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Gas permeability of thermoplastic films at low temperature: effect of glass transition and crystallinity

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Abstract

Recent interest in hydrogen technologies has led to many questions, including how to store hydrogen. Some fields, such as aeronautics, are considering storing hydrogen in the liquid state, i.e. at cryogenic conditions ($T < 120\text{K}$) and atmospheric pressure. Polymers and composite materials are good candidates for these storage tanks (high mechanical performance/weight ratio), but the phenomena of gas transport at these temperatures are still poorly understood. This study therefore aimed to characterize the permeability, diffusion and solubility of polymers materials at cryogenic temperatures. A specific experimental permeability test setup was developed for this purpose, which temperature can be controlled down to 55K (-220°C). This original device was used to study the effect of glass transition and crystallinity of semi-crystalline thermoplastic materials on permeability temperature-dependence. The results show that the glass transition reduces the barrier effect of PVDF, while the crystallinity improves PEKK impermeability at low temperature. Comparison of these two polymer families shows that PVDF has an excellent helium impermeability property that is better than PEKK's.

1. Introduction

In the current context of ecological transition, the use of hydrogen as new energy vector will help reduce greenhouse gas emissions. Depending on the type of application, hydrogen will be used and stored in different ways. For long-distance travel, aircraft manufacturers such as Airbus have opted for the use of liquid hydrogen (LH₂) [1]. This choice is motivated by the higher energy density of hydrogen (67 g/L) in its liquid form (20K at atmospheric pressure), than in its gaseous state (20g/L at 300bar). Currently, due to the small size of hydrogen, cryogenic storage tanks for this type of liquid are mainly metallic. The development of organic matrix composite tanks able to store LH₂ at low temperatures is therefore essential for the deployment of these technologies in the aeronautical industry. The low temperature permeation process through organic matrix composites is thus of prime importance as the main property required in a tank is its tightness (especially for hydrogen of very low steric hindrance). In order to better understand the mechanisms of permeability in composite materials, this study first focuses on the behavior of composite matrices, and more specifically of semi-crystalline (SC) thermoplastic (TP) matrices since their toughness, processability and repairability make them promising gas barrier candidates for such applications. Permeability of SC thermoplastics of various natures and glass transition temperatures were investigated from room temperature down to cryogenic conditions using a homemade permeability setup. A particular analysis of the influence of polymer crystallinity and physical relaxations (glass transition particularly) on permeability was achieved, since these physical properties are key factors of gas solubility and diffusion in polymers and composites [2]. Their effects on permeability have actually never been studied at very low temperature, and only few data are available in literature [3], [4], [5].

2. Materials and methods

2.1 Materials

In this study, the permeability behavior of PEKK and PVDF polymers were investigated. PEKK samples with different Terephthaloyl/ Isophthaloyl (T/I) ratios (6002, 7002 and 8002 grades) and PVDF samples were supplied by ARKEMA in the form of 100 μ m thick films. As film extrusion induces high cooling rates, initial PEKK films were globally amorphous (A). Therefore, semi-crystalline film samples were prepared by applying a one-hour heat treatment between 250°C and 200°C depending on the T/I ratio [6]. Doing so, the resulting Cold Crystallized (CC) film samples could be compared to the As-Received samples (AR). PVDF films were also investigated in this study, but contrary to PEKK films, only the as-received PVDF films were characterized. Indeed, thanks to the material's excellent ability to crystallize (even when applying high cooling rates), the films were already highly crystalline and a heat treatment was insufficient for modifying PVDF crystallinity.

2.2 Materials characterization

To establish a correlation between permeation behavior, the crystalline microstructure and phase transitions, the materials were characterized by differential scanning calorimetry (DSC Perkin Elmer 8000). Measurements were performed on polymer samples of 8-10 mg using a heating ramp of 10°C.min⁻¹.

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{100\%}} \quad (1)$$

DSC measurements were used to determine the mass crystallinity ratio X_c using Eq. 1, with ΔH_m , the melting enthalpy in J.g⁻¹, ΔH_{cc} , the cold crystallization enthalpy, $\Delta H_{100\%}$, the theoretical melting enthalpy of 100% crystalline polymer (130 J. g⁻¹ for PEKK [6], 105 J. g⁻¹ for PVDF [7]). DSC results can also be used to measure the transition temperatures, and in particular glass transition and melting temperatures. The results obtained for the various PEKKs and PVDF samples are summarized in the Table 1.

Table 1. Physico-chemical properties (degree of crystallinity X_c , glass transition temperature T_g , melting temperature T_m , Monomer) of PEKK films (AR: As-Received; CC: Cold-Crystallized) and PVDF film (SC: Semi-Crystalline).

Specimen	State	$X_c(\%)$	T_g (°C)	T_m (°C)	Monomer Chemistry	Film Thickness (μ m)	
PEKK6002	A	1.1	160	305	(C ₂₀ H ₁₂ O ₃) _n	100	
	CC	22					
PEKK7002	A	3.6	162	332			
	CC	28					
PEKK8002	A	6.2	165	358			
	CC	33					
PVDF	SC	53	-40	169			(C ₂ H ₂ F ₂) _n

2.3 Cryogenic gas permeability apparatus

Permeability was measured using a test device specially developed for the project. As described in Figure 1, it is based on the principle of partial pressure difference between an inlet and a detection chamber that are separated by the tested sample. For safety reasons, the gas used in this study for permeability is helium 6.0, which is smaller in size than hydrogen [8] and is therefore giving conservative results as regards to hydrogen. The absolute pressure was set to $p=0.5$ bar in the inlet chamber and $p < 10^{-5}$ mbar in the detection chamber. The gas passing through the material was detected by a mass spectrometer (100u, tungsten filament).

To be cooled down, the permeability cell is connected to a cryocooler (77K/34W) by copper braids and coupled to a resistive heater up to 100W for temperature regulation. This cold/heat combination provides a thermal power balance leading to thermal levels between ambient temperature and 55K (temperature

measured with a platinum thermometer) on the permeability cell (Figure 2). To reach these temperatures, the cell was thermally isolated in a vacuum chamber (Figure 1) which is equipped with a second turbomolecular pump to create a vacuum of at least 10^{-5} mbar.

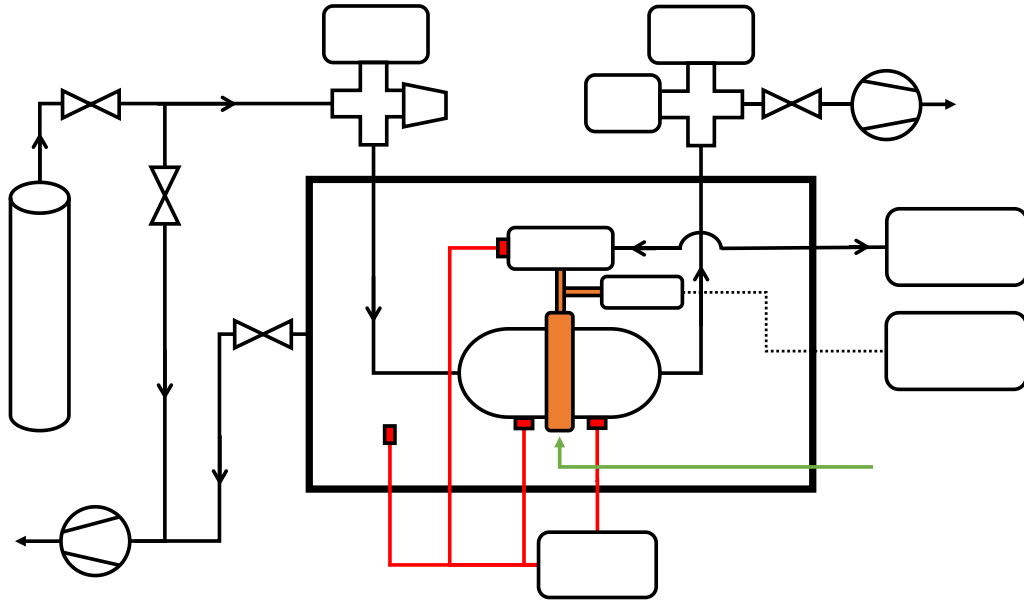


Figure 1. Schematic diagram of cryogenic permeability measurement setup

During a permeability experiment, the mass spectrometer measures the helium partial pressure over time (Figure 3) and the steady-state partial pressure p_{∞} can then be easily determined. This value was used to determine the polymer permeability with Eq. 2.

$$P = \frac{p_{\infty} \dot{V} t h}{A \Delta p R T} \quad (2)$$

In Eq. 2, \dot{V} is the turbomolecular pump volumetric flow rate (m^3/s) for helium, th the thickness of the sample, A the sample area (m^2), Δp the difference of upstream and downstream pressures (MPa), R the molar gas constant (J/K/mol) and T the temperature (K). The diffusion coefficient was then determined from the time at half steady-state partial pressure value $t_{0.5}$ with Eq. 3 [9].

$$D = \frac{t h^2}{7.199 t_{0.5}} \quad (3)$$

Finally, the solubility coefficient was deduced from P and D with Eq. 4 [2].

$$S = \frac{P}{D} \quad (4)$$

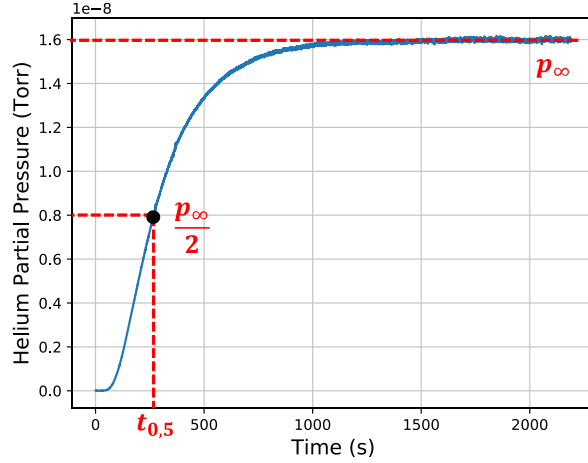


Figure 3. Raw curve obtained by mass spectrometry with identification of the steady-state partial pressure in red

Permeability, diffusion and solubility coefficients are temperature-dependent according to an Arrhenius law (Eq. 5, 6 and 7). The coefficients can therefore be defined from the pre-exponentials P_0 , D_0 and S_0 factors, and from E_p , E_D and H_S , the activation energies of permeation, diffusion and solubility in kJ/mol (with $E_p = E_D + H_S$ and $P_0 = D_0 S_0$) respectively. To be noted that $H_S = H_{\text{cond}} + H_{\text{mix}}$ represents the enthalpy of condensation (<0 and a low value for gases with low condensability such as helium or hydrogen) and the enthalpy of mixing (>0 and a high value when the gas/polymer cohesion is high) respectively [2].

$$P = P_0 e^{-\frac{E_p}{RT}} \quad (5)$$

$$D = D_0 e^{-\frac{E_D}{RT}} \quad (6)$$

$$S = S_0 e^{-\frac{H_S}{RT}} \quad (7)$$

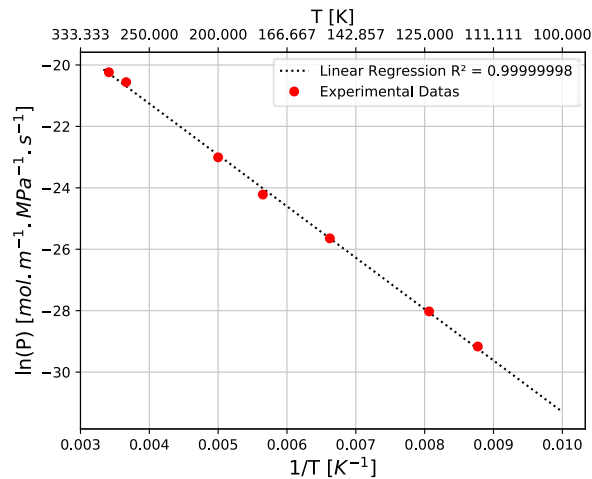


Figure 4. Permeability data of a PAEK film as a function of temperature

Figure 4 shows a reference curve obtained for a Poly(Aryl-Ether-Ketone) film between room temperature and 114K. Since the test time reached one week at 114K, the thermal study was not performed for lower temperatures. The results obtained for this polymer of high glass transition exhibit a perfectly linear trend in the full range of temperature ($R^2 > 0.99$). On the one hand, this demonstrates

the instrument's ability to control temperature isotherms and the accuracy of the mass spectrometer, and on the other hand it allows extrapolating permeation data to lower temperatures.

3. Analysis of permeability, diffusion and solubility of PVDF and PEKK grades

Permeability, diffusion and solubility measurements were carried out between room temperature and 100K, which is the lowest temperature reached within the maximum limit of one week per test. For each polymer reference, at least 4 temperatures were explored to ensure the accuracy of the linear regression of the Arrhenius law. The permeability results are plotted in Figure 5 and the corresponding values of P_0 , D_0 , S_0 , E_P , E_D and H_S are summarized in Table 2.

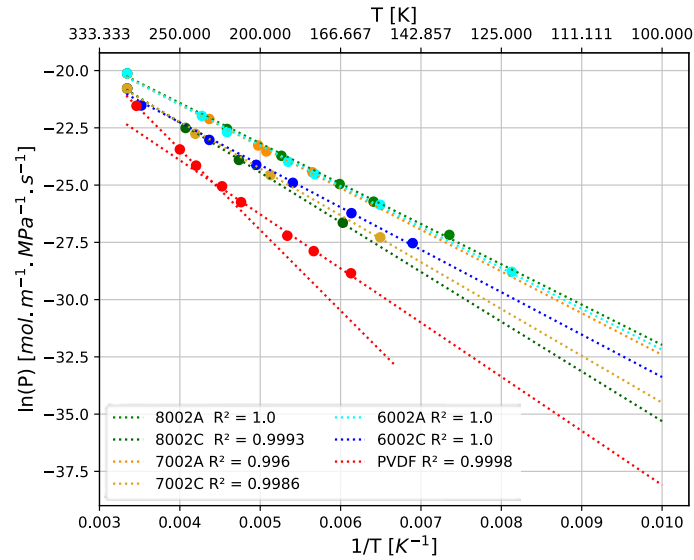


Figure 5. Temperature dependence of He permeability of PEKKs and PVDF films

Figure 5 compares the cryogenic permeability of PEKKs and PVDF as a function of temperature. The results show that for these specific temperatures, PVDF has much better barrier properties than PEKK polymers. This can be related to the crystalline content since PVDF has a much higher degree of crystallinity than the most crystalline PEKK sample.

Contrary to PEKK, PVDF temperature dependence is not linear over the full range of temperature, but bilinear with a change in thermal dependence at around 230K which corresponds to the glass transition temperature T_g of PVDF. This bilinear trend demonstrates the sensitivity of the experimental setup and its ability to capture slight changes. Despite this change in temperature dependency, PVDF remains more impermeable at cold temperatures than any of the PEKK grades.

As explained by Yasuda et al. [12], the permeability behavior can be related to the change in free volume within the polymer as regards to the gas size. A lower permeability in the glassy state than in the rubbery state was therefore expected. The change in permeability activation energy is actually in line with the change in thermal expansion of polymers at glass transition and the reduction of free volume [2].

Concerning the permeability of PEKKs, the results from Table 2 show that the activation energy E_p increases with the degree of crystallinity, independently of the T/I ratio. A comparison of the three cold crystallized 6002, 7002 & 8002 PEKK grades shows that the most crystalline possesses the highest activation energy, while their amorphous variants exhibit equivalent permeability behavior.

Table 2. Values of pre-exponential factors and activation energies obtained by linear regression of permeability, diffusion and solubility values.

Material		P_0 (mol/m/s/MPa) $\times 10^7$	E_p (kJ/mol)	D_0 (m ² /s) $\times 10^7$	E_D (kJ/mol)	S_0 (mol/m ³ /MPa)	H_S (kJ/mol)
PEKK6002	AR	5.92	14.8	1.03	15.7	4.31	-1.26
	CC	3.55	15.4	0.64	15.8	3.73	-0.99
PEKK7002	AR	6.77	15.1	1.69	16.5	3.99	-1.39
	CC	7.89	17.0	1.61	17.4	4.90	-0.40
PEKK8002	AR	5.72	14.6	1.26	16.0	2.76	-2.05
	CC	12.6	18.0	0.98	16.0	4.04	-0.02
PVDF	T > T _g	863	29.2	8.38	22.3	85.7	6.68
	T < T _g	5.24	19.7			1.30	-1.56

By decoupling permeability into diffusion and solubility coefficients (Figure 6 and 7), it appears that whatever the polymer, diffusion continuously decreases over the entire range of temperature. The linearity of the diffusion curves is almost perfect for all materials with correlation coefficients close to unity, which confirm the validity of Eq. 6 to define the temperature dependency of diffusion coefficient. For PEKK polymer, although crystallinity improves the barrier effect according to the permeability coefficients [2], crystallinity has very little effect on the thermal dependence of the diffusion coefficient. Indeed, the identified D_0 and E_D parameters (Table 2) are almost identical for all grades and only a slight decrease of the pre-exponential factor can be noted for CC samples. Surprisingly, the results for PVDF also indicate that glass transition has no effect on helium diffusion.

Regarding solubility, experimental data led to very different behaviors. For PVDF, the change in permeation behavior at 230K is directly related to a change in solubility. The activation enthalpy H_S is first positive above T_g which is in agreement with the results of Flaconnèche et al. [10]. Indeed, in their study of the thermo-dependence of P, D and S at elevated temperatures, i.e. above T_g between 370K and 312K, they observed a decrease in solubility with the decrease in temperature. However, it is interesting to note that the solubility activation energy turns negative below glass transition, indicating an increase in solubility as temperature decreases.

Decades ago, Meares, in his study of the diffusion and solubility of PolyVinyl Acetate, already observed such sign inversion of solubility enthalpy at the glass transition [11]. Assuming that solubility results from the ability of gas molecules to create and fill sorption sites, he concluded that the enthalpy of solution was negative because of the existence of available micro-pores within free volume that are still accessible for helium solubilization below T_g, although gas diffusion is hindered when decreasing temperature. The negative enthalpy of solubilization then would be the consequence of a decreased enthalpy of mixing and a higher enthalpy of condensation per unit volume of polymer.

Even if H_S values are small and the solubility coefficients more scattered than diffusion ones, the sorption activation enthalpy is also negative for all PEKK films. Regarding PEKK solubility results, it appears that the higher the crystalline ratio, the higher the solubility enthalpy. Nevertheless, differences between CC and AR samples are not only related to crystallinity. Indeed, it seems that the T/I ratio also affects solubility with increasing differences between CC and AR solubility S_0 and solubility enthalpy H_S as the T/I ratio increases.

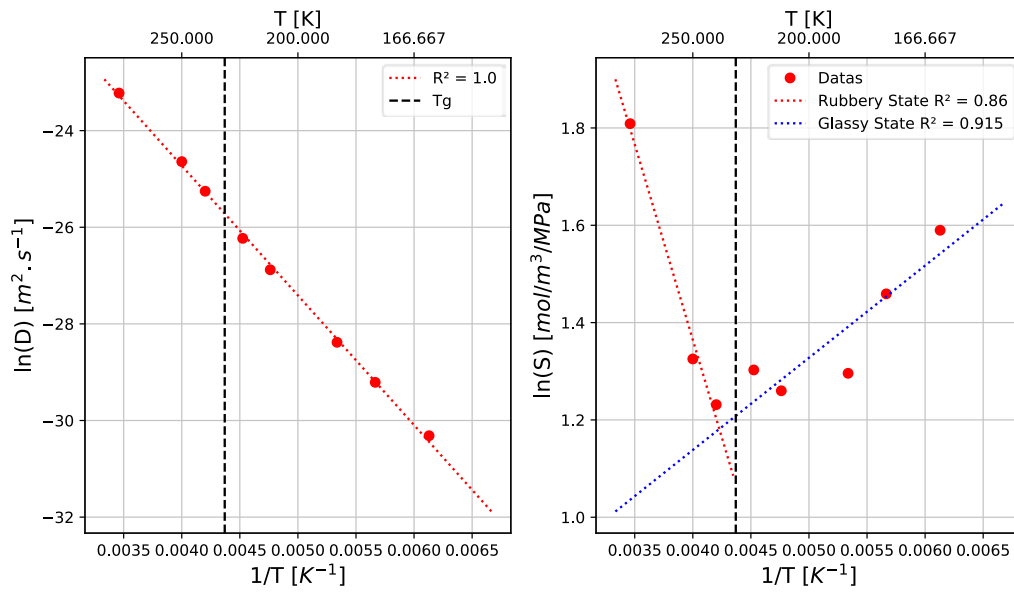


Figure 6. Evolution of helium diffusion (left) and solubility (right) in PVDF as a function of temperature.

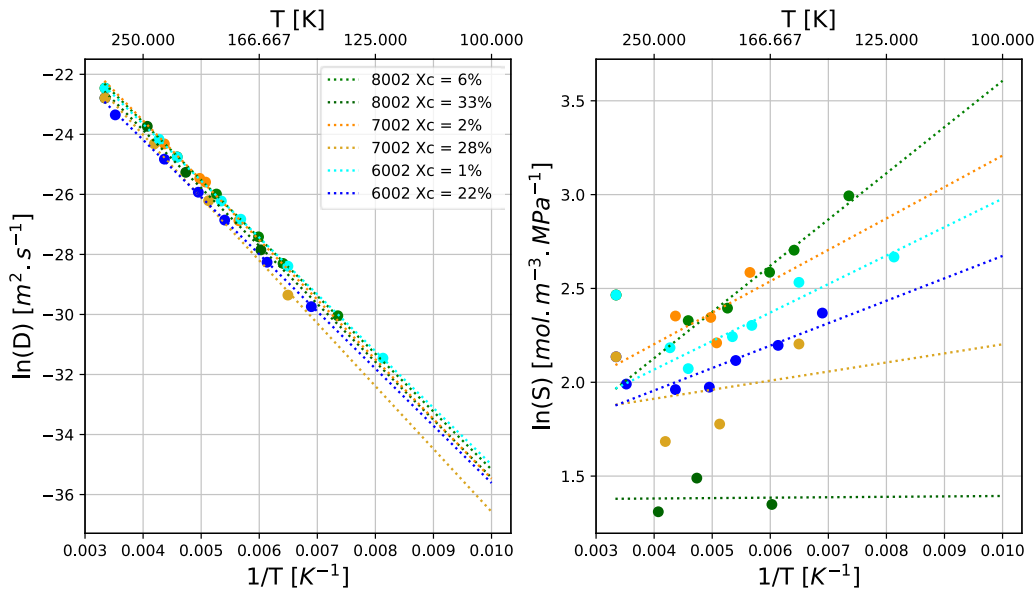


Figure 7. Evolution of helium diffusion (left) and solubility (right) in PEKKs as a function of temperature.

4. Conclusions and perspectives

The development of an apparatus for measuring cryogenic gas permeability has made it possible to study the influence of temperature for various polymer materials with low and high glass transition temperatures. Although these materials are highly impermeable when the temperature decrease, the ability of the test device to control temperature and to capture slight changes allowed revealing original features never highlighted before, like the influence of PVDF glass transition. In addition, the study of materials with different crystalline fractions confirmed what had already been studied at room temperature: semi-crystalline thermoplastic polymers are much more impermeable as the degree of crystallinity increases. However, some questions remain, such as why does the activation enthalpy of

gas solubility in the glassy state increase when the temperature decrease? To answer these questions, more detailed analysis such as quantifying the free volume in glassy materials with positron annihilation spectroscopy could be carried out to help understand these phenomena.

Acknowledgments

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