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Thin Polymer Films: Simple Optical Determination of Molecular Diffusion Coefficients*Paola Lova,^{1*} Heba Megahd,¹ Davide Comoretto^{1*}*

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KEYWORDS: Diffusion coefficient, polymer packaging, molecular diffusion, sensing.

ABSTRACT: The possibility to assess diffusion coefficients of small molecules in packaging polymer films directly on the shelf, or even along the fabrication line, without the use laboratory equipment commonly employed for gravimetric methods would represent a paradigm changer in the evaluation of barrier properties and byproduct formation in goods packaging and device encapsulation. In this work, we demonstrate a simple, effective and versatile method for the determination of the molecular diffusion coefficients that exploits simple UV-Vis spectroscopy and is suitable for any polymer film. This simple method also allows the direct identification of the intercalating molecule without the need for chemical targeting or of complex laboratory equipment. For this purpose, we report on the assessment of diffusion coefficients of both polar and non-polar molecules including water, ammonia, methanol, ethanol, toluene, and even hexafluorobenzene into polyvinyl chloride wrap commercialized for food packaging.

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5 Assessing the diffusion coefficient of small molecules in the vapor and gas phases through polymer
6 thin films is important to evaluate barrier properties of packaging systems in food industry, in device
7 encapsulation, and even for artwork protection.¹⁻² Monitoring these properties directly on the shelf or
8 along the fabrication line can indeed provide significant information on both the polymer barrier
9 properties, and on the formation of degradation byproducts, that could be harmful for human health. In
10 fact, polymers are efficient absorbers for a large amount of chemicals,³⁻⁵ often used to for pollutants
11 absorption in water.^{2, 6-7}

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14 The diffusion of molecular species into polymer matrices is usually measured on bulky
15 materials via gravimetry and pressure decay methods⁸ or by techniques based on refractive
16 index variations.⁹ Conversely, when small polymer masses are involved, dedicated expensive
17 and time consuming laboratory techniques such as nuclear magnetic resonance,¹⁰⁻¹¹ infrared
18 spectroscopy,¹² and neutron reflectometry¹³ are frequently needed. Some attempts to
19 measure diffusivity in thin films via UV-Vis spectroscopy have been done using chromophore
20 analytes,¹⁴ but the use of these colored compounds aims to detect opportunely labelled
21 molecules and then, it cannot be employed for uncolored species. Alternatively, the
22 characterization of the chemico-physical variations induced in the polymer matrix by the
23 diffusing molecules would be more versatile and potentially applicable to any polymer-solvent
24 couple.

1 In a previous work, we demonstrated that the simple UV-Vis spectroscopy performed with portable
2 and low-cost detectors and light sources can be used to easily assess the molecular diffusion coefficients
3 through polymer multilayered photonic crystals.¹⁵⁻¹⁷ In these structures, periodical alternation of two
4 polymers with different refractive index interacts with light to generate a diffraction pattern
5 characteristic of the structure.¹⁸ The diffusion of an analyte within the multilayer can swell polymers,
6 modifying the diffraction pattern proportionally to the mass intake, and with kinetics depending on the
7 polymer-analyte chemico-physical interactions. This phenomenon also leads to label-free selectivity to a
8 variety of analytes,¹⁵⁻²¹ and makes these structures effective sensors and actuators,²²⁻²³ besides their
9 most common applications.²²⁻³³ The dynamic of the spectral changes in the diffraction pattern during the
10 intercalation of a molecular species, also allows the use of classical models to estimate diffusion
11 coefficient values full agreement with gravimetric data.³⁴ These structures could then be used as
12 integrated smart sensing tags in packaging system, but possess some disadvantages related to
13 implementation within packaging systems. In this work we demonstrate that a similar approach method
14 can be extended to any unstructured polymer films used in packaging. In this case, the packaging itself
15 can be used as an active detection medium, making the method suitable for bare or multilayered
16 polymer films used in both food industry and device encapsulation, allowing the assessment of
17 properties that cannot be studied with standard techniques neither in-situ, nor for very small amounts of
18 material.

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41 When their roughness is small enough, thin films provide interference patterns that depend on their
42 thickness and on their refractive index. Such patterns typically arise from the constructive and
43 destructive interference between light beams reflected and refracted from the upper and bottom film
44 interfaces. As depicted in Figure 1a, for a film with thickness L and refractive index n , when a light
45 beam (I_1) hits the film, it is partially reflected (R_1) and partially refracted (T_1) through the interface.
46 Since the refractive index of the polymer is always larger than the one of air, $n > n_{air}$, the phase of R_1 is
47 shifted by $\lambda/2$ with respect to I_1 .³⁵ The refracted beam T_1 hits instead the lower interface of the thin
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1 film where it is again partially reflected within the polymer (R_2) and partially transmitted (T_2). In this
2 case, no phase shift occurs for the reflected beam R_2 .³⁵ The beam R_2 reaches then the upper interface
3 where it is transmitted and can interfere with the beam R_1 . Whether the interference between the beams
4 R_1 and T_2 is constructive or destructive depends on their phase difference. At normal incidence, without
5 any phase shift, we would obtain constructive interference when the difference of the optical path $2nL$
6 equals a multiple of the beam wavelength ($m\lambda$). Because the phase of the beam R_1 is shifted by 180
7 degrees, R_1 and T_2 are in-phase when the path difference $2Ln$ equals $\lambda \left(m + \frac{1}{2}\right)$.³⁶ This condition
8 corresponds to full constructive interference between the two beams, that arises in the thin film
9 spectrum as relative maxima (Figure 1b). The beams are instead out-of-phase (destructive interference,
10 corresponding to minima in the spectrum of Figure 1b) when the path difference equals $m\lambda$.³⁶ When a
11 small molecule diffuses into a polymer film, the macromolecules can swell so that the thickness
12 variation modifies the position of the interference maxima and minima. Then, the spectral variations
13 occurring in the interference pattern during intercalation of molecular species can be directly linked to
14 the variations of film thickness. As a proof of principle, we exposed a commercial polyvinyl chloride
15 (PVC, cling wrap) thin film (see supporting Information S1 for details), to different solvents including
16 some found in foods. This PVC wrap is commonly used in food packaging for preservation, and
17 protection from chemical (gases, moisture, and light), biological (microorganisms, insects and animals),
18 as well as physical and mechanical damages.³⁷

42 **EXPERIMENTAL**

43 Commercial PVC thin films with thickness of 8.5 μm was used as purchased. For the measurement
44 the film was cut in different sections of about 5 mm^2 and supported on a reflecting substrate to increase
45 the background reflectance.
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47 For all the samples, reflectance data were collected at normal incidence at set time intervals with a
48 homemade setup based on optical fibers. The sampling intervals were established on the basis of the
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1 sensor response kinetics to the different analytes. For analytes showing slow response the sampling
2 intervals was longer than for faster systems to avoid collection of redundant spectra. For the
3 measurement, the sample was placed in the holder of a Y-bundle immersion probe purchased from
4 Avantes. The probe has a bundle of optical fibers that takes the light from the illumination sources to the
5 sample with normal incidence. Another fiber collects the light specularly reflected from the sample with
6 the same angle and take it to the detector. The light detection system is an Avantes AvaSpec-2048
7 spectrometer (200–1150 nm, resolution 1.4 nm) which allow to register the entire spectral range in a
8 single measurement. The light source is a deuterium–halogen Micropak DH2000BAL lamp. The
9 measurements were registered during the exposure to water, ammonia, methanol, ethanol and toluene
10 vapors at ~26 °C, 1 atm, and humidity within 65–80%. This was achieved by immersion of the probe
11 containing the sample in a sealed tube saturated with the analyte vapor by placement of 0.5 mL of
12 liquid analyte.
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30 **RESULTS AND DISCUSSION**

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32 Figure 1b shows the variations occurring in the interference pattern of the pristine commercial PVC
33 cling film (red line) and after 5 min in toluene vapors (black line). The variations consist in a reduction
34 of the reflectance intensity of the interference pattern and in a densification of the fringes. The latter
35 characteristic is assigned to the increase of thickness of the film induced by the swelling.¹⁵ The intensity
36 reduction can be instead linked to two phenomena: first, the reduction of the optical quality of the PVC
37 film and second, the decrease of the dielectric contrast at the PVC-air interface. Figure 1c shows the
38 dynamic of these variations during the exposure to toluene as a contour-plot. There, the x-scale
39 represents the wavelength and the y-scale represents the exposure time. The reflectance intensity is
40 conversely reported as a color scale so that we can distinguish any interference fringe as an oscillation
41 between green and blue colors. In this plot we notice that the interference pattern is smoothly modified
42 during the exposure to toluene. Indeed, all the fringes shift to the longer wavelengths side of the
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spectrum, in agreement with an increase of the film thickness. In this system, the volume variation induced by the intercalation of molecules can be described as the thickness variation. Moreover, dealing with vapor analytes $\Delta d/d(0) \gg \Delta n/n(0)$,^{20, 38-41} we can assume that the refractive index variation is negligible during the swelling process, $n(0) \approx n(t) \approx n(\infty)$ ¹⁵. To better clarify this point, one can consider as an extreme case the total replacement of a polymer film with refractive index ~ 1.6 and which does not modify its geometrical thickness with a solvent with index ~ 1.33 . In this case the error performed on the optical thickness of the material (n times d) would approach 20%. In the real case the effective variation of refractive index is lower than 5%^{15, 17, 40-41} for swelling approaching 100% of the initial thickness,^{15, 17} implying a way smaller error on the thickness variation and in turn on the evaluation of D . Then, for additive volumes the polymer mass intake (M) can be related to the film thickness (L) as follows:

$$\frac{M(t)}{M(t_\infty)} = \frac{L(t) - L(t_0)}{L(t_\infty) - L(t_0)} = \frac{\Delta\lambda(t)}{\Delta\lambda(t_\infty)} \quad (1)$$

Where t is the exposure time, so that t_0 is $t=0$ s (before the exposure), and t_∞ represent the steady state.³⁴

Then we can derive the molecular diffusion coefficient within the polymer film from the fringes spectral position during the vapor exposure from:^{15, 34}

$$\frac{M(t)}{M(t_\infty)} = \frac{\Delta\lambda(t)}{\Delta\lambda(t_\infty)} = \frac{2}{L} \sqrt{t} \sqrt{\frac{D}{\pi}} \quad (2)$$

Equation 2 described the linear part of the sorption curves commonly retrieved by gravimetric measurements, where $M(t)/M(\infty) < 0.5$,^{34, 42-47} and no accumulation occurs. In this range, D

1 is commonly evaluated from the angular coefficient of the sorption curves reported as
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4 $\Delta\lambda(t)/\Delta\lambda(\infty)$ vs. \sqrt{t} . Such curves can be retrieved from the data reported in Figure 1c by
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7 extrapolation of the fringes spectral position (relative maxima) during the exposure. Due to the
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10 small film thickness (8.5 μm), concentration gradients that could affect the local diffusion coefficient can
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13 be neglected, as demonstrated in previous works on molecular diffusion in multilayered thin films.^{15, 20}
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15 Figure 1d shows the retrieved data as the variation of spectral position ($\Delta\lambda$) normalized by the spectral
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18 shift registered at the steady state for one of these relative maxima (λ_∞). There, the spectral position of the
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21 fringe moves initially with fast kinetics to the longer wavelength side of the spectrum and then the shift
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24 slows down until the position is stable. These data have been extracted tracing the position of the relative
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27 maximum initially positioned at ~ 800 nm (marked with “*” in Figure 1b). We would like to highlight that
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30 the choice of this maximum was completely arbitrary. Indeed, once normalized the spectral behavior of
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33 all the pattern maxima is identical, and the retrieved curves are perfectly superimposable, as reported in
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36 Supporting Information S2, panels c of Figure S2-S7. Then, this method can be applied to thin films
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39 showing light interference in any spectral region unaffected by light absorption and scattering phenomena,
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42 making the method applicable to a large variety of materials.
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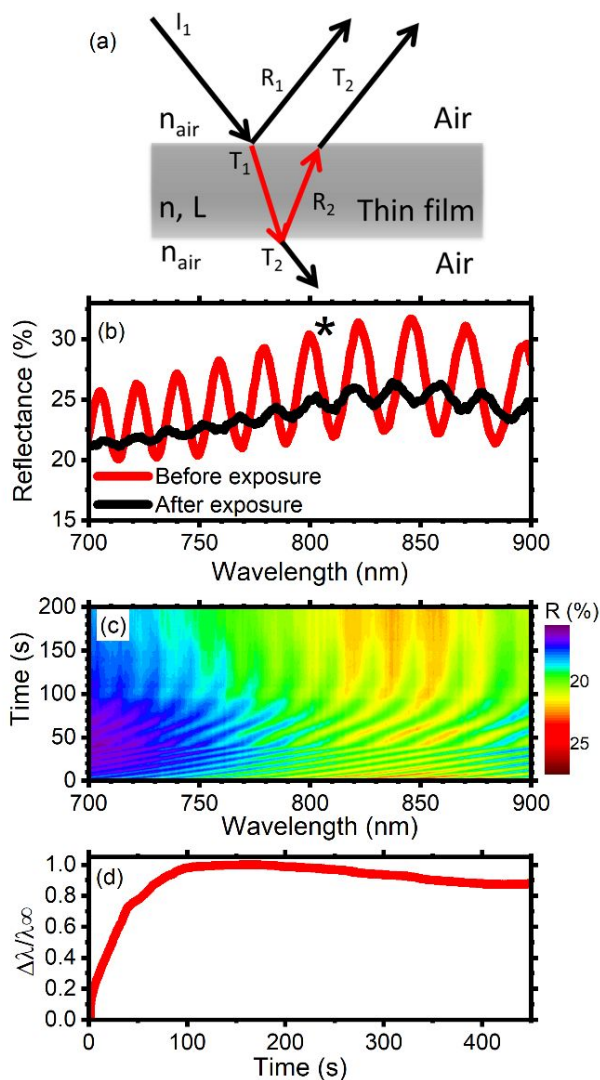
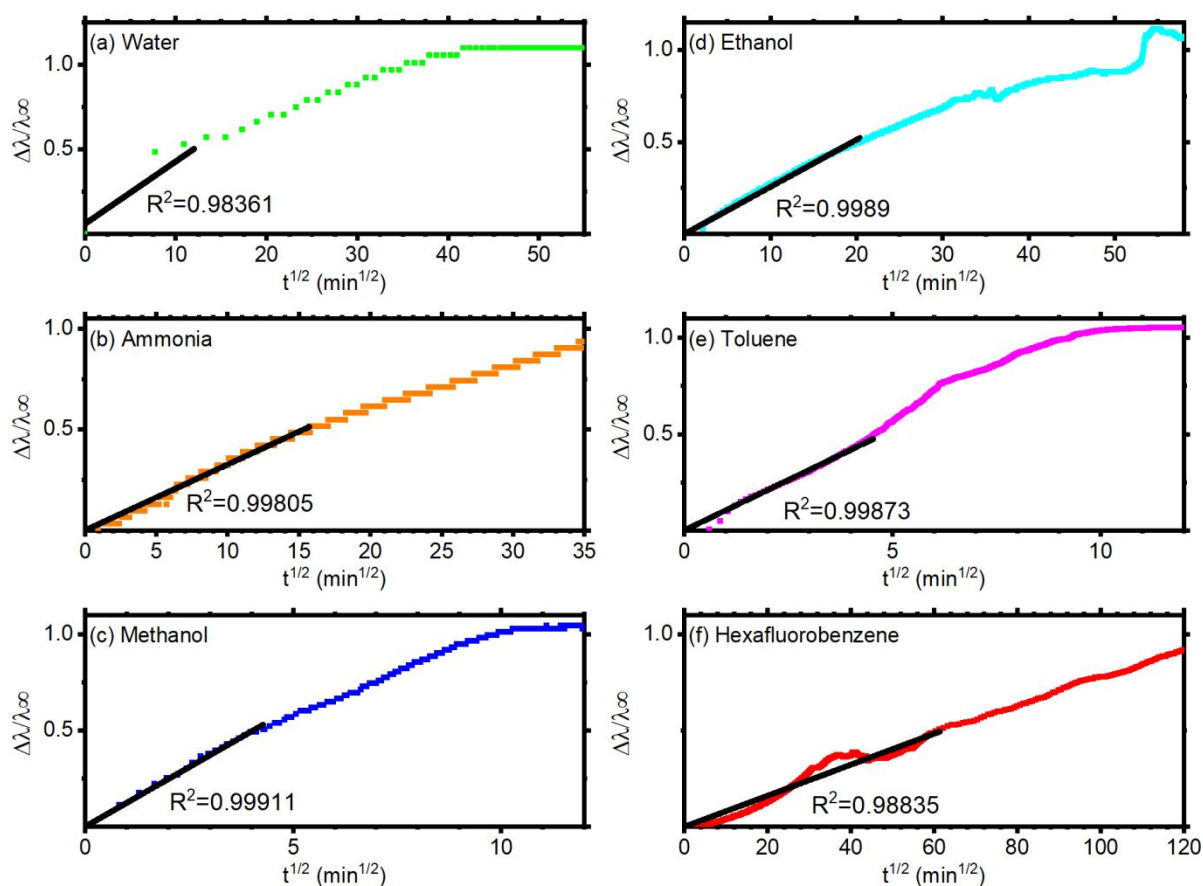


Figure 1: (a) Scheme of thin film reflectance. (b) reflectance of PVC film before (red line) and after (black line) ~5 min in toluene vapor. (c) Dynamic PVC spectral response during toluene exposure. (d) normalized spectral shift of the relative maxima initially positioned at ~800 nm during the exposure.

Notwithstanding PVC films are used for their barrier properties for food preservation, this material strongly interacts with many compounds. Indeed, Figure 2 reports the spectral evolution of the fringe

maxima marked with “*” in Figure 1b in environments enriched with vapors of water (a), commercial ammonia (4% in water, b), methanol (c), ethanol (d), toluene (e) and even of a perfluorinated compound (f). The behavior of the other fringes in the interference patterns is reported in Supporting Information S2. In all the cases, we see that the spectral position of the maxima shifts towards longer wavelengths with different kinetics that depends on the different chemical species. The detailed description of the sample responses is reported in Supporting Information Figures S2-S7. We would like to add a comment to the data of Figure 2. The large interaction between the PVC cling film with solvents commonly present in food such as water and ethanol can increase the migration of plasticizers,⁴⁸ which are largely present in these films,⁴⁹ into the food. Then, decreasing such interaction could make the use of these materials safer and healthier.



1 **Figure 2:** Optical sorption curves for the PVC film during exposure to water(a), commercial
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3 ammonia solution (4% in water), b), methanol (c), ethanol (d), toluene (e), and
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7 hexafluorobenzene (f). The black line represents the linear fit of the optical sorption curves
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11 retrieved for $\Delta\lambda(t)/\Delta\lambda(t_{\infty}) < 0.5$.

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16 The data of Figure 2 were analyzed accordingly to Equation 2 to retrieve the diffusion coefficients (D)
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18 for the intercalation of the species investigated within the PVC film. Notice that the sorption curves
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20 were retrieved for single concentration (saturated vapors: 23 mg/ml for ammonia, 23 mg/ml for water,
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22 155 mg/ml for ethanol, 238 mg/ml for methanol and 120 mg/ml for toluene, see also Supporting Table
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24 S1) and that concentration dependence of D was not investigated. We did not extract the coefficient for
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26 hexafluorobenzene because the system did not reach the steady state even after 4h of exposure. The
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31 calculated data are reported in Figure 3a (as black squares) and compared with different
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35 analyte properties and with the Flory-Huggins, Hansen and Hildebrand parameters for the
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39 polymer-solvent pairs. Notice that commercial packaging polymers such as PVC cling wrap
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42 contains a large amount of unknown plasticizers such as di-ethyl-hexyl-phthalate and di-ethyl-
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45 hexyladipate that give hard plastics like PVC the desired flexibility and durability.⁵⁰ Then, we
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49 can only provide a qualitative analysis of the polymer-solvent interactions, as the actual Flory-
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52 Huggins and Hildebrand parameter of the PVC film are unknown. On the other hand, to be
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56 compatible with PVC, the parameters of the latter and those of the plasticizers should
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necessarily be similar, then we do not expect large variation of the actual values from the data we could retrieve for pristine PVC. We would like to highlight that the possibility to apply this method, that was already reported for structured neat polymer films,¹⁵ on commercial systems with unknown composition is an important achievement because it allows to assess diffusive processes in both pristine polymers and packaging polymers directly on the shelf of the market.

In Figure 3a, we notice that the diffusion coefficients for the different diffusing chemicals appears inversely proportional to the Flory-Huggins parameter of the pristine PVC-solvent pairs (green squares). Such parameter is evaluated as the product of the van der Waals size of the solvent multiplied by the quadratic difference of the pristine PVC-solvent Hildebrand parameters, that decreases with the solubility of the polymer-solvent pairs (Figure 3b). Hence, we can reasonably state that the diffusion of the molecular species within the complex PVC film could be affected by the molecular dimensions and by their solubility within the polymer.⁵¹

The value of D seems indeed to increase when the solubility increases; Figure 3b also reports the quadratic difference between the Hansen parameters calculated for all the analytes with respect to pristine PVC. For this data, we notice that the Hildebrand parameter is dominated by Hydrogen bonding forces (orange squares in Figure 3b), while dispersive and polar forces (blue and green squares respectively in the same figure) have a secondary role. We can then

1 state that the diffusion coefficient in PVC is lower for highly polar molecules (ammonia and
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4 water), that are characterized by strong hydrogen bonding which makes their solubilization in
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7 PVC unfavorable and the diffusivity lower. Conversely the value of D increases when
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10 hydrogen bonding within the solvent is weaker or absent and other intermolecular forces,
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13 which also present in the PVC film, become predominant. Then, we can reasonably state that
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16 the formation of weak intermolecular interactions between polymer and analyte increases the
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19 efficiency of the diffusion process. Concerning instead the volume of the molecule, it does not
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22 seem to be strictly correlated to the diffusion parameter. On the other hand, it perfectly
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25 matches with the optical shift of the interference maxima measured at the steady state, which
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28 is proportional to the swelling degree, 1% for water, 1.5% for ammonia, 5 % for methanol, 7%
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31 for ethanol, 20% for toluene, 40% for hexafluorobenzene. As previously stated, the data
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34 regarding the latter have not been reported in Figure 3 as the system does not reach the
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37 equilibrium even after long exposure time. This data indicate that the larger the molecular
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40 volume, the larger is the spectral shift, and in turn the swelling. This characteristic also allows
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43 to use this simple method to discriminate molecules in the vapor phase without the use of any
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46 chemical target and complex laboratory equipment,⁵² and could be used to assess the
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49 presence of degradation byproducts.
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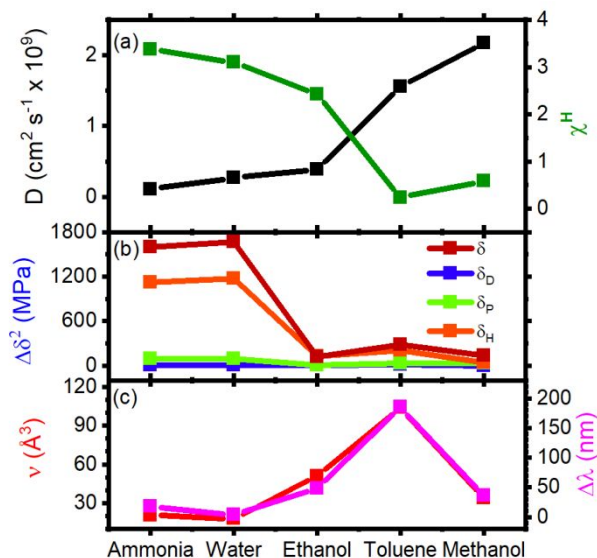


Figure 3: (a) Diffusion coefficient (black squares) and Flory Huggins parameter (green squares) for ammonia, water, ethanol, toluene and methanol in the PVC film. (b) Quadratic difference between the polymer-solvent Hildebrand parameters (red), and Hansen Parameter for dispersive (blue), polar (green) and Hydrogen-bonding (orange) forces. (c) comparison between the van der Waals volume of the diffusing species and the spectral shift of the relative maximum detected at 850 nm in the PVC reflectance spectra at the steady state.⁵¹

The values of diffusion coefficient retrieved optically (see also Supporting Information Table S1) are in good agreement with literature data where available. For instance, the literature coefficient for the two alcohols varies between 10^{-9} and 10^{-12} cm^2/s ,⁵³ while the value for water ranges from 10^{-5} to 10^{-9} cm^2/s .^{45, 53} We would like to highlight that the differences in the coefficient retrieved for water may arise because we performed the measurement in equilibrium with the environmental humidity instead of

1 on dry films. This makes the water concentration larger than zero in the PVC, and thus the diffusion
2 driving force smaller and the process slower. Moreover, the diffusion coefficient can vary by orders of
3 magnitude depending on the polymer molecular weight,⁵⁴ thickness,^{14, 55-56} and on the use of additives
4 and plasticizers that are widely used in these commercial films.
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10 **CONCLUSIONS**

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13 We demonstrated a new simple methodology for the assessment of the diffusion coefficient of
14 molecular species in the vapor phase into polymer thin films used for food packaging by mean of simple
15 reflectance spectroscopy. This method is based on the thickness variation of the polymer thin film
16 induced by the diffusion of molecules and on the variation of the interference pattern of the film itself.
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18 The procedure allows the simple extraction of optical sorption curves that can be employed to assess the
19 diffusion coefficient of the molecular species and the polymer barrier properties, paving the route to a
20 new smart packaging technology. Moreover, this approach allows to easily distinguish different
21 penetrants, providing a smart tool for assessment of goods quality directly in the shelf.
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32 **ASSOCIATED CONTENT**

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37 Supporting Information:

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42 RAMAN characterization of the commercial wrap film (S1); complete optical response of the
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45 PVC film during exposure to the six analytes (S2). Diffusion coefficients van der Waals
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48 volumes, Hildebrand parameters, Flory-Huggins parameters, percentual spectral shift of the
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51 fringes maxima and concentration for the different chemical species (S3).
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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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FOR TABLE OF CONTENT ONLY

Thin Polymer Films: Simple Optical Determination of Molecular Diffusion Coefficients

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