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MPA Horizon Application Note 110

Analyzing Multicomponent Permeation Through Barrier Membranes Using the Membrane Permeation Analyzer (MPA Horizon)

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Analyzing the multi-component permeation of gases and vapors through materials is crucial for optimizing barrier properties and enhancing barrier performance across various applications such as food packaging, electronics, textiles, and construction materials. Yet such studies pose challenges such as accurately replicating real-world environmental conditions, such as temperature, humidity, and pressure, in a controlled laboratory setting. Also, identifying interactions between permeating substances within the polymer, requires intricate mixing and detection of multiple components. This study demonstrates the use of the Membrane Permeation Analyzer Horizon (MPA Horizon) for characterizing the permeation of water and toluene through barrier material membranes, as relevant molecules for moisture and organic compound transmission rates (MVTR/WVTR). It demonstrates PET's increased permeability at higher temperatures (>70 ° C) compared to Kapton caused by differences in glass transition temperatures of materials. Enhancing the barrier properties of PET by using a 9 µm aluminum coating to create a composite material was shown to protect the membrane against changes at a higher temperatures and humidity. This modification effectively enhanced the barrier properties, mitigating the effects of the glass transition to ensure the protective properties are maintained. The MPA enables precise analysis of single and multi-component permeation, revealing competitive interactions between toluene and water molecules within the polymer. The MPA Horizon was shown to be a comprehensive permeation analyzer capable of complex, industrially relevant, multicomponent permeation experiments.

Introduction

Understanding and analyzing the permeability of membrane films for use as barrier materials is critical in various industries, ranging from food packaging to environmental protection and healthcare. The ability of these films to regulate the passage of gases, liquids, and ions directly influences product quality, shelf life, and in some cases medical efficacy. By analyzing permeability properties, researchers and engineers can modify barrier materials to improve functionality and enhance the stability of a protected product. Having a greater understanding of permeability and how it can be affected by barrier performance can be used to identify the most suitable materials for a given application. This knowledge can be used to optimize material characteristics or direct the use of an optimum combination of materials.

This study focuses on characterizing the permeation of water and organics through Polyethylene terephthalate (PET) and Kapton using the Membrane Permeation Analyzer (MPA Horizon).

PET is a major synthetic polymer used globally, primarily in industries such as textiles, packaging, and beverages [1]. The global production of PET has been estimated to range from 50 million metric tons to over 87 million metric tons annually [1]. In the food industry, PET can act as a barrier to prevent contamination from environmental factors which helps in maintaining food quality by preventing the sorption of gases, which can lead to spoilage. For example, sulfur dioxide, often found in industrial emissions, can penetrate packaging, and accelerate the spoilage of foods like dried fruits by altering their flavor and nutritional content [2]. In the field of electronics, it is increasingly used in the encapsulation of flexible electronic devices and just like food materials, electronic components can be susceptible to oxidation and degradation from components in the atmosphere. For example, in OLED materials, when using PET to protect components the barrier was enhanced when using multilayer structures that combine inorganic (SiOx and AlOx derivatives) and hybrid organically modified ceramic polymers, further improving barrier performance against moisture and gases [3].

The environmental impact of PET waste has driven a significant shift towards recycling efforts. Industries are now focusing on innovative recycling methods to retain the material's integrity and effectiveness as barrier materials. Advanced techniques such as chemical recycling, which breaks PET down to its monomers for re-polymerization, and enhanced mechanical recycling processes, are being developed to produce high-quality recycled PET (rPET) that matches the performance of virgin PET [4]. These efforts aim to create a sustainable lifecycle for PET, minimizing environmental harm. Given the vast scale of production, it has become increasingly important to develop methods to analyze its performance as a membrane material, ensuring successful barrier performance across a range of applications.

Kapton, a polyimide film, is extensively used as a barrier material in the electronics industry, exploited for its high-temperature stability and chemical resistance. These attributes make Kapton ideal for various applications including flexible circuits, insulation for wires, and as a material for printed electronics [5]. Understanding the permeability of barrier materials is essential because it directly influences the longevity and reliability of electronic devices.

Alongside humidity, the MPA can measure the permeability of organic vapors and its effects on changes in temperature and vapour concentration.

This study looks at the permeation of toluene through PET. Toluene is an important solvent to study because, in the electronics industry, toluene can affect the performance of insulated materials or lead to the degradation of protective coverings. Also, since it is an environmental pollutant, toluene permeation in the food industry could cause contamination affecting safety and quality. Also, due to its ability to dissolve a wide range of organic compounds, toluene is frequently used during polymer synthesis therefore, even after appropriate purification steps there can be some residual toluene found within polymer structures [6]. Toluene can also serve as an effective simulant for aromatic flavor molecules commonly found in food and fragrance compounds used in personal care products. This means that the permeability of barrier materials to toluene can be indicative of their effectiveness in preventing the loss of taste and smell in packaged goods. Toluene's permeability through packaging materials can impact the integrity of fragrance formulations, leading to the gradual loss of scent over time. Barrier materials that effectively block the permeation of toluene can help maintain the potency and longevity of fragrances, ensuring that products retain their desired scent profiles throughout their shelf life.

The permeation of gases and vapors through a polymer is affected by several factors. Permeability mechanisms can be influenced by temperature, humidity, and the diffusion of molecules into the materials' structure. With regards to PET, some of these interactions may lead to chemical or physical changes for example undergoing a glass transition phase or changes in crystallinity. Challenges with Kapton lie with its high-temperature applications and replicating experiments that provide real-world accurate data. This application note identifies these challenges and uses the MPA Horizon and the permeation technique to provide a better understanding of real-world applications using single and multicomponent permeation studies.

Methods

All experiments were conducted using the MPA Horizon, a cross-flow permeation instrument produced by Surface Measurement Systems. Prior to sample exposure, operators select the desired concentration and temperature of gas or vapor molecules, which are monitored by detectors. The principles of the MPA involve directing a controlled flow of the desired solvent/water vapor or gas concentration in an inert carrier gas over the surface of a membrane. Throughout the experiment, one side of the sample is subjected to these conditions, and detectors are positioned to measure the permeation of permeate molecules that pass through the membrane and into the cross-flow gas. The detectors can accurately identify and quantify the permeating species in the cross-flow gas, generating a permeation curve. Figure 1 shows a schematic of the principles of the MPA.

For the comparison of water permeation through PET and Kapton, experiments were carried out at 130 °C using a constant absolute humidity of 21.9 g m^{-3}. To observe any temperature-induced changes in PET, aluminum-coated PET, and Kapton, the experiment was repeated at a range of temperatures from 25 °C to 110 °C. Where appropriate, the permeation of humidity was reported as the water vapor transmission rate (g m^{-2} day^{-1}). This water vapor transmission rate is calculated using the MPA inlet and outlet humidity probes. The flow rate of water on the permeate side (a product of mole fraction and sweep gas flow rate) is divided by the membrane effective area to produce a volumetric flow rate per area (cm^3 m^{-2} day^{-1}). The volumetric flow rate is converted into a molar flow rate by dividing by the molar volume of a gas and multiplying by the molar mass of water shown in Equation 1:

$$\left({}^{Volumetric\ flow/m^2}/_{22400\ cm^3mol^{-1}}\right) \times 18\ g\ mol^{-1} \qquad (1)$$

In the MPA, the range of WVTR measurement is between 0.009 - 800 g m^{-2} day^{-1}, making use of the inline humidity probes to provide kinetic and equilibrium data. To investigate any changes to PET with respect to toluene permeability as a function of temperature, further experiments were carried out above its T_g at 110 °C, 120 °C, and 130 °C keeping toluene concentrations constant at 35000 ppm (corresponding to 95% p/p0, 25 °C). The diffusion coefficient for water and toluene were calculated using Equation 2 the slab model (4.23) proposed by Crank [7].

$$ln\left(\frac{M_t}{M_\infty}\right) = -\,ln\left(\frac{8}{\pi^2(2n+1)^2}\right) + \left(\left(\frac{D(2n+1)^2\pi^2}{l^2}\right).t\right) \qquad (2)$$

Where m is the amount of a species passing through the film, l is the sample thickness, t is time, and D is the diffusion coefficient. Diffusion activation energies were calculated via an Arrhenius type-plot, following Equation 3.

$$D_A = D_{0A}exp\left(-\frac{E_{DA}}{RT}\right) \qquad (3)$$

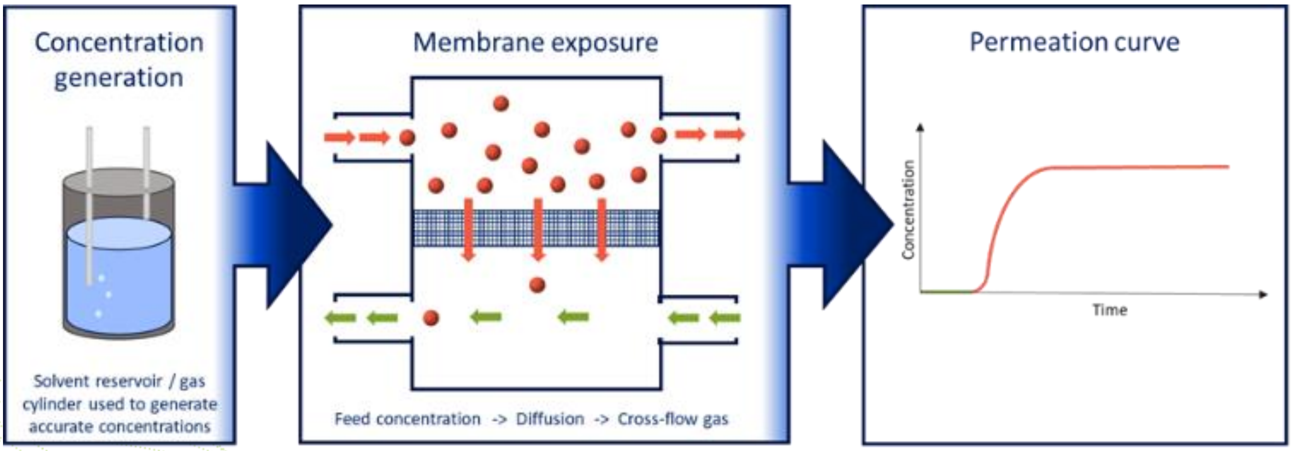

Figure 1. Schematic of the basic principles of the MPA

Where, E_{DA} is the diffusion activation energy, R is the ideal gas constant, and T is temperature.

For the multi-component permeation through PET, two variable studies were carried out at 130 °C. The first involved maintaining water vapor at 50 %RH (T=25 °C) and varying concentrations of toluene from 200 ppm to 1000 ppm and the other involved varying RH (T=25 °C) from 10 %RH to 40 %RH and keeping toluene concentrations constant at 2000 ppm. PET was obtained from Terphane, Al-PET was obtained via a collaboration with Imperial College London, Kapton was obtained from RS Components Ltd, and solvents were obtained from Sigma-Aldrich.

Results

The first part of the study compared the transport of water through the two membrane materials, shown in Figure 2. Materials were subject to conditions of 130 °C and 21.9 g m^{-3} absolute humidity (95 %RH, 25 °C). The results show that both Kapton and PET allow water to pass through the membranes. PET allows more water through compared to Kapton and at a faster rate, confirmed by the higher permeability and diffusion constants, displayed in Table 1. This is due to PET having a lower glass transition temperature which ranges between 75 °C and 80 °C whereas Kapton has a T_g above 300 °C. Therefore, at 130 °C, PET has undergone a transition from a glassy polymer, in which the amorphous phase is tightly packed, to a rubbery polymer, with more conformational freedom in the polymer chains. This increased conformational freedom in the polymer releases some of the trapped free-volume between polymer chains, which allows for the increased movement of molecules through the polymer [8]. This facilitates a greater permeability of water through the film.

The MPA Horizon was then used to observe changes in the polymer morphology, during its glass transition, by varying the membrane temperature between 20-110 °C and using absolute humidity as a probe, as shown in Figure 3. PET can be an effective barrier below 70 °C, however, above this glass transition temperature, the water vapor

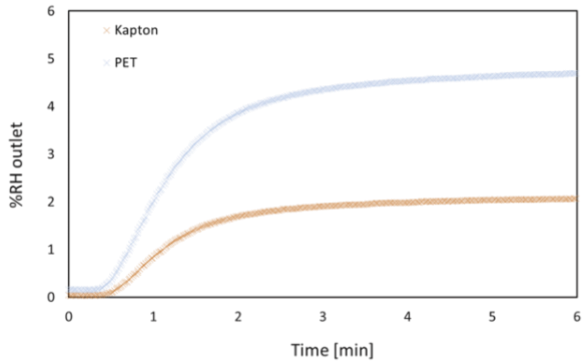

Figure 2. The comparison of water permeation on Kapton and PET

transmission rate increases (WVTR), and its functionality as a barrier material against moisture collapses. This trend is similar to the phenomena of the Tortuous Path Model where measured values of water vapor transmission rates increase linearly with the decreasing semi-crystallinity of a polymer, arising from an increase in polymer free-volume increasing available pathways or creating less tortuous routes for moisture diffusion through the polymer [9]. This is expected in semi-crystalline polymers where the free-volume in the amorphous regions increases with temperatures above the T_g value. The results show that Kapton maintains the strong interactions between the amorphous polymer chains and is less affected by temperature changes which are below its glass transition temperature. Multilayer composite materials are often used to overcome the permeation properties of polymers. Aluminum is effective since it has good thermal stability that can act as a protective layer for PET. With an attempt to decrease its WVTR an aluminium layer on the PET material was applied and experiments were repeated, shown in Figure 3. Results show that even a small coating of 9 µm on top of 15 µm of PET creates an effective barrier to humidity even at temperatures above 70 °C with little-to-no water vapor transmission observed.

The next study looks at the permeation of toluene through PET. Figure 4 shows the permeation curves of ~35,000 ppm toluene (95% toluene at 25 °C) through a PET membrane at 110 °C, 120 °C and 130°C. The presence of toluene can interact with the PET matrix, potentially acting as a plasticizer. Therefore, physical changes occur allowing for greater number of toluene molecules to diffuse into the material. The diffusion activation energy for the diffusion of toluene into PET materials is high, meaning higher temperatures are necessary to overcome this activation energy to observe permeation. Above its T_g (>70 °C), at 110 °C the kinetics of this interaction is slower and increases with increasing temperatures with significant permeation at 130 °C.

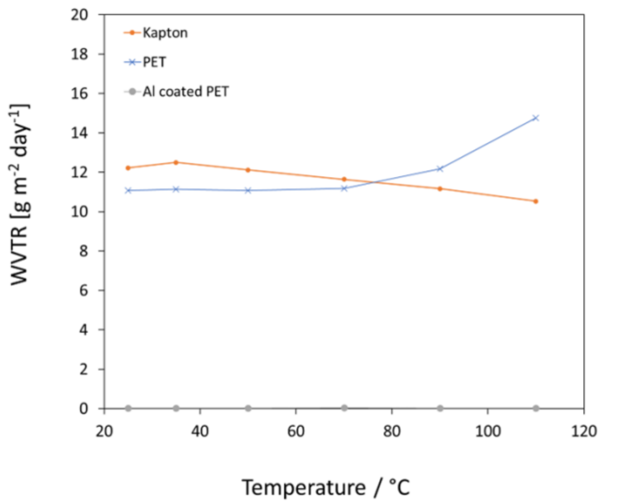

Figure 3. The glass transition effects on Kapton, PET, and multi-layered aluminium PET using water

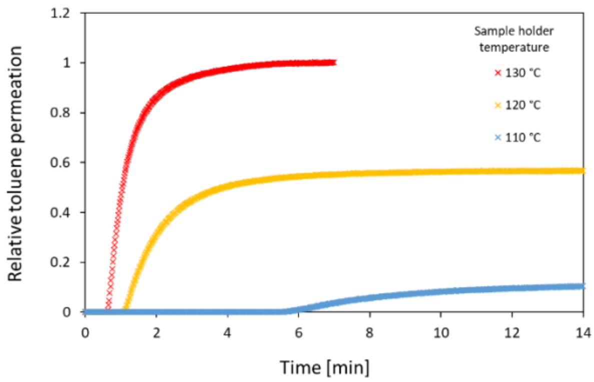

Figure 4. Analysis of toluene permeation in PET at 110 °C, 120 °C and 130 °C, relative to equilibrium permeation at 130 °C.

Table 1 shows the diffusion constants calculated using the MPA Horizon using organic solvents on both PET and Kapton materials. These values are comparable to those found in the literature and are consistent with multiple diffusion models.

Multi-component permeability

The capabilities of the MPA are not limited to single permeation analysis, it can also characterize materials based on realistic multi-component permeation. A comprehensive permeability study has been carried out to measure the competitive permeation of toluene and water through PET. Figure 5 presents the results of water permeability measured in relation to the percentage of relative humidity, determined while increasing toluene concentrations under a constant flow of 50% RH.

*Table 1. Diffusion constants calculated using the MPA Horizon compared to those found in literature. *N/D = Non-determined (no permeation observed at lower temperature)*

Material	**Solvent $_0$**	**Transmission rate (g m^{-2} day^{-1})**	**Diffusion coefficient (standard model) / x10^{-10} cm^2 s^{-1}**	**Literature diffusion coefficient / x10^{-10} cm^2 s^{-1}**	**Activation energy / KJ mol^{-1}**	**Literature activation energy / KJ mol^{-1}**	**References**
PET	Toluene (130 °C)	2.5	5.65	6.4	103.4	107	[10]
	Water (25 °C)	26.4 (110 °C)	42.1	39.5	6.9	36	[11,12]
Kapton	Toluene	N/D	No Permeation	Not found	N/D	Not found	-
	Water (130 °C)	10.5 (110 °C)	28.8	22.6 (60 ^{o}C)	21.1	~(20-40)	[13]

Increasing the toluene concentration leads to a slower permeation of water as toluene competes for adsorption and diffusion through the polymer-free volume.

A reverse study was also carried out by varying RH and keeping the toluene concentration constant. Figure 6 shows that increasing the moisture in the

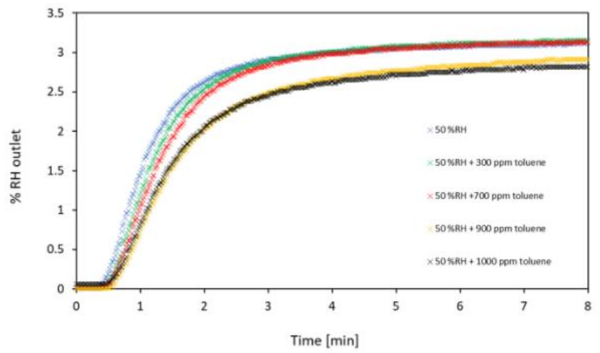

Figure 6. The effects of competitive permeation of toluene and water keeping water concentrations constant.

environment restricts toluene permeation. This is likely due to water molecules occupying or blocking the pathways that toluene would otherwise use. Although we are above the materials T_g, at 130 °C and below 40% RH, there are no plasticization effects observed suggesting that the structural integrity and barrier properties of the PET remain stable under these conditions. By analyzing how increased moisture restricts toluene permeation, the experiment highlights the competitive behavior between different types of permeants within the

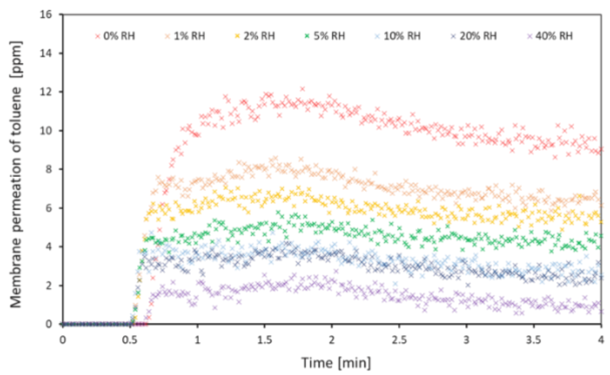

Figure 5. The effects of competitive permeation of toluene and water keeping toluene concentrations constant.

polymer matrix, which can influence the material's overall effectiveness as a barrier. Such insights are essential for applications requiring robust barrier performance under fluctuating humidity conditions, common in real-world environments.

Conclusion

The study's comprehensive approach, including single and multi-component permeation analyses, shows that the Membrane Permeation Analyzer (MPA Horizon) can be used as an essential tool to characterize the permeation behaviors of materials. The system was able to determine differences in temperature-dependent permeation properties of Kapton and PET. The MPA has also shown to be useful in analyzing composite multi-layer effects on permeation by demonstrating the effectiveness of an aluminum coating on PET to enhance its barrier properties. By investigating the permeation of water and toluene through various membrane materials, valuable insights have been gained that underscore the importance of multicomponent measurements. Single component measurements can lead to incomplete results since it fails to capture the full spectrum of performance dynamics, leading to potentially inadequate material selections and suboptimal product protection. Multicomponent measurements ensure a holistic evaluation of barrier properties, thereby enhancing the reliability of materials in real-world applications.

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