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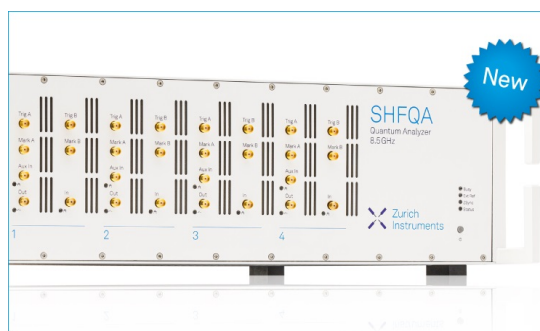
# A versatile technique for *in situ* investigation of the effect of thin film cracking on gas permeation of coated flexible polymers

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**ABSTRACT**

In this work, we report the development of a measurement chamber linked with a quadrupole mass spectrometer (QMS) for *in situ* investigation of the effect of thin film cracking on the gas permeation of coated flexible polymeric substrates. The chamber enables the establishment of a bulged state of the substrate/coating system, which causes the cracking of the coating layer. The increase in the gas permeation rate due to the presence of cracks can be monitored precisely using the QMS without movement or re-clamping of the samples between each measurement step. This method eliminates the probability of uncontrollable mechanical changes in the sample, and with the mass spectrometer, high sensitivity, reliability, and reproducibility of the experimental data become available.

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Measurement of gas permeation through thin film coated flexible polymer membranes is crucial for applications in food packaging, chemical separation, medicine, and micro- and nano-electronics.[1–3] To cover temperature-sensitive substrates, the most frequently used materials are metal–oxides, metal–nitrides, and carbides.[4–6] Among these, $Al_2O_3$ is the most extensively studied passivation layer.[7–10] Permeability measurements of ultrabarriers with the most widespread devices from Mocon (coulometric sensor) and Brugger (piezoresistive pressure sensor) suffer from sensitivity problems as their lower detection limit does not meet the requirements for OLED encapsulation: water vapor transmission rate less than $10^{-6}$ g m$^{-2}$ day$^{-1}$ and oxygen permeability lower than $10^{-3}$ cc m$^{-2}$ day$^{-1}$. More precise evaluation of water permeation data can be made by the radioactive HTO (hydrogen–tritium–oxygen) tracer method and with electrical or optical Ca tests.[2] Mass spectrometry offers short experimental times and high sensitivity, down to ppb levels, and uniquely, by measuring the permeant partial pressure instead of the total pressure within the system, simultaneous determination of permeability for gas mixture components with different mass to charge (m/z) ratios is possible.[12,14] Mechanical stability of the deposited films is especially important for applications where flexibility is a criterion, as in thin film encapsulation

of organic light-emitting diodes (OLEDs). Cracking is a major issue in ultra-barrier films as they form penetration paths, thus increasing water and gas permeation, which, consequently, must be considered when barrier films are applied to flexible substrates as the films are required to bend, flex, or roll during production or end-use.[11–13] The visualization and characterization of thin film cracking, and revealing the consequence of these defects on permeation could be quite challenging on nanofilms.[1,14] The failure mode of brittle films on flexible substrates, such as channeling/cracking or debonding, mainly depends on the substrate modulus, layer adhesion, and film cohesion. Experimental approaches based on cracking analysis of stressed films (fragmentation testing) are a very efficient way to characterize the mechanical performance of thin films on compliant polymers.[15] Bulge testing is a 2D biaxial fragmentation test (equibiaxial plane stress), which provides a more precise reflection of the actual stress state conditions during packaging fabrication processes. Imposing the coated membrane to uniform pressure and following the corresponding out-of-plane deflection, mechanical properties of oxide films can be extracted.[16–18]

In this work, we demonstrate a method based on mass spectrometry and on the concept of the membrane bulge test to evaluate the changes in barrier usefulness caused by the cracking of

thin layers. In the literature, thin film cracking is usually carried out separately from the transmission measurement, or re-clamping of the sample is needed between the two sub-steps.[15,19–21] Our novel approximation utilizes an *in situ* cracking process during the gas transmission experiments, which eliminates the probability of uncontrollable mechanical changes in the substrate/coating systems, for example, movement or re-clamping of the samples between each step. Therefore, high sensitivity, reliability, and reproducibility of the experimental data become available, which could be very useful in practical applications and has significant relevance in theoretical calculations.

The fundamental parts of the permeation measurement system are illustrated in Fig. 1. Uncoated and coated polymer substrates [Fig. 1, (a)] with an oxide layer facing the measurement gas inlet (b) (or inversely, if needed), mounted between two separate chambers, are indicated with darker and lighter shades of gray in Fig. 1 and are sealed against each enclosed volume with Viton™ gaskets (c). These gaskets define the sampling area: $0.0085$ m$^2$. The volume ratio of the two chambers permits fast gas diffusion while suppressing the dilution of the test gas. Initially, the closed butterfly valve (d) separates the atmospheric pressure test gas [$CO_2$ in our case], and the sample. The volume between the sample and the butterfly valve is negligible compared to the volume of the test gas container. After placing the specimen, both sides of it are flushed with atmospheric pressure N$_2$ (99.99%) gas to remove any residual gas contamination from the two chambers and from the test piece. The flushing can be monitored by the QMS (e) as it is connected to the sample holding volume via a membrane inlet (f) (SILPURAN® FILM 2030, 20 $\mu$m thickness). This membrane is used as an interface between the sample to be analyzed (atmospheric pressure) and the vacuum of the mass spectrometer ($10^{-7}$ mbar). With the help of this diaphragm, we can avoid the pressure difference induced damage in our oxide layers. The membrane inlet has a suitable transmission rate ($<5 \times 10^{-6}$ cm$^3$ s$^{-1}$ at standard temperature and pressure) and very short response time compared to the sample; therefore, the detected changes in the ion fluxes in the quadrupole mass spectrometer (QMS) are directly related to partial pressure variation created by the removal of gases from chamber volumes. Furthermore, the gas diffusion across the inlet does not change the atmospheric pressure of the test gas, which accumulated in the volume between the sample and the inlet.

After the flushing, the background signal of the test gas is recorded. By opening the butterfly valve (d), the measurement is started, the gas and the sample are connected, and due to the partial pressure difference of the gas, a diffusion process is initiated. The partial pressure increase on the spectrometer side can be recorded with a gas flow calibrated QMS (e). During the experiment, the partial pressure of the test gas at the inlet side was kept constant at an atmospheric level.

The measured flow rate, $Q$ (atm cm$^{-3}$ day$^{-1}$), is proportional to the number of diffused molecules that are permeated through the sample at a given exposed surface area, $A$ (m$^2$).[22] From the kinetics of the process, i.e., from the time lag or by the evaluation of steady state flow, the transmission properties of coated substrates can be deduced.[23,24]

Commercial-grade low-density polyethylene (LDPE) films with a thickness of 10 $\mu$m were chosen as substrates. The plasma-enhanced atomic layer deposition (PEALD) of Al$_2$O$_3$ films was carried out using a Beneq TFS 200-186 reactor. The precursors used for thin films were trimethylaluminum (TMA, 97%), and O$_2$ (99.999%).
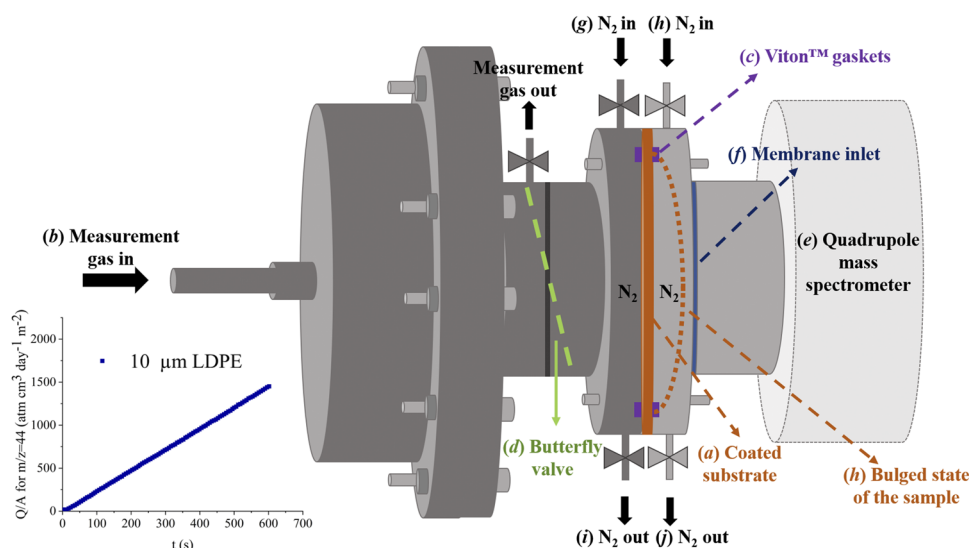


**FIG. 1.** (a) Permeation measurement system consisting of two chambers (darker and lighter gray parts) separated by the tested sample. Valves on both sides of the specimen [(g), (h), (i), and (j)] permit the N$_2$ (atmospheric pressure) flushing. From left to right, one can see the volume in which the high purity atmospheric pressure test gas, carbon dioxide (CO$_2$) in our case, is accumulated before the measurement. A butterfly valve (d) detaches this gas from the sample. The partial pressure increase can be monitored using the QMS (e), which has a membrane inlet (f) to avoid the pressure difference induced deformation of the test piece. The insert shows the recorded flux of CO$_2$ across the uncoated LDPE substrate.

Nitrogen was used as a carrier and purging gas, the reactor pressure was maintained around 1.2 mbar, and the reactor temperature was 38 °C. Plasma was produced by flowing $O_2$ into the reactor at 100 SCCM, plasma power of 50 W. 10 s of $O_2$ plasma pre-treatment was applied before deposition. The sequence of pulses for one deposition cycle was: (1) a TMA source for 0.15 s, (2) a $N_2$ purge for 2 s, (3) an $O_2$ plasma pulse for 2 s, and (4) a $N_2$ purge for 2 s. Two thicknesses, 25 nm and 50 nm, were investigated with and without cracks.

To investigate the effect of cracking of the coating layers on the gas permeability properties, we have to follow the described procedure and record the spectrum for the "uncracked" film, as can be seen in Fig. 2. After that, the butterfly valve and all the "$N_2$ in" [(g) and (h)] and "$N_2$ out" [(i) and (j)] valves (see Fig. 1) are closed. With the help of a compressor, a buffer tank is filled with compressed air, and this tank is linked with the closed "$N_2$ in" (g) valve, which is coupled to the oxide-coated face (left-hand side) of the LDPE via a precise digital pressure gauge. The overpressure in this volume can be adjusted to the mechanical response of the substrate/coating systems, which ranges from +2 mbar up to +2000 mbar. Then, after strictly adjusting the overpressure, the "$N_2$ in" (g) valve is opened, and the chamber volume between the butterfly valve (d) and the coated sample (a) is pressurized. The coated LDPE is bulged (h), and due to this, cracks in the oxide layer appeared. This over-pressurized state is held as desired – in this study, it is 10 s. The over-pressurized state ends by closing the "$N_2$ in" (g) and opening the "$N_2$ out" (i) valve. In the following step, all the "$N_2$ in" an "$N_2$ out" valves are opened, the $N_2$ source is reconnected,

and the flushing-permeability testing steps are repeated. The temperature of the test chamber system can be increased up to 150 °C using a heating jacket; accordingly, the temperature dependence of the permeability properties can be evaluated. The measurement process was repeated both with the uncoated LDPE substrates and for several times (at least three independent measurements) with the oxide-coated LDPE foils. The gas transmission rate of the uncoated substrate did not change considerably (within 10%) after the over-pressurization, which is necessary if we want to examine the effect of oxide layer cracks. Because of the cracks in the barrier layers, the measured fluxes of the test gas increased for both +10 and +20 mbar, and that was recorded with high accuracy and sensitivity (Fig. 2). The presented technique gives a unique way to study gas transmission under mechanical strains. This gas transmission rate–bulge test combined system permits investigation of how different conditions alter the mechanical response of the system and hence the transmission properties, such as the composition and thickness of different coating/substrate composites, or the coating technique.
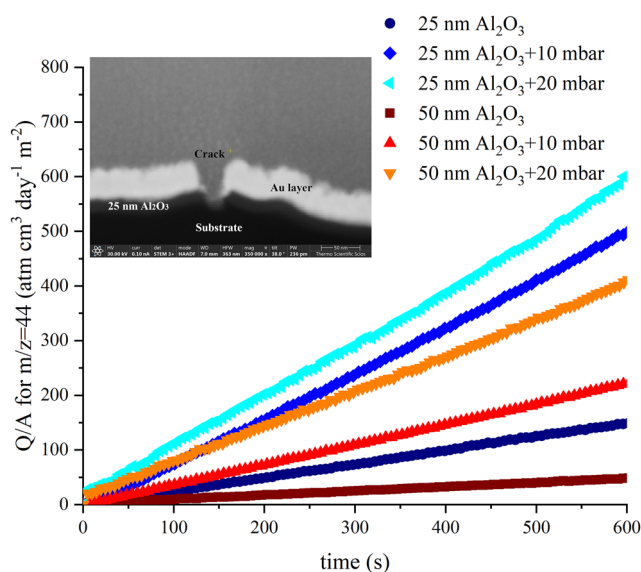
## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.



**FIG. 2.** Measured fluxes of $CO_2$ diffused through 25 nm and 50 nm $Al_2O_3$ coated LDPE. As the thickness of the $Al_2O_3$ increases, the slope of the function decreases because of the prolonged diffusion paths in the thicker layer. After the cracking process, the corresponding fluxes increased significantly. As the pressure increased to +20 mbar, a gradual increase in the flow rate can be observed, which corresponds to high defectiveness and small defect spacings in the coating layer.[25] The inset shows the focused ion beam assisted microscopic (FIB/SEM) picture of the LDPE coated with a 25 nm $Al_2O_3$ after the cracking, proving that the LDPE remains intact. The conductive gold layer decreases the charge buildup in the specimen.

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