed before the metal coating process. In many occasions, however, the metal coating process is a baking process in itself.

6. Conclusion

Outgassing characteristics of the polycarbonate as the VIP core material have been investigated theoretically and experimentally. Outgassing rate is measured using the pressure rise method. It is shown that the measured outgassing rate firstly decreases as \( r^{-1/2} \), and after some time decreases as \( \exp(-D_t) \). This behavior corresponds to the theoretical outgassing rate, which is derived from the Fick’s second law. The major gas sources of the outgassing from the polycarbonate are water, nitrogen, hydrogen, carbon dioxide and oxygen. The diffusion coefficients for nitrogen, oxygen, carbon dioxide and water vapor are separately obtained using the short-term outgassing rate and initial gas concentration. Desorption from the initially adsorbed layer on the surface significantly adds uncertainty in the obtained diffusion coefficient for carbon dioxide and water vapor. This remains to be further investigated. Temperature dependence of diffusion coefficients is evaluated for nitrogen. Based on these results, outgassing rate of the polymer VIP’s core material can be lowered to a negligible level by baking pre-treatment and/or metal coating on the polymer surface in vacuum.

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References