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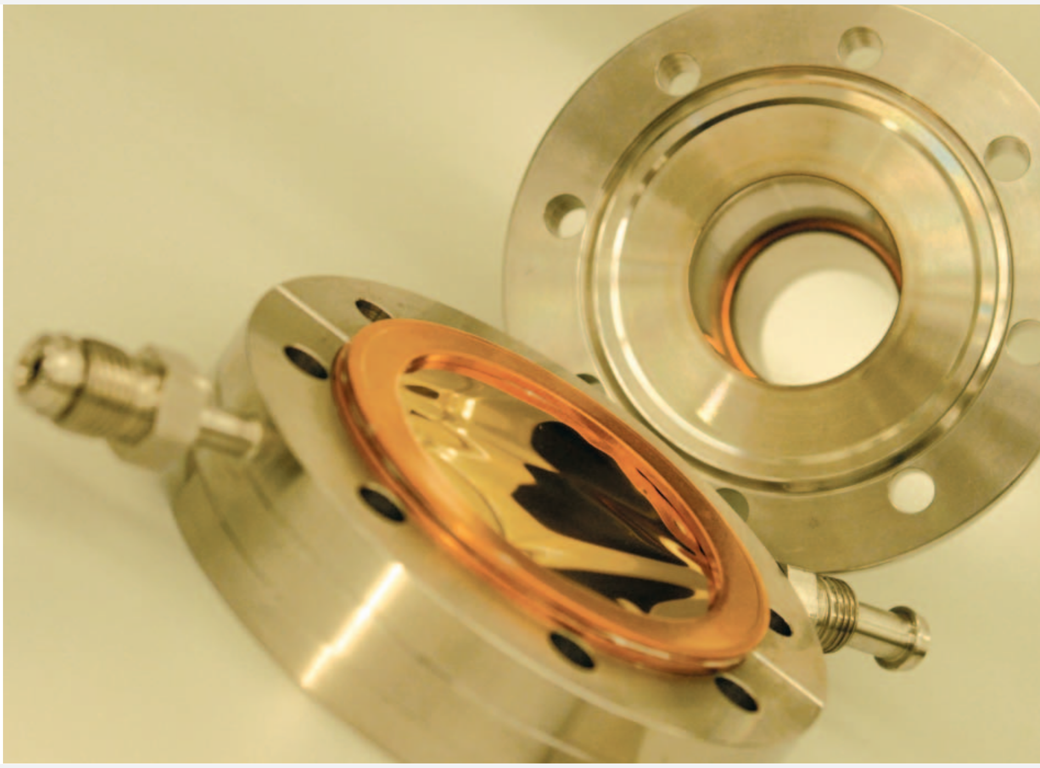
Numerous applications of polymers are critically dependent on the rate at which various molecular species permeate. MiPlaza Materials Analysis has developed an experimental set-up to measure the water vapor transmission rate of thin polymer sheets in a simple and effective way. Using different detectors, the permeability of polymer sheets for many other gases and vapours can be measured as well.

Materials Analysis

Permeability of polymer sheet materials

- Materials properties
- Quality control
- Permeability
- Mass transport through polymers
- Gases and vapors



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Introduction

A critical function of flexible packaging is to keep dry products dry. In many applications (e.g., food, semiconductor and electronics) moisture has disastrous effects on product characteristics. Without protective packaging, products will quickly accumulate moisture until they are at equilibrium with the environmental relative humidity. At this point, crispy food products become soggy and electronic components fail as a result of corrosion.

Water vapor transmission rate (WVTR) is the standard measurement by which films are compared with respect to their ability to resist moisture transmission. Lower values indicate better moisture protection. However, the WVTR value is only valid under the conditions applied in the experiments (specific film thickness, partial pressure donor gas, temperature). It is therefore preferable to use a parameter that is independent of the experimental conditions: the permeability.

Permeability

The general concept of the ease with which a permeant passes through a barrier is referred to as the permeability. This general term relates to the rate of transmission and is characteristic for the polymer and the permeant. The permeability can be directly measured by determining the rate of mass transfer through a polymer film, as shown in the following equation:

$$P = \frac{\text{(amount or permeant) (film thickness)}}{\text{(area) (time) (partial pressure drop across the film)}}$$

$$[m3_{(STP)}\ ^{1)}.m/m^2.s.Pa]$$

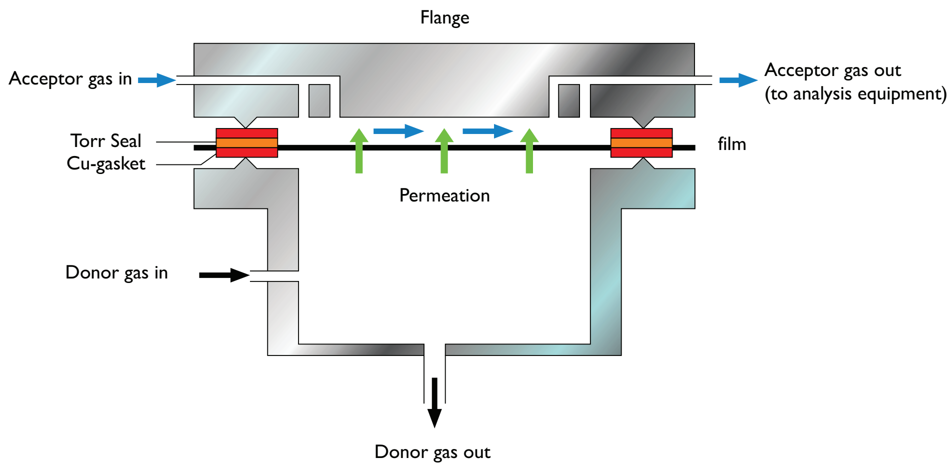
1) STP = Standard Temperature & Pressure (273 K, 1 atm)

The permeation process consists of two steps. In the early stages there is a transient response owing to the unsteady state penetration of gas into the polymer. This is followed by steady state permeation when a stationary concentration of the permeating gas has been established inside the polymer. Mass transfer through the polymer in the second state can be used to calculate the permeability coefficient P.

Measurement set-up

Several methods have been developed to measure the permeability of sheet materials. Our method is based on procedures described in the American Standards of Testing Materials (ASTM). In this method the sheet material is mounted as a sealed semi-barrier between two chambers at ambient atmospheric pressure (figure 1). One chamber is slowly purged by a stream of nitrogen (acceptor gas). The other chamber is purged with a humidified gas (donor gas). As moisture permeates through the film into the nitrogen carrier gas, it is transported to the moisture analyzer where the concentration is recorded. Mass spectrometry (MS) and a moisture sensor based on Near Infrared Diode Laser Spectroscopy (NIR-DLS) are used to measure the moisture content in the acceptor gas. The permeability coefficient is calculated from the moisture concentration in the steady state phase using the above-defined formula.

Fig. 1: Measurement set-up for permeability measurements of thin sheets.



Excellent WVTR detection sensitivity

The method described above is ideally suited for permeability measurements of sheet material used in the packaging industry (figure 2). The lowest detectable moisture permeability equals 3.10^{-18}(m$^3_{(STP)}$/s.m.Pa) which is two decades below the moisture permeability of many sheet materials. This makes the method very suitable for testing barrier coatings to prevent moisture permeation.

Applications

- Protective packaging (e.g., food, semiconductor and electronics)
- Controlled dosing of specific components using permeation devices
- Controlled ventilation of in-situ released gasses in enclosures
- Separation of volatile hydrocarbons from stack emissions using membrane technologies

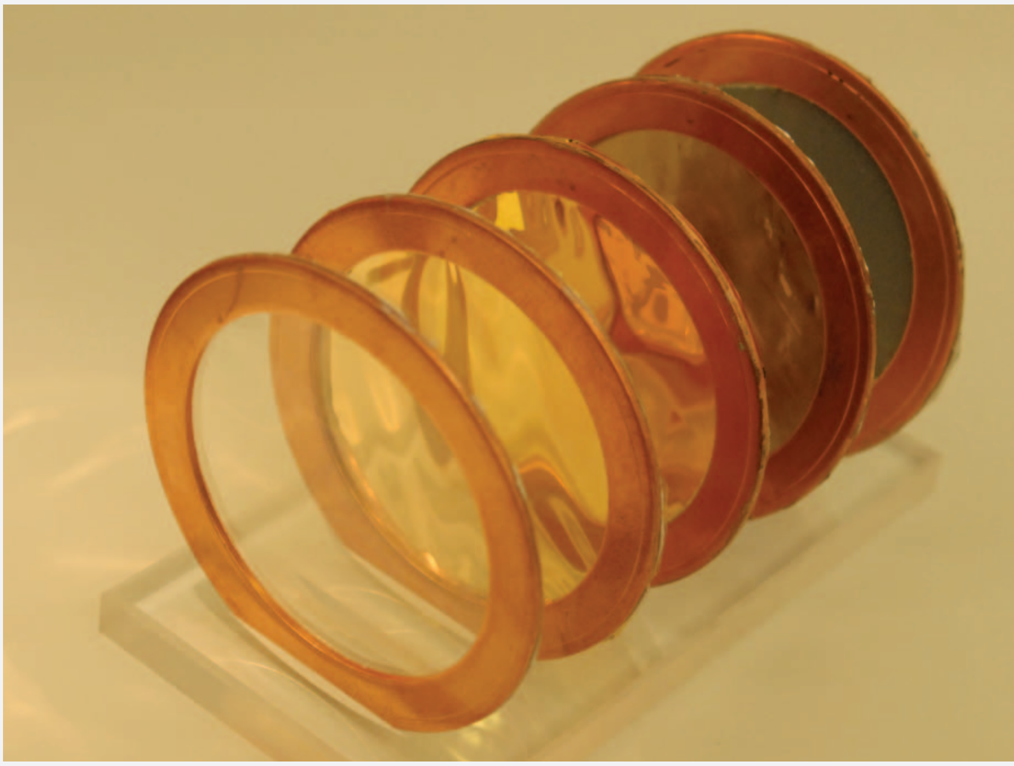
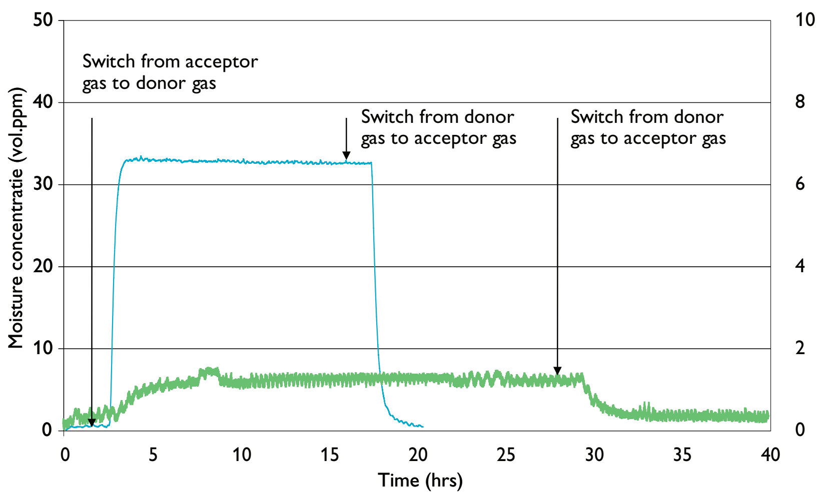


Fig. 2: Blue line: WVTR measurement of a polymer sheet (film thickness 25 µm). Concentration moisture measured using NIR-DLS. Moisture permeability 3.6x10^{-16} [m^3/s.m.Pa]. Green line: WVTR measurement of polymer sheet + additives (film thickness 50 µm). Concentration moisture measured using NIR-DLS. Moisture permeability 1.2x10^{-17} [m^3/s.m.Pa].



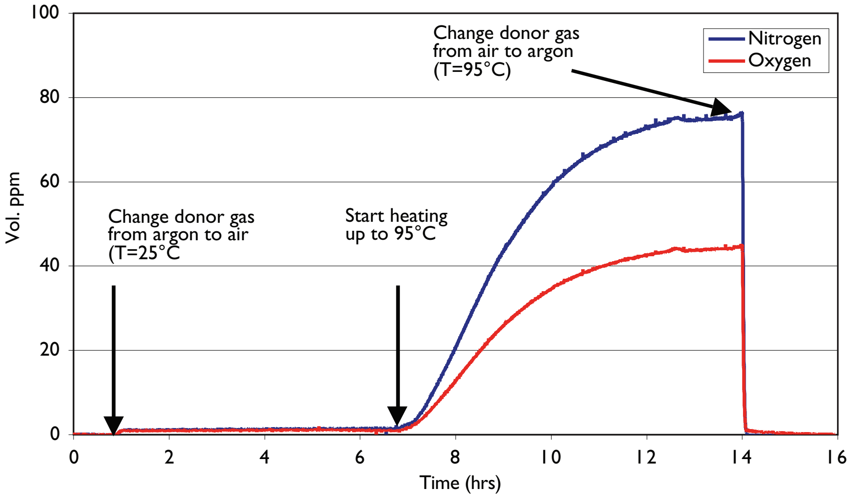


Fig. 3: Nitrogen and oxygen transmission rate measurement through a polypropylene sheet (film thickness 100 µm) at 95 °C.

The concentration of nitrogen and oxygen is measured using mass spectrometry.

Advanced methods

Besides the above mentioned method, which is most commonly used, more advanced methods have also been developed and optimised;

- Measurements can be performed at *elevated temperatures*. The maximum applicable temperature depends on the sheet characteristics (figure 3).
- MS is used to monitor different permeants *simultaneously*.
- The use of specific gas monitors makes the measurement of *transmission rates of gases and vapors* possible with a lower detection limit. The use of a CO gas monitor based on infrared absorption spectroscopy will result in a sensitivity 2 decades better than that of the MS detector.
- *Transmission rates of organic components (solvents)* can be measured by replacing the donor gas by a small amount of liquid at the bottom of a sealed donor compartment. The result is a donor compartment filled with a saturated vapor phase of the specific component.
- The use of pre-concentration techniques combined with off-line analysis can *improve the detection limit*. For organic components, gas chromatography with thermal desorption injection is used after trapping the component of interest on Tenax adsorption tubes. Quantification and positive identification of the target component is performed using the MS detector.

MiPlaza Materials Analysis
offers a full range of analytical methods and expertise to support both research and manufacturing, serving customers by taking an integral, solution-oriented approach.

making the invisible visible

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Characteristics

Information
- Permeability of different gases and vapors through sheet material

Sample type
- All sheet materials

Sample size
- Maximum applicable sample surface: Approximately 30 cm² (i.e. a circle with a diameter of 7 cm) with a maximum thickness of 1-2 mm

Detection limit
(target component depending)
- Moisture: 2.10^{-18} ($m^3_{(STP)}$/s.m.Pa) for direct analyses
- NMP: 1.10^{-20} ($m^3_{(STP)}$/s.m.Pa) when pre-concentration techniques are used

Accuracy
- 5% relative in general, dependent on target component

Precision
- 3% relative in general, dependent on target component

Destructive
- yes (sample holder is limited to 7cm diameter)

Routine analysis
- yes

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