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► To cite this version:

David Chapelle, Liping Feng, Philippe Nardin, Jean Rauch. Assessment of the gaz permeation through thin coated polymeric membranes: improvement of the gas barrier ability for hydrogen storage. International Conference on Diffusion in Materials (DIMAT 2011), Jul 2011, Dijon, France. 10.4028/www.scientific.net/DDF.323-325.393 . hal-02300554

HAL Id: hal-02300554

<https://hal.science/hal-02300554>

Submitted on 9 Jan 2020

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Assessment of the gas permeation through thin coated polymeric membranes; improvement of the gas barrier ability for hydrogen storage.

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Keywords: Hydrogen barrier, gas permeation, hydrogen storage

Abstract. We investigate and simulate the permeation behavior of PET membranes on which thin coatings are deposited. Depending on the parameters of deposition and on the thin coating thickness, we assume this alteration could make it possible to decrease by one order of magnitude the permeation coefficient. Some specific developments have been necessary, all the more not only a decrease of permeation is expected but also the mechanical strength of the thin coating during severe mechanical loadings. We consequently design devices dedicated to the permeation test but also to the bulge and blister tests which permit to check the mechanical properties of the film and its adhesion on the PET surface. This paper focuses on the permeation test.

Introduction

The emerging of a hydrogen energy world requires developing new materials and new technologies (but also standards) whether it be for hydrogen production, storage or utilization [1]. When hydrogen storage or utilization is accounted, one of the main challenges to overcome is to design materials which prevent structure from any leakage or for which the kinetics of the leak could be controlled. Thus, for high pressure vessel, two types of liner, it means barrier envelop, are commonly used, a metallic liner or a polymeric liner. The latter one allows the structure to fulfill the standards requirements for cycling loading while presenting a 10 times permeation increase compared to a metallic liner.

Poly (ethylene terephthalate) (PET) is a very valuable polymer because PET is lightweight, optically transparent, unbreakable and also recyclable [2, 3]. PET materials can be blown into containers and bottles used as the packaging of food and water. However, the application of PET containers to some products like gas or water involves significant difficulties because of the insufficient gas barrier properties of PET. Thus, developing new films or processes to improve gas barrier properties of PET are highly demanded in the market [2, 4].

Previous studies focused mainly on the improvement of barrier properties of PET applications in food and drink packaging industry. Therefore, many coatings were investigated, such as AlOx [5], SiOx [6], AlOxNy [7] and carbon films [8], because of their excellent oxygen and water vapour barrier performance. Presently, PET can be formed into pipelines used as the conveyance of high pressure gas or petroleum products. However, there are very few studies of the barrier properties of PET applications in high pressure hydrogen transportation. The microstructural and gas barrier properties of thin coatings deposited on polymer substrates are of great importance to the high pressure hydrogen transportation. Additionally, the process and surface treatment of polymers prior to coating are efficient ways of modifying the surface ability of PET to then produce a good deposit. In this study, metallic films are deposited on PET substrates by RF magnetron sputtering and

evaporation. Pre-treatments of Ar plasma and Ar beam are adopted for RF magnetron sputtering and evaporation, respectively. Current work is focused on investigating the pressure hydrogen permeation behavior of metallic films prepared on PET by different processes.

Theory

Gas permeation through a membrane is a rather well known phenomenon which could be depicted in three stages. The first one refers to the gas penetration on the inlet side, the second is the matter transportation from one side to the other and for which the driving-force is the concentration gradient, the third one is the exit of gas on the outlet surface. The permeation test relates to the technics which allow quantifying the matter transportation. This can be fulfilled using easily accessible manometric method or less affordable, but more accurate, technics as mass spectroscopy. In literature, background on diffusion is well documented [9] and its field of application is large [10]. Fig.1 introduce a schematic representation but also the characteristic curve of such an experiment.

Figure 1: Principle scheme (left) and characteristic curve (right) of the permeation phenomenon through a plane membrane.

The following expression provides the gas volume crossing the plane membrane according to time while steady-state is reached, the permeability and the gas concentration at surface, respectively:

$$Q(t) = \frac{DC}{e} \left(t - \frac{e^2}{6D} \right), \quad (1)$$

$$P = DS, \quad (2)$$

$$C = Sp. \quad (3)$$

Physical quantities are (*STP*: Standard Pressure and Temperature) Q , the gas volume at time t ($\text{cm}^3(\text{STP})$), D the diffusion coefficient (cm^2s^{-1}), e the membrane thickness (cm), C the gas concentration at surface ($\text{cm}^3(\text{STP})\text{cm}^{-3}$), P the permeability ($\text{cm}^3(\text{STP})\text{bar}^{-1}\text{cm}^{-1}\text{s}^{-1}$), S the gas solubility in the membrane ($\text{cm}^3(\text{STP})\text{bar}^{-1}\text{cm}^{-3}$) and p the gas pressure (bar).

The time-lag, defined as the intercept between the steady-state linear plot and the time axis, is expressed as:

$$L = \frac{e^2}{6D}. \quad (4)$$

Experimental

As polymer substrates, 1 mm thick PET disc membranes with a 50 mm diameter are prepared (Fig 2.a). Metallic thin films (Al, Ti and Cr) with thickness less than 300 nm are deposited on the PET substrates by RF magnetron sputtering and evaporation. PLASSYS MP500 system is used for RF magnetron sputtering and EVA 450 equipment is used for evaporation. The PET substrates are dipped in ethanol solution and cleaned using ultrasonic apparatus. After that, samples are dried to remove adsorption dust on the surface, and finally present mirror like surface on the metallic thin coating side (Fig 2.b). The purity for metallic target is greater than 99.99%. The substrate-to-target distance is about 6.0 cm and 40 cm for the sputtering and evaporation deposition, respectively.

Figure 2: 1 mm thick PET disc membranes with a 50 mm diameter a), with metallic thin coating b)

LEICA INM20 optical microscope measurements are performed to observe the films surface. Hydrogen permeation measurements were carried out using in-house developed permeation device (Fig. 3), having three permeation cells and allowing monitoring the inlet pressure from 1 to 10 bar by means of a Brooks 5866 pressure regulator. The hydrogen transport is assessed by pressure measurement using 0-250 mbar Baumer transducers.

Figure 3: Permeation device with 3 parallel permeation cells (4th is for swelling measurement)

Results and discussion

Al, Cr and Ti deposition

This section is dedicated to the comparison of the gas barrier potential of three different metallic thin coatings, i.e. Aluminum coating, Chromium coating and Titanium coating. The composition of the film is expected to significantly modify the behavior of the so-made composite membrane, regarding the gas flow. At the same time, evaporation and sputtering methods to deposit the thin films are performed for comparison and the influence of surface preparation with respectively Ar beam or Ar plasma pre-treatment is investigated. Table 1 gives the parameters used in order to carry out these pre-treatments or depositions.

Table 1: Pre-treatment (PT) and deposition (D) parameters

	Sputtering		Evaporation	
	PT	D	PT	D
Pressure (10^{-3} mbar)	7	7	0.4	0.005
Power (W)	150	-	350	300
Intensity (A)	-	1	-	-
Time (s)	120	300	90	-
Speed (A/s)	-	-	-	5/40(Al)
Gas flow (sccm)	56	56	10	-

Before having permeation experiments on those samples, some observations with an optical microscope have been carried out. These reveal relevant discrepancies of the resulting thin film depending on the parameters and on the metal. Thus, results are clearly distinct according to the metal deposited: optical aspect of Ti and Cr films is far from Al film aspect. For Ti and Cr thin coatings, observations show a network of cracks. The worst results are obtained when the deposition is made using evaporation method, even worse when there's no pre-treatment. Fig. 4 illustrates these comments showing images of Ti and Cr thin coatings by evaporation method, with or without any pretreatment.

Figure 4: Optical observations of Ti and Cr thin coatings

- a) Ti evaporated without pretreatment, b) Ti evaporated with Ar beam pretreatment
- c) Cr evaporated without pretreatment, d) Cr evaporated with Ar beam pretreatment

At the opposite, on the Al thin coating never any failure has been observed. Visual aspect of the surface is clearly dependent on preparation process but no drastic defect has been evidenced during observations. Fig. 5 presents images of the Al thin coatings obtained on the PET substrate with evaporation method and no pretreatment, and with sputtering method and Ar plasma pretreatment.

Figure 5: Optical observations of Al thin coatings

a) Al evaporated without pretreatment, b) Al sputtered with Ar plasma pretreatment

Obviously, such reports lead to predict a poor efficiency of Ti and Cr thin coatings whatever the deposition process is. Failures observed on those coatings involve easy ways for gas flow. This is confirmed by the permeation tests performed consecutively. At the opposite, regardless of the applied process to get Al thin coatings, permeation tests show homogeneous results with a fourfold reduction of the permeability in comparison with permeability of the PET membrane.

Al thickness effect

In accordance with previous results, we decided to focus on aluminum thin coating deposition using sputtering method. The following investigations aim to assess the effect of the Al thin coating thickness on the barrier efficiency. Thus, new samples have been prepared with parameters as detailed in Table 2 (pressure is 7×10^{-3} mbar). The applied pretreatment is identical to the one used in the above section for sputtering, i.e. pressure is 7×10^{-3} mbar, power is 150 W and process time is 120 s.

Table 2: Sample sets depending exposure time and measured thickness

	Set 1	Set 2	Set 3
Intensity (A)	1.5	1	1.5
Exposure time (s)	60	120	120
Estimated Al thickness (nm)	< 75	100	150

For each set of samples, three permeation tests have been performed using the three available cells. The hydrogen inlet pressure is monitored and fixed at 4 bar. Fig. 6 plots the mean values of the gas quantity which passed through the composite membrane versus time. It is worth to immediately point out that the results for 150 nm thin coating should be consider with real caution. Pressure monitoring during this experiment is clearly defective and involves in our opinion an underestimate of the amount of gas which goes through the membrane. This justifies the choice made in Table 3 to give an estimation of the slope, which gives the gas flow trend, for these specimens (**bold italic**).

Except the check of the monitoring pressure for 150 nm thin coating, the previous option is motivated by results from the two other thin coating thickness experiments. Contrarily to our first hypothesis, the thickness increase of the thin coating leads to a decrease of the gas barrier efficiency.

Figure 6: Permeation measurements on PET substrate with Al deposition (75, 100 and 150 nm) Mean hydrogen quantity (cm^3 (STP)) is plotted versus time (h).

Table 3: Sample sets depending exposure time and estimated thickness

	Slope $10^{-3} \text{ cm}^3 / \text{h}$	L <i>heure</i>	D $\text{cm}^2 \text{s}^{-1}$	C $\text{cm}^3(\text{STP}) \text{cm}^{-3}$	S $\text{cm}^3(\text{STP}) \text{bar}^{-1} \text{cm}^{-3}$	P $\text{cm}^3(\text{STP}) \text{bar}^{-1} \text{cm}^{-1} \text{s}^{-1}$
PET 1 mm	15.8	4,8	9.64×10^{-8}	4.32	0.7	8.77×10^{-8}
PET + 75 nm Al	2.9	8	5.79×10^{-8}	1.39	0.35	2.01×10^{-8}
PET + 100 nm Al	5.8	7	6.61×10^{-8}	2.43	0.61	4.03×10^{-8}
PET + 150 nm Al	6.8	6	7.72×10^{-8}	2.45	0.61	4.71×10^{-8}

Thus, the assessed efficiency of a 75 nm Al thin coating is more than 3 times the efficiency of the single PET membrane, while the 100 nm Al thin coating is twice less efficient compared to the 75 nm Al film. The next investigations should help us to establish the relevance of such a conclusion by controlling the residual stresses in the thin coating, the amount of defect correlated to the previous measurements. Another controversial issue is the permeability mentioned in literature for PET membrane. In [11], at 25°C , permeability is equal to $39.4 \text{ cm}^3(\text{STP}) \text{mm atm}^{-1} \text{m}^{-2} \text{day}^{-1}$, i.e. $4.56 \times 10^{-9} \text{ cm}^3(\text{STP}) \text{bar}^{-1} \text{cm}^{-1} \text{s}^{-1}$, and in [12], the given value at 50°C is 1.31 Barrer ($10^{-10} \text{ cm}^3(\text{STP}) \text{cmHg}^{-1} \text{cm}^{-1} \text{s}^{-1}$), i.e. $9.96 \times 10^{-9} \text{ cm}^3(\text{STP}) \text{bar}^{-1} \text{cm}^{-1} \text{s}^{-1}$.

Conclusions

This paper investigates the permeation through polymeric membrane on which thin coating is deposited in order to increase the gas barrier efficiency. Ti, Cr and Al films have been tested in order to address their suitability as a gas barrier. This study reveals that only Al thin coating is acceptable with the deposition parameter range which was taken into account. In an unexpected way, the increase of the Al thin coating thickness seems to lead to a decrease of the barrier efficiency. Regarding at the initial goal, the decrease of the global composite permeability is far from one order of magnitude. Following investigations involve checking the above mentioned results but also estimating the durability of such a barrier when used on a structure subjected to severe environmental and mechanical loadings.

Acknowledgement

This work is supported through ‘Region Project’ by Région Franche-Comté. A financial support has been brought for device development but also for a post-doctoral position.

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