$^4\text{He}$ permeation and $\text{H}_2\text{O}$ uptake of cyanate ester resins — an alternative to commonly used epoxy resins at low temperature

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Abstract. Cyanate ester (CE) thermoset is a polymer with a high glass-transition temperature of $\approx 300$ °C. CE is expected to be an alternative to Stycast 1266 as a sealing and casting glue for low temperature experiments, especially for adsorption experiments where baking of the substrate at $T > 100$ °C before cooling is required to eliminate surface contaminations. We experimentally confirmed that thermosets of CE monomers are non-porous and absorbs/desorbs water very little from measurements of (1) $^4\text{He}$ permeation properties at temperatures from room temperature (RT) to 77 K and of (2) weight gains ($\delta W$) after storage for days in water and in air at RT. The $^4\text{He}$ permeation is rather large at RT but negligibly small at $T \lesssim 130$ K where the diffusion constant of $^4\text{He}$ in CE is vanishingly small. $\delta W$ in water and air are 0.3–0.5% and 0.5–1.0%, respectively, which are much smaller than those of Stycast 1266. Therefore, cyanate ester is an excellent alternative to commonly used epoxy resins especially in surface-sensitive experiments at low temperature.

1. Introduction

To seal, glue, and cast parts of experimental apparatus used at low temperature, Stycast 1266 and 2850FT epoxy resins (EPs) [1] are the most commonly used materials. However, since their glass transition temperatures ($T_g$) are below 115 °C, the EPs are unusable for some applications which require baking at $T > 100$ °C to obtain higher vacuum before cooling down. Cyanate ester thermosets (CEs) [2] are a high temperature compatible and low outgassing polymer cured at 230–250 °C. Its $T_g$ ($\approx 300$ °C) is much higher than that of EPs. CE is also distinctive for small dielectric constant and small loss tangent among various thermosetting resin systems. In addition, with reinforcing carbon fibers, CE is focused on for its excellent cryogenic durability to microcracking [3]. For other properties such as mechanical properties, processability, and thermal expansion coefficients [4], CEs are almost similar to EPs. Thus CEs should be an excellent alternative to EPs in many applications at low temperature. However, current usage

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of CEs is almost limited to a matrix resin of FRPs (Fiber Reinforced Plastics) in electronic and aerospace industries, due to the lack of characterization and precedent. Recently, pure CE thermoset is also becoming available thanks to massive consumption as a matrix resin and 3D printing technologies.

Since we are planning to use CEs as a construction material and sealing glue in experimental apparatus for adsorbed helium [5], we measured various properties of thermosets of different species of CE monomers (TA: 2,2-bis(4-cyanatophenyl)propane, P201: 1,1-bis(4-cyanatophenyl)ethane, NCN: aralkyl type cyanate ester resin, and copolymer of TA and NCN [6]), along with Stycast 1266 and other polymers. Helium leak tightness is required for chamber walls at low temperature. Polymers sometimes have microcracks or pores which become more significant at low temperature. In addition, thermal stress can generate microcracks, which actually occurred for our nylon cell after a few thermal cycles. Thus permeability of 4\(^\text{He}\) through CEs was measured from room temperature to 77 K. Although finite solubility and diffusivity of 4\(^\text{He}\) were observed at \(T \geq 130\text{K}\), we did not find leakage due to microcracks or pores. Second, water/moisture uptake were measured because, if the material of the chamber walls uptakes water from dew or air, chamber walls can desorb water which contaminates the surface of the adsorption substrate. Other properties such as specific heat, thermal conductivity, and magnetic susceptibility at low temperature will be reported elsewhere [7]. Briefly, the thermal diffusivity is rather low among thermosets and magnetic susceptibility is as low as Stycast 1266.

2. \(^4\text{He}\) permeation properties
Permeation of \(^4\text{He}\) through polymer plates was measured using two experimental settings. One, hereafter RTcell, made of brass is for measurements at room temperature as shown in figure 1, and the other, VTcell, made of copper is for those at variable temperatures between 77–340 K. The temperature of VTcell was measured using a T-thermocouple and controlled using a ribbon heater with a temperature controller or using cold vapor from liquid nitrogen. In both settings, a polymer plate (20 mm-square or \(\phi 20\text{mm-circular}\) is sandwiched by a pair of face-seal caps with O-rings. In RTcell, the O-rings are P-12 rubber rings while in VTcell, indium rings were used.

One side of the plate, upper side in figure 1, is exposed to \(^4\text{He}\) gas of a pressure \(p_1\) (0.1–1 bar). The other side is evacuated to a pressure \(p_2\) (\(< 10^{-2}\text{ mbar}\)). The \(^4\text{He}\) flow rate \(Q\) through the plate was measured using a \(^4\text{He}\) leak detector. The measured \(Q\) was between \(10^{-9}–10^{-6}\text{ mbarL/s}\). Background \(^4\text{He}\) flow rate \(Q_0\) through the seals instead of the plate was estimated using a metal plate sample through which \(^4\text{He}\) does not permeate. The \(Q_0\) is less than the detection limit of the leak detector, \(10^{-11}\text{ mbarL/s}\). Different samples of different thickness (0.3–1.6 mm) were measured for each CE monomer type. Beside them, Stycast 1266, Stycast 2850FT, two types of BT resins (copolymers of TA and bismaleimides), nylon 6, PTFE (polytetrafluoroethylene, Teflon), and PVDC (polyvinylidene chloride, Saran) were measured as shown in Table. 1.

Figure 2 shows an example of measurements of the flow rate \(Q\) for a 1.12-mm-thick TA plate. The supplying pressure \(p_1\) was abruptly changed at \(t = 0\). After a certain time lag (\(t_{\text{lag}} \approx 100\text{s}\)) due to the diffusion process through the sample, the flow rate \(Q\) begins to increase. After about 1,800 seconds, \(Q\) stops changing with the value of \(Q_{\text{sat}} \approx 1.5 \times 10^{-8}\text{ mbarL/s}\).

To derive permeation properties from such measurements, we develop a simple model for time (\(t\)) evolution of \(^4\text{He}\) concentration \(\phi\) at a position \(x\): \(\phi(x,t)\). We take the origin of \(x\) at the end of the plate of the detector side. At the sample surface of the supply side (\(x = d\), where \(d\) is the sample thickness), \(^4\text{He}\) atoms dissolve from the gas phase into the solid sample. \(\phi(x = d)\) is conveniently expressed as \(p_1S\) in terms of the gas phase pressure \(p_1\) and solubility \(S\). According to the Fick’s first law, diffusion flux in the \(x\) direction \(Q\) is described as

\[
Q = -D \frac{\partial \phi}{\partial x} \tag{1}
\]
Figure 1. Schematic view of the experimental apparatus for measurements of $^4$He permeability at room temperature (RTcell).

Figure 2. Time evolution of $^4$He flux $Q$ when the inlet pressure $p_1$ increased stepwisely at $t = 0$ for a 1.12-mm-thick sample of TA measured with RTcell.

Table 1. Permeability $P$, diffusivity $D$, solubility $S$ of $^4$He in various polymers, and number of samples $N$ measured at room temperature using RTcell.

|        | $P \times 10^{12}$ (m$^2$/s) | $D \times 10^9$ (m$^2$/s) | $S$     | $N$ |
|--------|-------------------------------|---------------------------|---------|-----|
| CE     |                               |                           |         |     |
| TA     | 6.7(7)                        | 4.1(5)                    | 0.0017(2) | 7   |
| P-201  | 3.6(8)                        | 2.8(2)                    | 0.0013(2) | 4   |
| NCN    | 3.1(8)                        | 3.1(2)                    | 0.0011(2) | 4   |
| TA+NCN | 4.6(4)                        | 3.2(4)                    | 0.0015(2) | 4   |
| BT resin |                              |                           |         |     |
| TA+BMI70 | 6.4(5)                      | 4.1(1)                    | 0.0016(1) | 3   |
| TA+BMI2300 [8] | 2.5(3)                  | 1.4(9)                    | 0.0020(11) | 3   |
| EP     |                               |                           |         |     |
| Stycast 1266 | 0.5(1)                  | 1.20(6)                   | 0.00044(5) | 6   |
| Stycast 2850FT | 0.4(1)                 | 0.11(2)                   | 0.0031(3) | 2   |
| Nylon  |                               |                           |         |     |
| MC901 [9] | 0.1                         | 0.6                       | 0.0002   | 1   |
| PTFE   |                               |                           |         |     |
| Teflon [10] | 21                         | 9.4                       | 0.0022   | 1   |
| PVDC   |                               |                           |         |     |
| Saran wrap [11] | 0.3                   | 0.004                     | 0.067   | 1   |

using the diffusion constant $D$. Thus, in the steady state with constant $p_1$, the saturated flow rate $Q_{\text{sat}}$ is described as

$$Q_{\text{sat}} = DSA \frac{A \Delta p}{d},$$

(2)

where $A$ is the area inside the O-rings exposed to the inlet gas, and $\Delta p \equiv p_1 - p_2$ is the pressure difference ($\approx p_1$). For each sample, $Q_{\text{sat}}$ values were measured for several different $p_1$, and the permeability $P$ ($= DS$) was determined by least squares fitting.

$D$ was determined independently by analyzing $t$-evolution of $Q$ based on the following
diffusion equation with boundary conditions for sufficiently small $p_2$:

$$\frac{\partial \phi(x, t)}{\partial t} = D \frac{\partial^2 \phi(x, t)}{\partial x^2}, \quad \phi(x, t) = \begin{cases} 0 & (t < 0) \\ S\Delta p & (x = d, t > 0) \\ 0 & (x = 0). \end{cases}$$

(3)

The solution of the equation above is as follows:

$$\phi(x, t) = S\Delta p \left( \frac{x}{d} - 2 \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n\pi} \sin \frac{n\pi x}{d} \exp \left( -\frac{n^2\pi^2 D}{d^2} t \right) \right)$$

(4)

from which $^4$He flow rate $Q$ at the evacuated side is determined as

$$Q(t) = AD \frac{\partial \phi}{\partial x} \bigg|_{x=0} = DS \frac{A\Delta p}{d} \left( 1 - 2 \sum_{n=1}^{\infty} (-1)^{n-1} \exp \left( -\frac{n^2\pi^2 D}{d^2} t \right) \right).$$

(5)

Here high-$n$ terms are significant only when $t$ is small, and a simple equation: $Q = Q_{sat}(1 - \exp(-t/\tau))$ can represent the time evolution of $Q$ at $t \lesssim 1.5\tau$ very well as indicated by the thin dashed line in figure 2. We determined $D$ from the relaxation time $\tau$ through

$$D = \frac{d^2}{\pi^2 \tau}$$

(6)

and $S$ as well according to the relation $P = DS$. From numerical evaluation of equation 5, $t_{lag}$ is $\approx 0.5\tau$ and proportional to $d^2$. It is confirmed by the actual measurements of CEs.

The values of $D$ and $S$ at room temperature determined by the above mentioned way for different species of CE and other polymers are summarized in figure 3 and table 1. According to the $P$-contours in the figure, nylon has the lowest $P$, PVDC and Stycast resins come next, then CEs, and finally PTFE has the highest. Both $D$ and $S$ are rather high in CEs compared to Stycast 1266 presumably because they have a larger free volume in the molecular structure ($\approx 2.2\%$) according to previous Fourier transform infrared spectrometry measurements [12]. Note that the sample of PVDC is very thin (0.011 mm thick) and was largely deformed by the pressure difference. Thus the values of $P$ and $D$ for this material should be considered as an upper limit.

Because Stycast 2850FT is an epoxy resin mixed with alumina powders, $^4$He permeation proceeds in two steps in this material characterized by $t_{lag}$ much smaller than $0.5\tau$. $^4$He atoms first permeate through epoxy portion with larger $D$ and smaller $S$ and then alumina portion with smaller $D$ and larger $S$. Therefore, special care must be taken for leak testing on this epoxy: with $^4$He sprayed the permeability may look rather small but when packed in a bag filled with $^4$He gas, its long-time permeability is as large as that of Stycast 1266.

Next, using VTcell, we measured temperature dependencies of $P$, $S$, and $D$ for TA (0.9 mm thick), P201 (0.7 mm thick), and PTFE (0.5 mm thick) which is used in commercial demountable cryogenic seals. For PTFE, we had to retighten the screws of VTcell several times to compensate its large thermal contraction. The large dots in figures 4(a)–(c) are data taken at several discrete temperatures in the same way as at room temperature, while small dots in figure 4(a) are data taken on cooling by monitoring $Q$ with $p_1$ fixed. $Q$ responded immediately (within a second) to discrete changes of temperature through the whole temperature range investigated.

As shown in figure 4(a), $P$ diminishes exponentially with decreasing $T$ and becomes undetectable below 130 K. From figures 4(b) and (c), one can see that the exponential $T$-dependence of $P$ comes from that of $D$ not from $S$ nearly $T$-independent. It indicate that the permeation is associated with molecular scale diffusion not with gas flow through randomly-distributed microscopic pores where $D$ is expected to increase with decreasing $T$ due to decreasing viscosity [13] unlike the observation. Activation energy for the diffusion $E_d$ is $2,000 \pm 200K$ for all the polymers investigated here.
Figure 3. $D$ and $S$ of $^4$He in CEs and various polymers at room temperature measured using RTcell. The thin solid lines are contours for $P$.

Figure 4. Temperature dependencies of (a) $P$, (b) $S$, and (c) $D$ of $^4$He in CEs (TA, P201) and PTFE measured using VTcell. $P$ is normalized to the value measured using RTcell at room temperature because the exposed area $A$ is difficult to estimate with indium O-rings. Large dots are data obtained with temperature fixed, while small dots in (a) are those in cooling. Previous studies on $P$ for several species of epoxy glues are also plotted [14].

3. $H_2O$ uptake
$H_2O$ uptake of CE and other polymers was investigated by monitoring a weight change ($\delta W/W_0$) relative to the initial weight $W_0$ as shown in figure 5. In water at room temperature, $\delta W/W_0$ for nylon and Stycast 1266 are 4% and 5.5%, respectively, while those for CEs are only 0.5–1%. In air at room temperature (partial pressure of $H_2O$: 10–30 mbar), nylon still absorbs a large amount of $H_2O$ (3.5%) but Stycast 1266 does less (1.5%) and CEs do very little (0.3–0.5%).

Compared to helium-4, $H_2O$ dissolves very well in polymers. Even the lowest $\delta W/W_0$ (0.3%) in our measurements corresponds to a large $S$ ($\approx 10^2$). On the other hand, $D$ values of $H_2O$ are very small: $5.1 \times 10^{-13}$ (TA) and $3.6 \times 10^{-13}$ m$^2$/s (MC901) at room temperature, determined
Figure 5. Relative weight changes of small samples (10–20 mg, 5 mm square, 0.7–0.9 mm thick) of CEs and other polymers. The samples were baked first at 80°C in air (red shaded), dropped into water (blue shaded), baked again (red shaded), and then kept at room temperature in air.

from similar measurements on thicker samples. For example, it takes a whole month for moisture in air to permeate in a 5-mm-thick chamber made of TA at room temperature. Thus, water release from polymer bulk at room temperature should be treated not as permeation but as desorption of dissolved water. The dissolved water can be removed efficiently by baking, for example, at \( T \approx 160 \) °C, where both \( D^{-1} \) and \( \delta W/W_0 \) are expected to be reduced to one-tenth.

4. Conclusions

Permeation properties of \(^4\text{He}\) and \(\text{H}_2\text{O}\) uptake for cyanate ester resins (CEs) were measured and compared with those of other polymers including Stycast epoxy resins. Although the permeability of \(^4\text{He}\) in CEs are rather high compared to the epoxies, it becomes negligibly low below \( \approx 130 \) K. No vacuum leakage was detected for CEs even after 40 thermal cycles. It was found that CEs absorb \(\text{H}_2\text{O}\) very little (\(\lesssim 1\) wt%) both in water and in air. Also, CEs are bakeable up to 250 °C, while the epoxy resins are tolerable only up to \( \approx 100 \) °C. In conclusion, it is greatly advantageous to use cyanate ester resins as a sealing, gluing, and casting resin for surface-sensitive experiments such as adsorption experiments at low temperature in which one can reduce remnant moisture, a major contamination source, much more effectively than Stycast 1266 and 2850FT.

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