

Faster Results

Permeation Measurement of Films. By using helium instead of other gases such as oxygen and carbon dioxide, permeation measurement of films can be speeded up considerably. Measurement with helium is therefore a very suitable rapid test method for predicting gas permeability or monitoring film quality during production.

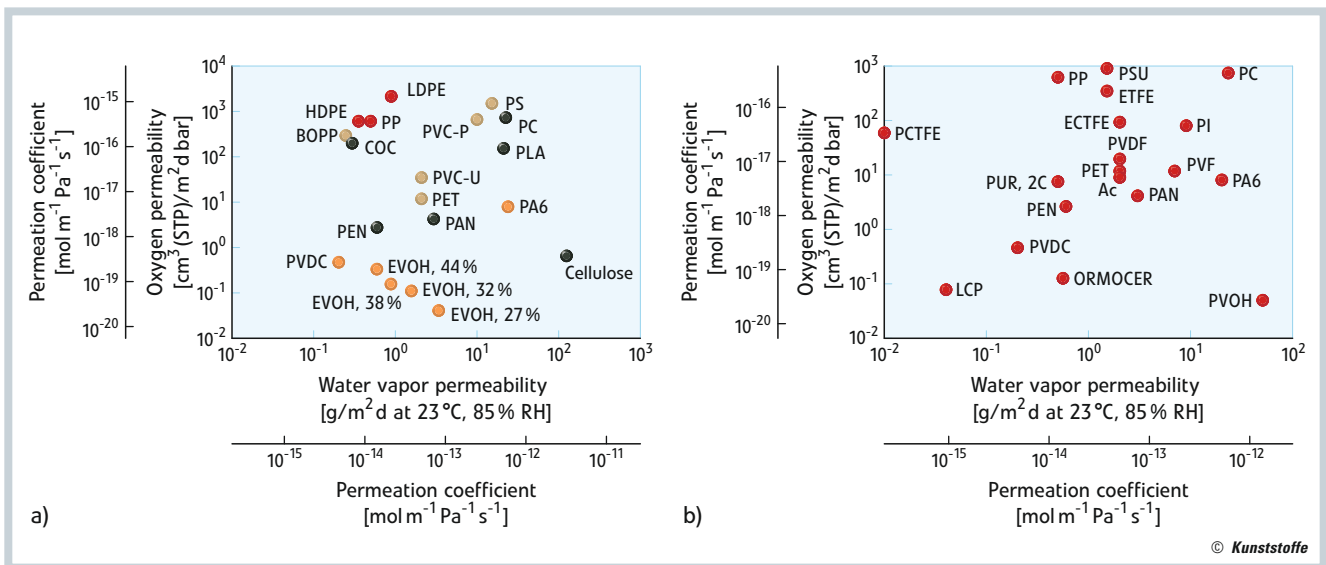


Fig. 1. Permeability and permeation coefficient at 23°C of typical packaging plastics for a) food and b) technical products according to [3]

(source: Fraunhofer IVV)

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The development of new formulations for film applications, including process optimization and the determination of barrier properties in quality monitoring, has until now been a time-consuming and cost-intensive process. Determining gas permeation, in particular, has proved a challenge in this respect, since these measurements can take several days and, for high-barrier technical applications, even several weeks. For this reason, it would be desirable to develop a method that would allow the barrier properties of polymer films to be measured during the actual production process. This would also dramatically accelerate the development of new materials and process configurations, since the rapid feedback of information on perme-

ation properties would make it possible to carry out continual iterative development directly on the production line.

One approach to speeding up permeation measurement is to use gases with small molecules or atoms – such as helium. Permeation processes can also be accelerated by increasing the temperature. By these means, measuring times can be reduced by several orders of magnitude as compared to standard measurements with oxygen or carbon dioxide.

This article describes a rapid test method based on the above principles for speeding up quality monitoring of films and the development of film materials. To provide meaningful values, the results of the helium permeation measurements must be correlated with those of standardized methods. This process is discussed as follows and used to evaluate the possibilities and limitations of the method. In conjunction with a direct film extrusion line, the feasibility of using this method for accelerated material and

process optimization and rapid determination of film quality is demonstrated.

Improving Barrier Properties

The permeability of commodity plastics and also most high-performance plastics to water vapor, oxygen and other molecules has already been intensively studied and documented [1, 2] but is too high for most technical applications. Figure 1 shows the permeability values of some typical packaging plastics. These values are standardized to a film thickness of 100 µm. Because of the poor barrier properties of these plastics, the development of measures to improve barrier performance started in the 1960s. Today, there are basically four approaches to improving barrier properties in the plastics packaging sector [3]:

■ Vacuum coating methods:

Barrier layers can be applied onto the plastics using vacuum coating methods. In the case of packaging film, the

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barrier layer is always covered by additional polymer layers or plastic films. Today, some 15 billion m² of packaging film are produced using this method. In most cases, PET or BOPP films are coated with aluminum, and a small proportion with transparent oxides (silicon oxide, aluminum oxide) [4].

- Plastic containers with different barrier layers:
In these cases, the primary material is usually PET. The vast majority of these containers with excellent barrier properties have a multi-layer structure. To further improve barrier performance, exfoliated plastic particles are increasingly being incorporated in the polymer. A smaller proportion of plastic containers are coated on the inner surface, e.g. with silicon oxides.
- Nanocomposites:
The third category has so far been used far less than the two previously mentioned categories. In this case, homogeneously dispersed nanoparticles are compounded into the polymer matrix as a barrier layer to inhibit gas permeability.
- Multi-layer films:
Finally, a fourth class of materials has been developed for packaging techni-

cal articles or sensitive foods, for which the very highest barrier requirements are specified. This class of materials for the protection of e.g. thin-film batteries or optoelectronic devices has a multi-layer structure. Here, inorganic and polymer layers are deposited alternately on a flexible polymer substrate.

about two days – owing to the relatively low diffusion coefficient. Measuring time can be considerably reduced with the rapid test described here.

Measuring time depends on the time required for a steady state to be reached and therefore on the dimensionless time or Fourier number F_0 [5]:

$$F_0 = \frac{D \cdot t}{l^2} \quad (1)$$

This means that the measuring time t is halved when the diffusion coefficient D is doubled and quadrupled when the layer thickness l is doubled.

In addition, diffusion D , solubility S and permeation P are dependent on the testing temperature T according to the Arrhenius equation, where ΔH_S is the heat of solution, E_D the activation energy and R the universal gas constant [6]:

$$P = D \cdot S = P_0 \cdot \exp\left(\frac{-(E_D + \Delta H_S)}{R \cdot T}\right) \quad (2)$$

where $P_0 = D_0 \cdot S_0$

Therefore, a gas with a high diffusion coefficient, such as helium, should be used for a rapid test. In addition, the equation shows that the measuring time can be

impermeable particles accounting for a volume fraction ϕ , then the gas molecules can essentially only diffuse through the remaining volume fraction of the polymer $(1-\phi)$. In this case, the diffusion path x can be lengthened.

The ratio of the permeation coefficient of a filled specimen P_1 to that of the unfilled specimen P_0 can be represented as follows [7]:

$$\frac{P_1}{P_0} = \frac{(1-\phi)}{\tau} \quad (3)$$

The lengthening of the effective diffusion path x can be described with the aid of τ , where τ is the ratio of the average length of the diffusion path of a gas molecule to the specimen thickness.

If now the geometry of the particles is considered to be the ratio of the length L to the width w (known as the aspect ratio), then the permeation coefficient P_1 can be estimated as follows [7]:

$$P_1 = \frac{P_0 \cdot (1-\phi)}{1 + \frac{a \cdot \phi}{2}} \quad (4)$$

Rapid Permeation Test Developed

At the German Plastics Center (Das Kunststoffzentrum SKZ) in Würzburg, Germany, a rapid permeation test (Fig. 2) was developed and introduced in collaboration with the Fraunhofer Institute for Process Engineering and Packaging (Fraunhofer IVV) in Freising, Germany. A manometric measuring system for tests as per DIN 53380-2 is coupled with a helium leak detector. With the integrated mass spectrometer, very small helium leakage rates down to below $5 \cdot 10^{-12}$ mbar·l·s⁻¹ can be detected. Direct helium detection has the advantage of increasing measuring accuracy by a factor of 10^4 as compared with manometric helium permeation measurement.

Figure 3 shows a schematic representation of the at-line permeation measurement. In this diagram, the helium flow is plotted logarithmically against the measuring time.

In this test, the top measuring cell is first flushed with nitrogen to desorb any dissolved helium gas molecules that might still be present in the polymer. As a rule, this operation takes 1 to 2 min with the tested film specimens. The required flushing time is, however, dependent on the material, thickness and quality of the test specimen. As soon as a constant val-

Table 1. Penetration times in measurement of O₂, CO₂ and helium permeation through some selected plastics

Material	Penetration time [min]		
	O ₂	CO ₂	He
LDPE	0.6	0.8	0.04
PVC	23	111	0.10
PET	62	335	0.14
PA11		15	0.08

further reduced by increasing the testing temperature. The diffusion coefficients of helium in different plastics are higher than for oxygen by a factor of 15 up to 500 [2]. This gives the penetration times shown in Table 1. To obtain the actual testing time (including zero point measurement and setting the permeation equilibrium), the penetration time must be multiplied by a factor of about 20. This means that the measurement of helium permeation through films with a thickness of 100 μm takes only a few minutes.

Permeation Coefficient of Filled Plastics

Permeation is dependent not only on dispersion but also on filler content (see equation 3). If a polymer is filled with largely

cal articles or sensitive foods, for which the very highest barrier requirements are specified. This class of materials for the protection of e.g. thin-film batteries or optoelectronic devices has a multi-layer structure. Here, inorganic and polymer layers are deposited alternately on a flexible polymer substrate.

Measurement of Permeation Properties

The oxygen and water vapor permeability of plastic films are most commonly measured using specific carrier gas methods. These test methods are standardized, such as DIN 53380-3 for oxygen permeability. The disadvantages of these test methods are costs and measuring time. For example, to determine the oxygen permeability of a 100 μm PET film takes

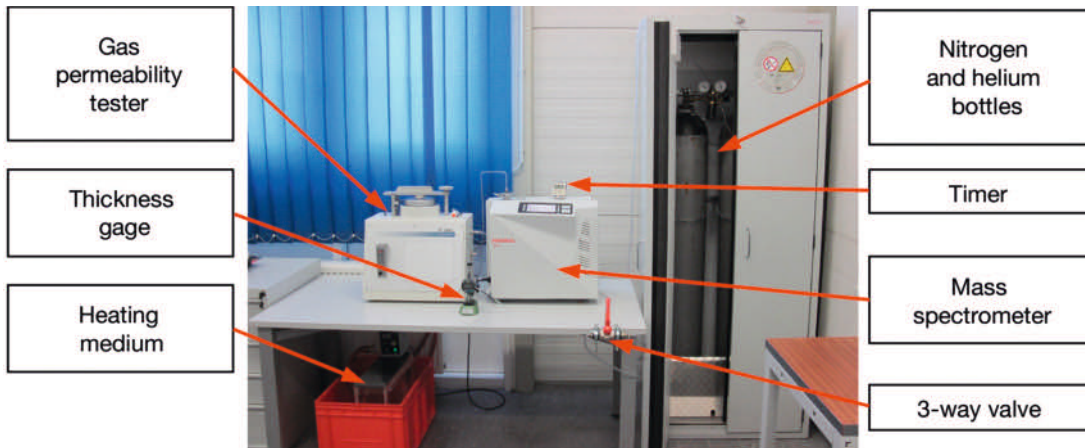


Fig. 2. Layout of the rapid permeation measurement system for at-line use (figure: SKZ)

ue is achieved with the nitrogen flushing (zero point measurement), it is possible to switch over to helium (see Fig. 3, A). The helium gas molecules now need a certain amount of time to diffuse through the polymer to the underside of the specimen. The measuring time until a steady state, i. e. constant volumetric flow rate, is established, ranges between 3 and 5 min for the monofilms tested.

The gas molecules now desorb in the lower measuring cell. The resulting helium leakage rates can be determined with the coupled mass spectrometer based on the change in quantity and concentration. The helium leakage rate when the final steady state is reached is used as a reference value for determining the permeation value in the rapid test (Fig. 3, B).

So the total measuring time for this gas permeation test is composed of the time required for nitrogen flushing plus the time for subsequent measurement of helium permeation (about 4 to 7 min).

With this rapid test system, the helium leakage rate \dot{Q} can be determined in mbar·l/s. However, helium permeability is generally quoted in the unit $\text{cm}^3 \cdot \text{cm} / (\text{cm}^2 \cdot \text{s} \cdot \text{bar})$. With the aid of test area A and pressure difference Δp , the he-

lium permeability Q can be calculated from the helium leakage rate:

$$Q = \frac{\dot{Q}}{A \cdot \Delta p} \quad (5)$$

Application in Direct Film Extrusion

Figure 4 shows the schematic layout of the direct extrusion line combined with the rapid permeation test system, which is integrated into the production line as an at-line measuring unit for accelerated material and process development.

The direct extrusion line was set up according to this layout in the processing laboratory of the SKZ (Fig. 5). This trial facility consists of a co-rotating twin-screw extruder (Leistritz ZSE 27Maxx, manufacturer: Leistritz, Nuremberg, Germany), a flat-film die (width approx. 350 mm) and a roll unit. For taking samples from the running production line and subsequent at-line permeation measurement, a special sampling device was developed and integrated into the extrusion line. Through the combination of a film storage device and specimen punch, it is possible to punch out film

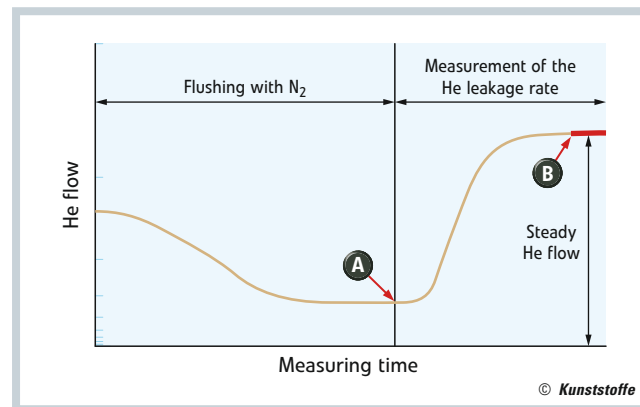
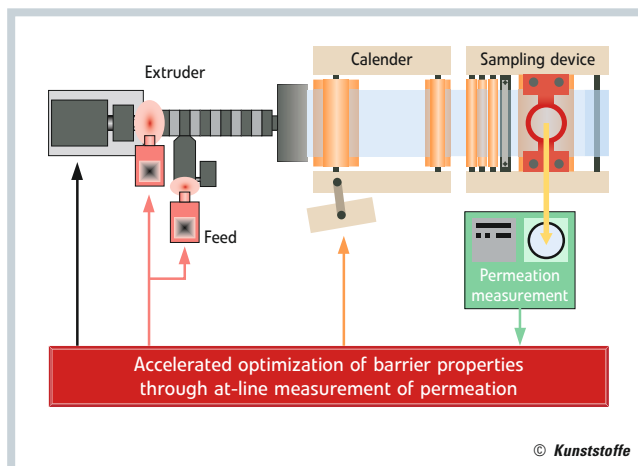


Fig. 3. Schematic representation of permeation measurement in the rapid test method (A: switching from nitrogen to helium (zero point measurement), B: helium leakage rate) (source: SKZ)

Fig. 4. Schematic diagram of the direct film extrusion line with the at-line permeation measurement system for accelerated material and process development (figure: SKZ)



disks from the moving film web during production.

Results

Measuring Time and Reproducibility: The previous estimates of measuring time were confirmed by the measurements. The time savings are illustrated by the measuring times for a 100 μm PET film. The total testing time for helium permeation measurement, excluding test specimen preparation, is about 7 min, which comprises about 3 min for zero point measurement and another 4 min for determination of the actual test value.

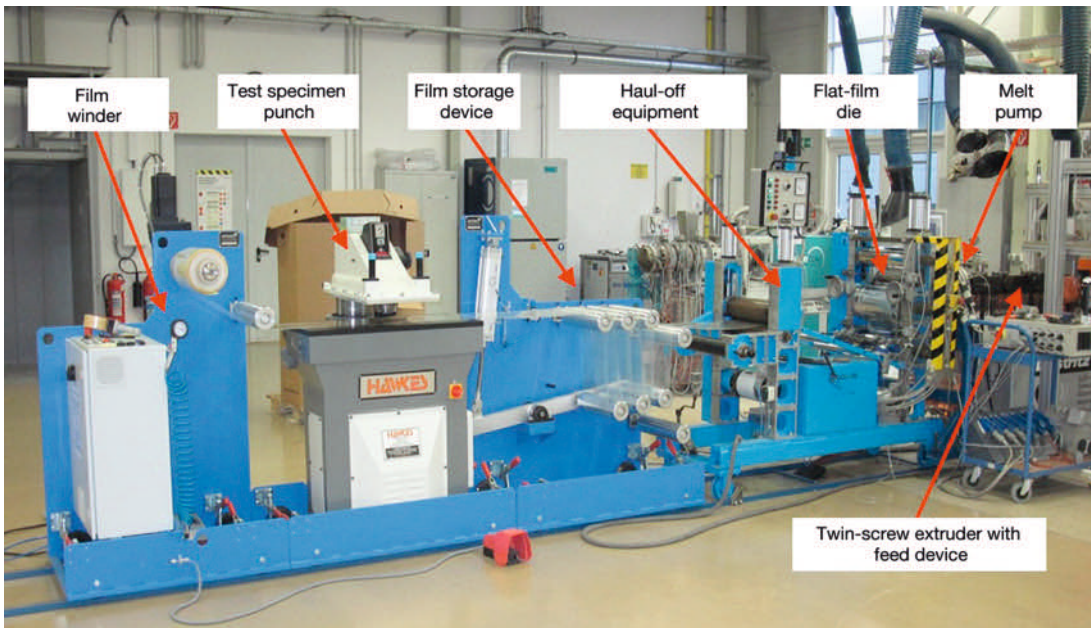


Fig. 5. Layout of the direct extrusion line
(figure: SKZ)

The total time required to measure the oxygen permeation through a similar 100 µm PET film according to the relevant standard is 48 h (= 2,880 min). So the helium rapid test method is 360 times faster than the conventional measuring time.

In **Figure 6**, the helium permeation coefficient P is plotted against filler content ϕ for various HDPE/talc compounds that were processed directly into film with a thickness of 250 µm by the direct extrusion process. In addition to the filler content, the filler feed position/method was varied. The polymer was introduced via the main feed opening and the talc either via a side feed opening, the main feed opening or as a 50 % masterbatch. Through repeat measurements, it was possible to achieve very high reproducibility in this measuring method, with a variance of about ± 1 %. So test specimen preparation and the way in which the measuring equipment is handled

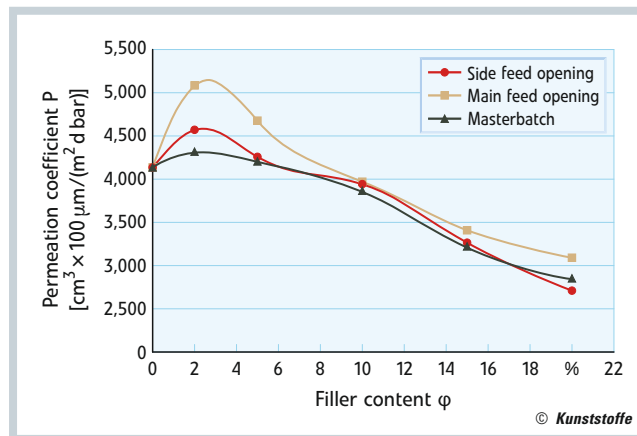


Fig. 6. Helium permeation coefficient (measured at 40°C) of HDPE/talc compounds as a function of filler content for different feed options
(source: SKZ)

have only minimal influence on the test values.

Influence of Filler Content on Helium Permeation: Up to a filler content of about 5 %, it may be assumed that the morphological properties of the polymer predominate, because with all three feed options there is a significant increase in the permeation coefficient (see **Fig. 6**). It may be concluded from this that the films in these cases have more amorphous regions and smaller spherulites. This phenomenon has already also been observed with polypropylene/talc compounds [8]. It is clear that, from a filler content of 5 %, the properties of the fillers ensure an appreciably lower permeation coefficient. In other words, the properties of the filler only start to predominate from a talc content of 5 %.

The relatively highest permeation coefficients were obtained when the fillers were added via the main feed opening (**Fig. 6**). In this case, reagglomeration (**Fig. 7**) of the filler particles takes place in the

melting range, which prevents homogeneous dispersion of the talc in the HDPE base polymer.

Calculation of the permeation coefficient of an HDPE/talc compound with a filler content of 10 % P_f according to **equation 4** gives a value of 3,321 $\text{cm}^3 \cdot 100 \mu\text{m} / (\text{m}^2 \cdot \text{d} \cdot \text{bar})$. The assignment of a value of 10 for the aspect ratio was taken from the literature [9]. In this example, the difference between the measured and estimated permeation coefficients for helium is about 2 %. Similarly accurate predictions were also obtained with other compounds of polyamide 6 and nanoclays. From this, it is clear that a good estimate of the permeation coefficient of a filled monofilm can be made in advance.

Correlation between Helium, Oxygen and Carbon Dioxide Permeation through Monofilms: **Figure 8** shows the correlation between oxygen and carbon dioxide permeation through talc-filled HDPE and helium permeation. Oxygen and carbon dioxide permeation were



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measured with a manometric measuring system according to DIN 53380-2. Helium permeation was determined using the helium rapid permeation test already described.

In a direct comparison of gas permeability, permselectivity must be taken into account. Permselectivity means in this case that the film has different barrier properties for different gases, with no linear correlation between the properties. There is a very good correlation between the oxygen and helium permeability, with oxygen/helium permselectivity being about 0.4 l. This corresponds to the typical value for unfilled HDPE [2]. There is also a correlation with carbon dioxide but with a somewhat lower coefficient of determination of 0.91 than for oxygen. These results demonstrate the suitability of helium permeation measurement as a rapid test method for the functional evaluation of filled plastics.

Correlation between Helium and Oxygen Permeation through Composite Films with EVOH Barriers: Three composite films with the structure PP/adhesion promoter/EVOH/adhesion promoter/PP with different EVOH layer thicknesses were produced at the Fraunhofer Institute for Process Engineering and Packaging (Fraunhofer IVV) on a

Figure 9 shows the correlation between the oxygen and helium permeability of these composite films. Just as with the previously described monofilms, there is again a very good correlation between the helium and oxygen permeability of the composite films. Consequently, the helium permeation measurement can also be used as a rapid test method in the development of barrier films with EVOH. As a result, development cycles and testing times in quality control can be significantly shortened.

Correlation Limits: Besides the advantages of the helium rapid test method, its limitations and special characteristics must also be taken into account. For this purpose, the helium and oxygen permeability values and permselectivities of a number of monofilms are compared in Table 2.

A crucial factor determining the suitability of helium permeation measurement as a rapid test method for predicting e.g. oxygen permeability is permselectivity $P(\text{He})/P(\text{O}_2)$, i.e. whether it is possible to define a fixed ratio between helium and oxygen permeability. Permselectivity differs significantly between different plastics. Whereas the permselectivity of non-polar polyolefins is 2 or 3, the permselectivity of polar plastics such as

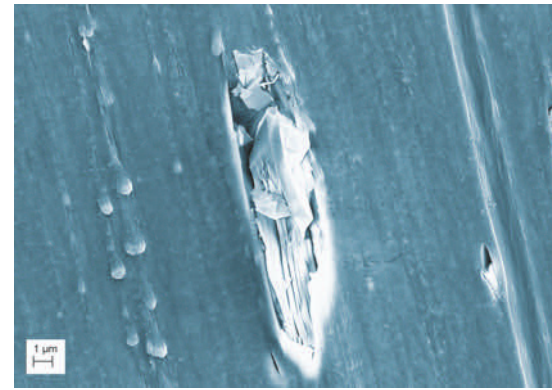


Fig. 7. Scanning electron micrograph of a talc agglomerate (figure: SKZ)

other hand, the permselectivity $P(\text{He})/P(\text{O}_2)$ of other barrier films, such as metalized PET films, is between 40 and 50, i.e. within the same range as the permselectivity of unmetalized PET.

Conclusion

The advantage of the helium rapid test over permeation measurement with other gases such as oxygen or carbon dioxide lies in the significantly shorter measuring time. Depending on the material combination, the measuring time with monofilms is only a few minutes and therefore some two orders of magnitude

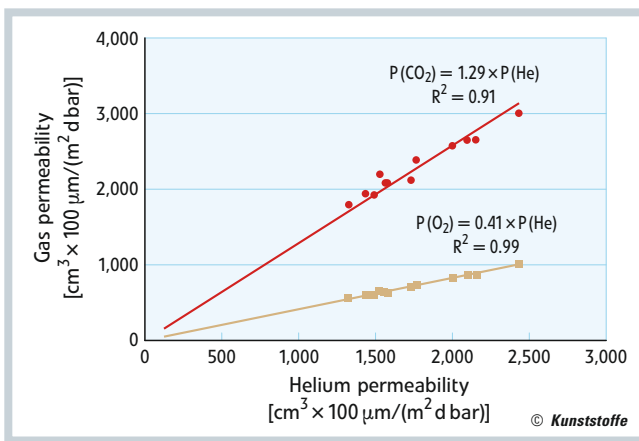


Fig. 8. Correlation of the oxygen and carbon dioxide permeability (measured at 23 °C) of HDPE/talc compounds with their helium permeability (source: Fraunhofer IVV)

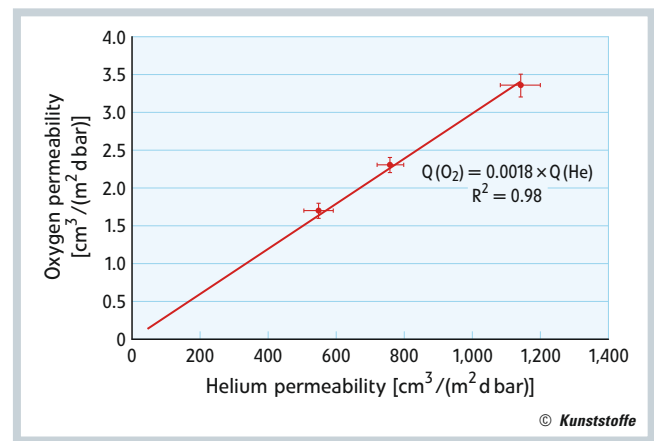


Fig. 9. Correlation of the oxygen permeability (measured at 23 °C) of PP/adhesion promoter/EVOH/adhesion promoter/PP composite films with their helium permeability (source: Fraunhofer IVV)

7-layer coextruder manufactured by the Dr. Collin company in Ebersberg, Germany. EVOH is commonly used as an oxygen barrier in packaging materials for sensitive foods. The EVOH grade selected here contained 38 % ethylene. The EVOH layer thickness, which is crucial for gas permeability, averaged 5 μm, 8 μm and 10 μm respectively for the three sample films produced. The total thickness of the films in all three cases was around 50 μm.

PET is much higher with a value ranging from 40 to 50. It can be concluded, that the helium permeation measurement cannot be used as a method for predicting oxygen permeability across the whole range of plastics but always only within a plastics group.

The same also applies to composite films. The permselectivity $P(\text{He})/P(\text{O}_2)$ of composite films with EVOH barriers typically ranges from 400 to 500. On the

faster than with e.g. oxygen permeation measurement by standard methods. It would therefore seem sensible to use helium permeation measurements as a rapid test method for predicting the permeability of mono- and composite films to other gases such as oxygen or carbon dioxide.

This is perfectly possible provided that some limiting conditions are observed. Only material combinations with approx-

Test specimen	Thickness	He	O ₂	P(He)/P(O ₂)
	[µm]	P [cm ³ ·100 µm/(m ² ·d·bar)]		
LDPE specimen 1	76	3,610	1,718	2.1
LDPE specimen 2	74	3,678	1,761	2.1
HDPE specimen 1	317	1,686	663	2.5
HDPE specimen 2	181	3,204	1,421	2.3
PS	175	10,745	1,509	7.1
PLA specimen 1	49	6,370	176	36.2
PLA specimen 2	47	6,580	166	39.5
ETFE	205	7,688	638	12.1
PET 12 µm specimen 1	12	629	15	40.9
PET 12 µm specimen 2	12,5	664	16	41.2
PET 100 µm specimen 3	99.5	672	16	41.7
PET 100 µm specimen 4	101	582	12	49.7
PEN 100 µm	97	371	4.5	82.4

Table 2. Comparison between the helium and oxygen permeability values and permselectivities of different monofilms

imately the same permselectivity can be compared. A typical field of application would be the further development of barrier systems, in which no fundamental changes to the film composition are being made, such as in the further development of composite films with EVOH barriers or with metalized aluminum barriers. Within these groups, there is comparable permselectivity. On the other hand, direct comparison between e. g. composite films with EVOH barriers and metalized composite films is not possible.

The helium rapid test method is also very suitable for at-line production monitoring of film quality in a product series after defined quality limits have been specified. With the rapid test method, possible shortcomings in gas permeability can be identified at an early stage, so enabling reject rates to be significantly reduced as compared with using the conventional, very protracted test methods. ■

This article is dedicated to Prof. Dr.-Ing. Dr.-Ing. E.h. Walter Michaeli on the occasion of his 65th birthday and his retirement.

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