Vapor Diffusion in Porous/Nonporous Polymer Coatings by Dielectric Sorption Analysis

M. Giacomelli Penon,[1] S. J. Picken,[1] M. Wübbenhorst,[2] J. van Turnhout[1]

[1]*Faculty of Applied Sciences, Department NanoStructured Materials, Delft University of Technology, 2628 BL Delft, The Netherlands*
[2]*Faculty of Exact Sciences, Department of Physics and Astronomy, BE-3001 Heverlee, Belgium*

ABSTRACT: The sorption of water vapor in various organic coatings (polyimide, polyamide 6.6 (PA6.6), epoxy, polymethyl methacrylate, low density polyethylene) and filters (polyvinylidene fluoride, polytetra-fluoro-ethylene, porous polyethylene, nitro cellulose, cotton linter) has been investigated by a technique called Dielectric Sorption Analysis (DSA). The technique is based on high-resolution time-resolved, capacitance measurements performed during exposure of an organic coating to humidified nitrogen. The DSA technique could distinguish between all samples, and the diffusion coefficient and maximum sorption is calculated for all samples. A frequency sweep with a dielectric analyzer showed that in all cases the water has no interaction with the polymer films, except PA6.6. For PA6.6 it is assumed that electrode polarization takes place. For filters a frequency sweep showed in two cases electrode polarization (porous polyethylene, cotton linter), two cases no interaction (polytetra-fluoro-ethylene, nitro cellulose) and two cases an intermediate effect (polyvinylidene fluoride 0.22 μm, polyvinylidene fluoride 0.45 μm). The filters described a desorption profile, likely due to swelling of the filters that caused the vapor to be pressed out of the pores of the filters. Mass transport properties derived from complementary weight measurements on epoxy films were in good agreement with the DSA results. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1471–1479, 2007

Key words: coating; diffusion; dielectric properties; films; moisture sorption

INTRODUCTION

Sorption of vapor or liquid into coatings are interesting issues for food packaging, beverage cans, pipes and tubes in process plants, protective paints, and composite materials in the aerospace industry.[1–3] Not only the diffusion coefficient (how quick the polymer absorbs) is of importance, but also the total sorption into the bulk material. For example, if in one case the rate of absorption is very high and the total absorption is not higher than 0.1%, it will have little effect on the ultimate material properties. A more serious change in material properties will be caused when the rate of absorption is very low, but eventually when the total absorption is more than 8%.[2,4,5]

In a previous article,[6] the concept of DSA (Dielectric Sorption Analysis) has been introduced as a useful method to investigate the sorption of vapor into Kapton® films by means of dielectric changes; instead of the more traditional techniques (isothermal weight measurements, thermogravimetric analysis, and permeability measurements[7]). The high sensitivity stems from the fact that water has a high dipole moment and high dielectric constant[8] causing a significant dielectric change at low moisture levels, i.e., when water starts to penetrate into the organic coating. This article will illustrate the full potential of the DSA by measuring a range of various organic coatings and filters/membranes. The DSA results show clear differences between all investigated organic films (and filters), by the maximum sorption and the calculated diffusion coefficients. For the filters an interesting desorption profile can be detected, where the filter first absorbs vapor and then, after some time, releases it. It will also become clear that measuring with the dielectric analyzer at different frequencies is an important and powerful tool to discover interactions of water with the polymer bulk material. The results in this article open the possibility to investigate in the near future degraded coatings, to detect the differences in vapor sorption compared with undegraded coatings. Besides measuring differences in degraded and undegraded coatings, also the sensitivity of the DSA will be an interesting issue.

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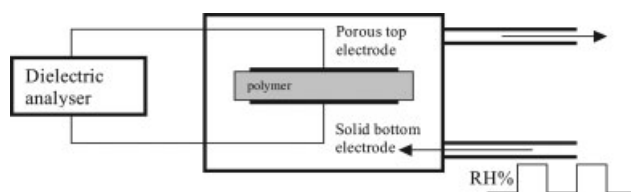**InterScience®**
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Figure 1 Schematic of DSA set up.

EXPERIMENTAL

Materials

To test the range of Dielectric Sorption Analysis (DSA) we used the following, with decreasing affinity towards water, films: Polyamide 6.6 (PA6.6), polymethyl methacrylate (PMMA), Polyimide (PI), epoxy resin, and low density polyethylene (LDPE).

The epoxy resin was received from Akzo Nobel, which is used as marine protective coatings with a thickness of 116 μm. Kapton® (Du Pont, Bad Homburg, Germany) of 50 μm thickness was used as PI. PA6.6 (75 μm), PMMA (39 μm), and LDPE (82 μm) films were made by pressing granules at 250°C, 250°C, and 190°C, respectively.

To expand the possibilities of the DSA we also used the following, with increasing pore sizes, filters (all from Millipore, Amsterdam, The Netherlands, except porous polyethylene and cotton linters): nitro cellulose (pore size 0.05 μm, thickness 76 μm) type VM; Durapore polyvinylidene fluoride (PVDF) membrane (pore size 0.22 μm, thickness 117 μm) Millex GV; PVDF membrane (pore size 0.45 μm, thickness 96 μm) Millex HV; polytetra-fluoro-ethylene (PTFE) (pore size 5 μm, thickness 133 μm) Mitex type LS; porous polyethylene (porous PE) Solupor (DSM, Herleen, The Netherlands) Solupor:3p07A from DSM (thickness 20 μm) and cotton linters (Schleichen and Schell, Dassel, Germany) (which have the appearance of normal paper filters) from Schleicher and Schell Gmbh 595 (thickness 100 μm). (It should be mentioned that for the last two filters the pore sizes are unknown, but by light microscopy it became clear that they were larger when compared with the other filters).

DSA set-up

The DSA set up, schematically shown in Figure 1, has been described more in detail in a previous article.[6] With DSA it is possible to measure the moisture uptake and drying of organic coatings by dielectric means, making use of a porous top electrode.

The dry flow was gaseous nitrogen and the ''wet'' flow gaseous nitrogen, humidified by passing the flow through a water flask. The flow speed of both dry and wet nitrogen flow was 7 mL/s.

The gas temperature was 27°, the dry gas was about 2% RH, and the wet gas was 86% RH. The dry and wet flow was controlled by a two-way valve, which leads either the dry or the wet flow across the sample. The sample was sandwiched between a solid bottom electrode and a porous electrode placed in a closed compartment.

The dielectric analyzer used for these experiments was a HP frequency analyzer with a frequency range between 20 Hz until 1 MHz.

The set up was placed in a temperature conditioned room of 24.5°C (±1°C).

Gravimetric experiments

For the validation of the DSA results, additional gravimetric measurements were performed. The epoxy samples were dried in dry nitrogen at RT for 5 days and then weighed by means of a precision balance. Subsequently, the sample was stored in a flow cell that was continuously flushed with moisturized nitrogen at 88% RH (at RT). The mass was measured by taking out the sample for a few seconds every 15 min (1st h), 20 min (2nd and 3rd h) and finally every 30 min until saturation of the mass was observed.

RESULTS AND DISCUSSION

Comparison of films

Frequency sweeps are shown for all films to discover whether interactions between water and polymer matrix occurs. Then, to illustrate the differences between the samples, PI, PA6.6, LDPE, epoxy, and PMMA are compared at 1 kHz, followed by gravimetric measurements on an epoxy coating.

Films: various frequencies

For all samples the difference in capacitance ($\Delta C'$) is used to plot the data. To compare the frequencies, the data has been normalized with respect to the saturation values (1).

$$|C'| = \frac{\Delta C_t'}{\Delta C_{sat}'} \qquad (1)$$

$|C'|$ is the normalized capacitance, $\Delta C_t'$ is the difference in capacitance ($C_t' - C_0'$) between time t and $t = 0$ (pF), $\Delta C_{sat}'$ is the difference in capacitance ($C_\infty' - C_0'$) at saturation (pF).

Presenting data this way will clarify whether vapor diffuses uniformly (with/without interaction) into the polymer matrix, or not.

The normalized capacitance versus frequency can be found in Figure 2 for various polymer films. For
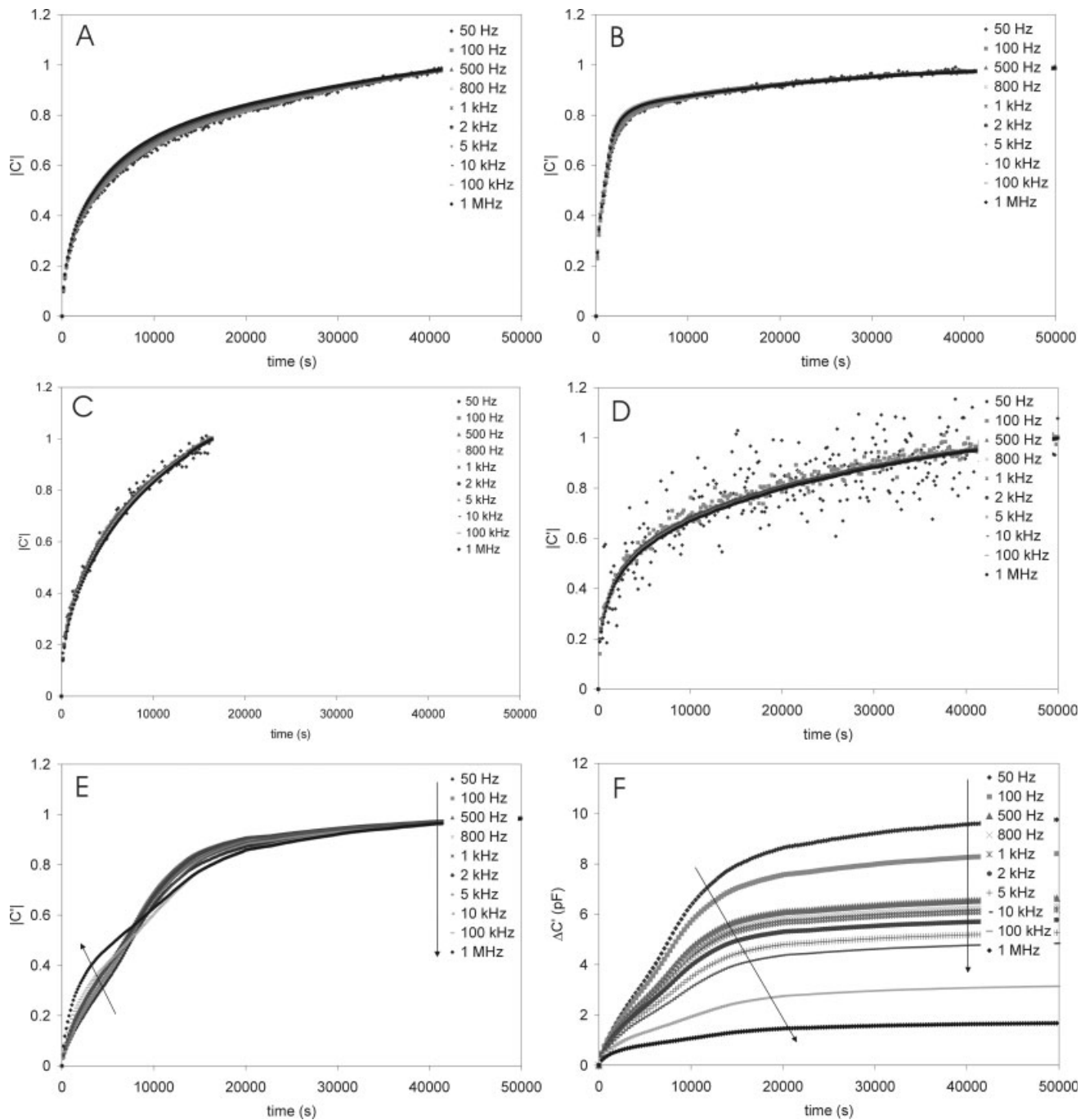
Figure 2 (A) Normalized frequency sweeps of PI; (B) normalized frequency sweeps of PMMA; (C) normalized frequency sweeps of epoxy; (D) normalized frequency sweeps of LDPE; (E) normalized frequency sweeps of PA6.6; (F) Non-normalized frequency sweeps of PA6.6.

PI, PMMA, epoxy, and LDPE it is clear that the data overlap perfectly, indicating that the vapor penetrates the matrix uniformly and does not interact with the polymer matrix. From these results it can be seen that, at the used frequencies, no dominant relaxation processes, and no polymer–water interactions, are detected. Only PA6.6 shows a deviation from this behavior that has a non-Fickian, more sigmoidal diffusion profile. This diffusion profile is present at all frequencies, where it is assumed that a slow establishment of equilibrium takes place at the surface of the film.[9] The slow establishment of equilibrium is not unlikely for nylon 6.6, since it is highly hydrophilic. From lower frequencies (50 Hz) up to high (1 MHz) a peak starts to appear at around 5000 s; whereas from 10,000 s on the diffusion behaves uniformly again. When the non-normalized data is shown [Fig. 2(F)], it becomes clear why the
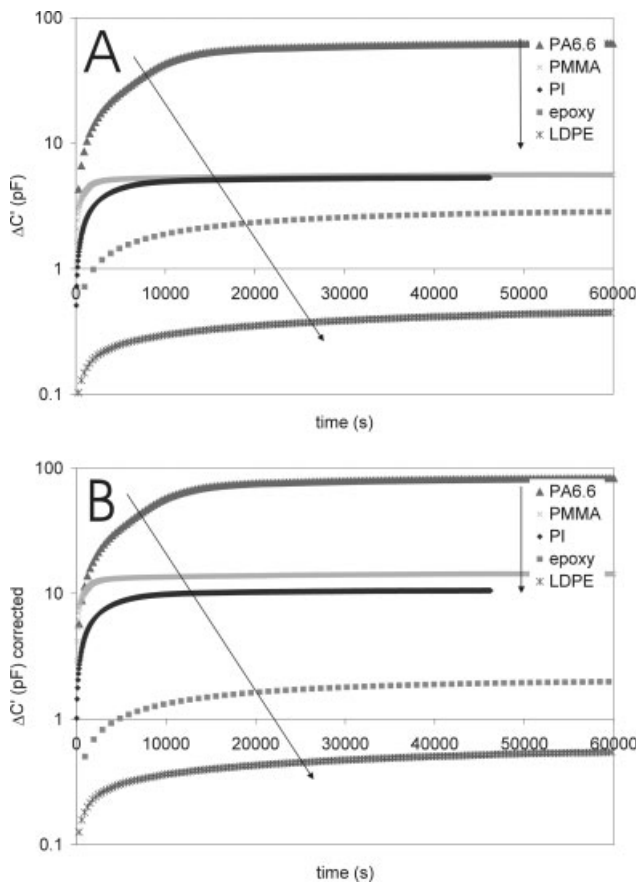
Figure 3 (A) Film comparison at 1 kHz: uncorrected; (B) Film comparison at 1 kHz: thickness corrected (100 μm).

''bump'' appears. Because of the high values of $\Delta C'$, at low frequencies normalizing the data results in a more pronounced signal at 1 MHz. We believe that at lower frequencies polarization is taking place at the electrodes, due to the high water uptake (up to 8–10%).[10]

Films: 1 kHz

Comparison between the films is not straightforward, since the thickness is not the same for all coatings; therefore corrections have to be made for the maximum sorption. In Figure 3(A) the data is shown without correction, in Figure 3(B) a thickness correction (all coatings have been corrected to 100 μm) is made for the maximum sorption. The equation used for maximum sorption correction is shown below (2).

$$C_1' = \frac{\varepsilon_r \varepsilon_0 A}{d_1}, C_2' = \frac{\varepsilon_r \varepsilon_0 A}{d_2} \Rightarrow C_1' = \frac{C_r d_2}{d_1} \qquad (2)$$

C_1' (C_2') is the capacitance for coating 1 (2) (F), ε_r is the dielectric permittivity, ε_0 is the permittivity of vacuum (8.85×10^{-12} F/m), A the measured area of

coating 1 (m^2), d_1 (d_2) thickness of coating 1 (2) (m). A small error is introduced by assuming the dielectric permittivity to be the same for all coatings.

As can be seen in Figure 3(B) no large changes can be seen after the correction, except PMMA and PI for which $\Delta C_t'$ became larger. As expected, PA6.6 has the highest absorption followed by PMMA, PI, epoxy, and LDPE.

To relate the dielectric response to the actual mass increase, which is assumed to be solely due to an increase by the water uptake, we have to model the dielectric response and the mass response. A two-stage sorption model [eq. (3)] with a relaxation term is used for this.[11] The first term in eq. (3) represents the ''perfect'' Fickian diffusion of water into a sample and the second term is the additional gradual uptake caused by the long-term relaxation of the sample due to structural rearrangements induced by the uptake of water.

$$M_t = M_{\infty,F}$$
$$\times \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-(2n+1^2)\frac{\pi^2 D t}{4d^2}\right)\right)$$
$$+ \sum_i M_{\infty,i}[1 - \exp(-k_i t)] \qquad (3)$$

M_t is the weight increase in time, $M_{\infty,F}$ is the equilibrium amount of sorption in the unrelaxed polymer (mg/g), d the half thickness (m), D the diffusion coefficient (m^2 s^{-1}), t the time (s), $M_{\infty,i}$ the equilibrium sorption of the ith relaxation process (mg/g), and k_i the relaxation rate constant of the ith relaxation process (s^{-1}). Note that the exponential series in eq. (3) converges fast, and a limited sum of three terms therefore suffices for the Fickian term. Only one relaxation process is assumed to take place in the polymer matrix, therefore only one relaxation term [eq. (3)] is used.
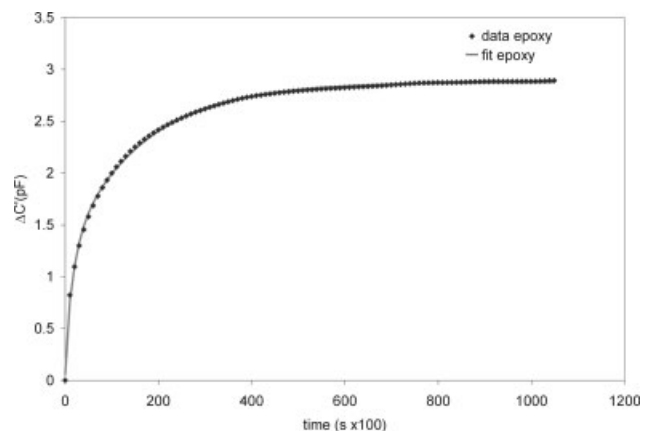

Figure 4 Viscoelastic diffusion model fit of epoxy.

TABLE I
Diffusion Coefficients, Model Parameters, and Total Sorption Calculated for Films

Film	Diffusion coefficient $(10^{-12}$ m^2 s$^{-1})$	$M_{\infty,F}$ (mg/g)	M_1 (mg/g)	k_1 (s^{-1})	Vol % DSA (vol %)
Epoxy	3.1	1.24	1.64	0.00622	2.1 (1.5)[a]
PI	0.44	4.60	0.72	0.00758	2 (2.2)
PMMA	1	4.94	0.68	0.00688	1.8 (–)
LDPE	1.2	0.26	0.29	0.00178	0.17 (–)
PA6.6	0.01	4.57	60.37	0.01189	21 (–)

[a] Values in parantheses indicate weights.

In Figure 4 a fit is shown for dielectric data of epoxy with eq. (3), assuming that the capacitance is linear dependent on weight; with a diffusion coefficient of 3.1×10^{-12} m^2 s^{-1}. For the gravimetric data of epoxy the fit results in a diffusion coefficient of 2.2×10^{-12} m^2 s^{-1}. For the other films the diffusion coefficients are given in Table I, along with the model parameters. For PA 6.6, the sigmoidal part of the sorption curve could not be fitted as perfectly as the other films, therefore other diffusion models will have to be checked in the future (e.g., variable surface concentration model[9]).

The lowest rate of sorption is found for PA6.6, which in turn has the highest sorption, indicating that both maximum sorption and sorption rate are necessary and important parameters. The maximum sorption is a good indicator for the affinity and wet ability of the polymer towards water (vapor); and the sorption rate shows how easy the water penetrates first the free volume of the polymer, followed by polymeric relaxation processes to increase its uptake (also linked with the wet ability).

From the DSA measurements maximum sorption values can be calculated by the following equation,[6] which is known as the Landau, Lifschitz, Looyenga (LLL) relation,[12,13]

$$\varepsilon_t'^{1/3} = v_w \cdot \varepsilon_w'^{1/3} + (1 - v_w)\varepsilon_d'^{1/3} \qquad (4)$$

ε_t' is the total dielectric permittivity of the saturated signal (water + polymer), ε_w' the dielectric permittivity of water (assumed to be 80), ε_d' is the dielectric permittivity of dry polymer; and v_w the volume fraction of water at saturation. The values of the calculated volume percentages of water in films can be found in Table I.

Weight measurements of (0.6533 g dry) epoxy show a mass water uptake of 8.7×10^{-3} g, which results in 1.3 wt % (1.5 vol %) vapor uptake. For DSA measurements the vapor uptake is 2.1 vol % calculated with eq. (4), which is in reasonable agreement with the weight measurements.

Because of the electrode polarization a too high value for water sorption in PA6.6 is calculated, whereas the other values are acceptable values for vapor sorption in polymer films.[14]

Gravimetric measurements

A direct comparison between the DSA response and the gravimetric data of the epoxy samples will be made. The gravimetric measurements were performed with epoxy coatings on a glass substrate to prevent double sided diffusion. In a previous article,[6] it was observed that Kapton® dielectric data was similar to weight (absorption) data.

The results of the normalized gravimetric ($|M| = \Delta M_t/\Delta M_{\mathrm{sat}}$) and dielectric ($|C'| = \Delta C'_t/\Delta C'_{\mathrm{sat}}$) measurements are displayed in Figure 5. The dielectric data can be treated as weight data, since the dielectric curve overlaps the mass curve.

Comparison of filters

In this section the results for filters are discussed and the same approach is used as for films. First an evaluation on measurements done at various frequencies has been done, followed by comparison of various filters at 1 kHz. Gravimetric measurements were not possible for filters due to too rapid desorp-
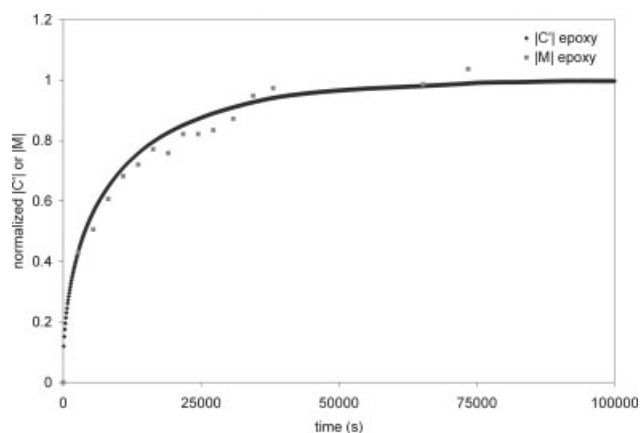

Figure 5 Gravimetric measurement versus dielectric measurement epoxy (1 kHz).
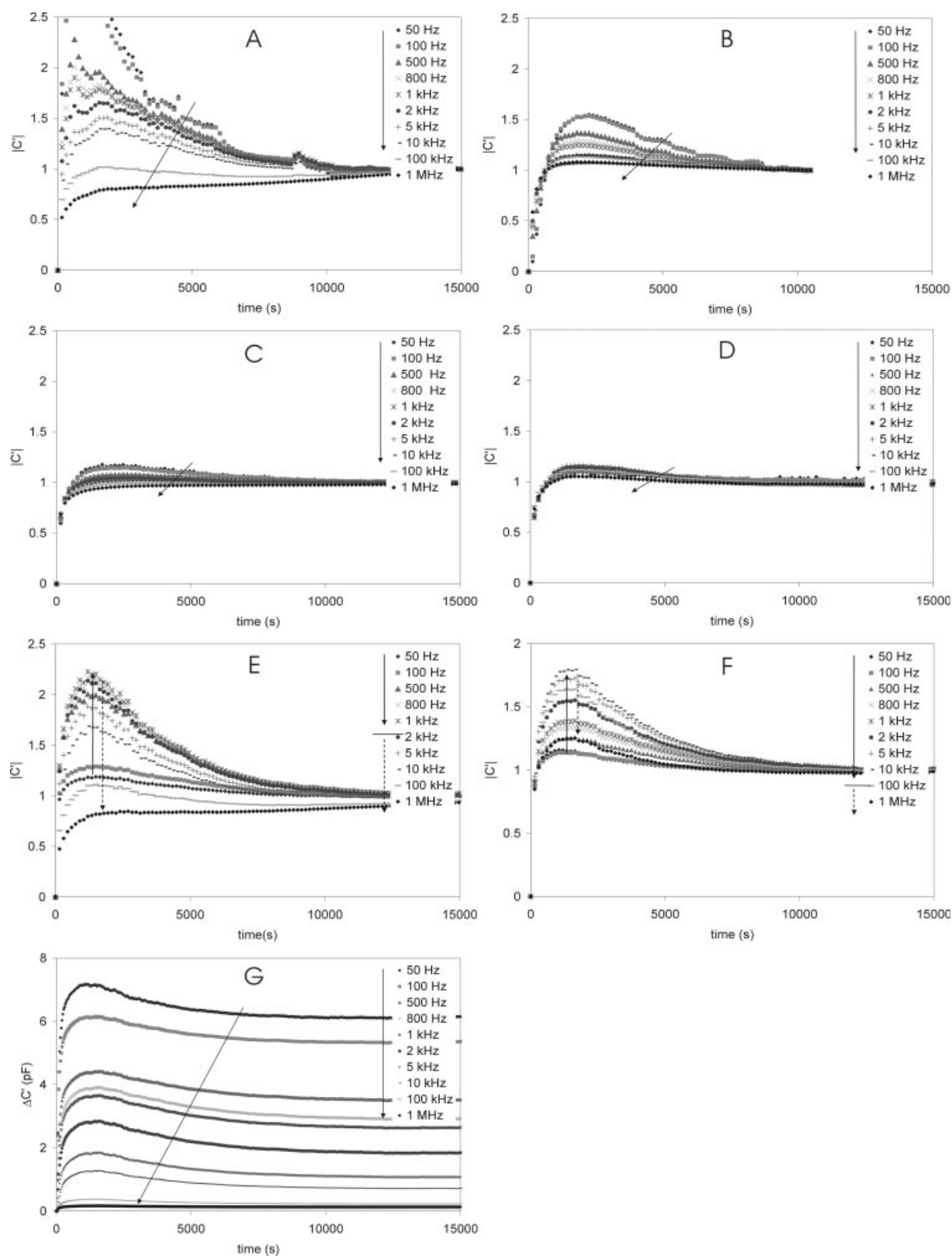
Figure 6 (A) Normalized frequency sweeps of porous PE; (B) normalized frequency sweeps of cotton linter; (C) normalized frequency sweeps of nitro cellulose 0.05 μm; (D) normalized frequency sweeps of PTFE 5 μm; (E) normalized frequency sweeps of PVDF 0.45 μm; (F) normalized frequency sweeps of PVDF 0.22 μm; (G) Non-normalized frequency sweeps of PVDF 0.22 μm.
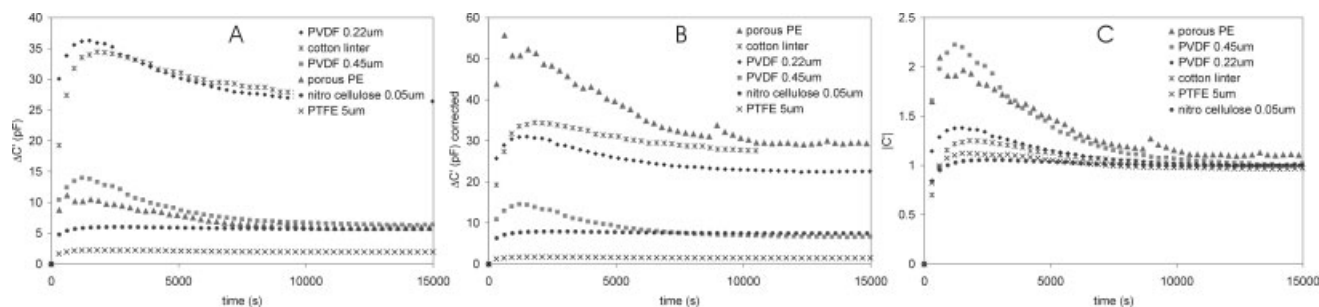
Figure 7 (A) Filter comparison at 1 kHz: uncorrected; (b) filter comparison at 1 kHz: thickness corrected (100 μm); (C) filter comparison at 1 kHz: normalized.

tion on removal from the flow cell flushed with moisturized nitrogen.

Filters: various frequencies

The normalized results for filters are shown at various frequencies in Figure 6.

For the filters another effect takes place during vapor uptake than the films. For porous PE and cotton linter a clear peak appears, which becomes smaller at higher frequencies. Berens and Hopfenberg found such behavior for sorption of methanol in PVC.[11] The assumption involves desorption of methanol due to collapse or deswelling of the glassy structure of PVC. It is not unlikely that also in this case desorption occurs for cotton linter, which is hydrophilic, due to softening (and finally collapse) of the matrix. On the other hand, for porous PE strong capillary forces caused by water, and strong hydrophobicity, deswells the structure. Porous PE has a low weight per surface area (3 g/m²) and is hydrophobic with a thickness of 20 μm, whereas cotton linter has a higher weight per surface area (78 g/m²), is hydrophilic and has a thickness of 100 μm.

Despite the fact that porous PE is hydrophobic, the low weight per surface area and small thickness causes electrode polarization. In some of the measurements nearly short-circuiting occurred, especially at low frequencies. Because of the low absorption of water in the PE polymer matrix, the water forms a thin layer in the continuous open structure of the pores. This also explains the fact that the peak becomes smaller from low to high frequencies due to polarization (decreasing from low to high frequencies). The same holds for the cotton linter, except in this case no short-circuiting appears due to the fact that the vapor easily penetrates the cotton, in combination with the higher thickness of the filter.

Nitro cellulose and PTFE shows a similar behavior, albeit to a much smaller extent than porous PE and cotton linter. Nitro cellulose is slightly hydrophilic and has pores of about 0.05 μm diameter. The formation of a water layer on the pore walls causes polarization at lower frequencies and finally due to

swelling of the polymer matrix the pores tend to close causing desorption of the water in the pores.

PTFE, a fiber structure (like cotton linters) and hydrophobic of nature, did not show polarization, observing the overlap at all frequencies, probably due to denser structure than porous PE; but desorption still occurs.

Finally PVDF 0.22 μm (pore size) and PVDF 0.45 μm (pore size) has a trend that starts with a low peak at low frequencies (50–500 Hz), to a maximum at higher frequencies (0.8–2/10 kHz) and ending low at the highest frequencies (0.05/0.1–1 MHz). This behavior is obviously not the result of polarization, which should increase with decreasing frequency. The structure is continuous and the matrix is hydrophilic PVDF. This material behaves similar to cotton linter, except the pore size is much smaller for PVDF. PVDF has been made hydrophilic, therefore the frequency has an important effect on the interaction of water to the matrix and finally the height of the peak, in this case the highest for PVDF between 2 and 10 kHz.

In Figure 6(G) the non-normalized data can be found for PVDF 0.22 μm. There is a general decreasing trend from high to low frequencies and also the peak has the same height over the frequency range 50–10 kHz. Compared to the other filters, PVDF, PTFE, and nitro cellulose show similar results. Cotton linter and porous PE show the trend from low to high frequency a high to low peak height, due to polarization.

Polarization does not play a role for PVDF, PTFE and nitro cellulose, because the peak heights are the same between 50 and 10 kHz; therefore the peak is likely an effect of desorption due to collapse of the matrix. The fact that higher frequencies (100–1 Mhz) show a smaller effect can be explained by different distribution of water, bulk water and bound water, in the polymer.

Filters: 1 kHz

For filters the same data presentation is used as for films, where in Figure 7(A) the data is plotted with-
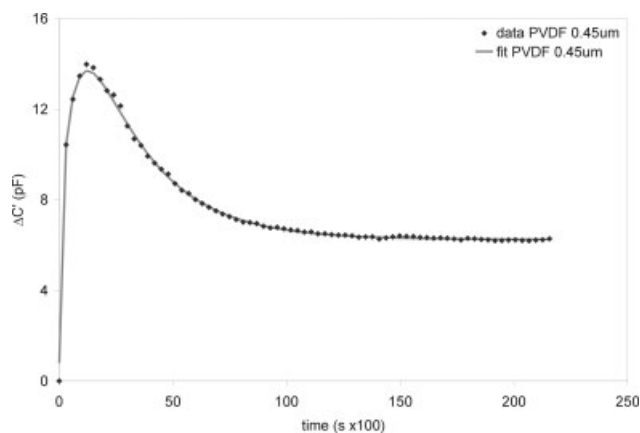
Figure 8 Viscoelastic diffusion model fit of PVDF 0.45 μm.

out any correction. In 7(B) the maximum sorption correction [eq. (2)] is given and 7(C) displays the normalized data for all filters.

Without maximum sorption correction [Fig. 7(A)] the order from high to low peak is: PVDF 0.22 μm, cotton linter, PVDF 0.45 μm, porous PE, nitro cellulose and PTFE. Corrected for the thickness this becomes now [Fig. 7(B)]: porous PE, cotton linter, PVDF 0.22 μm, PVDF 0.45 μm, nitro cellulose and PTFE. The most porous system (porous PE) and most hydrophilic (cotton linter) have the highest sorption; whereas the most hydrophobic (PTFE) has the lowest sorption, followed by the more hydrophilic nitro cellulose. The fact that PVDF 0.45 μm has 1.5 times higher density than PVDF 0.22 μm could explain higher water uptake of PVDF 0.22 μm.

The normalized graph [Fig. 7(C)] shows that porous PE and PVDF 0.45 μm have the largest desorption peaks. This large desorption peak might be the cause of high water uptake due to high porosity, causing electrode polarization on the electrodes and is followed by, for PVDF, a collapse of the matrix due to softening of the polymer; whereas for PE strong capillary forces and hydrophobicity causes the matrix to deswell. PVDF 0.45 μm has a higher density, but the pores are larger than that of PVDF 0.22 μm, resulting in larger electrode polarization for PVDF 0.45 μm.

Interestingly, the desorption peaks for all filters occur around the same time: 1000–2000 s [Fig. 7(C)]. A plausible explanation might be that the vapor penetrates the pores of all filters at the same rate, followed by diffusion in the polymer filter material causing the desorption peak to disappear due to swelling or collapse.

The diffusion coefficient has been calculated with the same fitting eq. (3), where the only difference is that two relaxation terms were used: one to account for the desorption process and one for the normal structural relaxation of the polymer matrix. In Figure 8 the fit is shown of PVDF 0.45 μm, resulting in a diffusion coefficient of 5.2×10^{-12} m^2 s^{-1}. The diffusion coefficients for the filter membranes are shown in Table II, along with the model parameters.

The most interesting result from the calculated diffusion coefficients in Table II is that they represent the real diffusion coefficients for the bulk polymer. This means that eq. (3) corrects the porous structure into a bulk polymer by using the two relaxation terms. This can be seen when the diffusion coefficient of PE (in Table I) is compared with porous PE (Table II), which are nearly the same. Also PVDF 0.22 μm and PVDF 0.45 μm have the same diffusion coefficients, although the pore sizes are different.

CONCLUSIONS AND OUTLOOK

The DSA is able to distinguish between all types of films and filters; which illustrates the capability of the device. The dielectric data can be used as mass data to calculate diffusion coefficients, since a good overlap was found when comparing gravimetric measurements and DSA measurements for an epoxy film (and also for PI). The diffusion coefficient can be determined by using a Fickian diffusion equation combined with a relaxation parameter. The maximum sorption can be determined by using a dielectric mixing-rule given by Landau, Lifschitz, Looyenga (LLL).

Frequency analysis showed that for polymer films the vapor penetrates the organic coating without interacting with the polymer. For PA6.6 this was not the case, where likely electrode polarization takes

TABLE II
Diffusion Coefficients Calculated for Filters, Along with Model Parameters

Filter	Diffusion coefficient (10^{-12} m^2 s^{-1})	$M_{\infty,F}$ (mg/g)	$M_{\infty,1}$ (mg/g)	k_1 (s^{-1})	$M_{\infty,2}$ (mg/g)	k_2 (s^{-1})
Porous PE	1.7	6.64	9.26	0.59	−10.25	0.031
Cotton linter	2.9	5.90	35.23	0.24	−15.28	0.021
PVDF 0.22μm	5.5	25.79	25.32	0.68	−24.97	0.035
PVDF 0.45μm	5.2	18.34	3.79	0.95	−15.88	0.036
Nitro cellulose	0.15	2.75	4.27	0.76	−1.37	0.035
PTFE	0.53	7.19	1.30	0.59	−5.97	0.0099

place due to the high water uptake of this material. Therefore, care should be taken with interpretation of the results for total water sorption. Also other diffusion models will have to be tried, to see whether the sigmoidal fit can be fitted better.

First observation of the DSA filter measurements showed that desorption seemed to occur. The largest desorption was found for the most porous systems (porous PE and cotton linter) and the smallest desorption for the least porous systems (nitro cellulose and PTFE). The relation between the size of the desorption peak and the porosity could indicate that electrode polarization occurs for the most porous systems and decreases for less porous systems.

Because of the high hydrophobicity of PTFE and small pore size of nitro cellulose, a negligible frequency effect (no interaction between water and polymer) of PTFE and nitro cellulose was found. For porous PE and cotton linter the electrode polarization takes place due to the high porosity of both materials. The intermediate case holds for PVDF 0.22 μm and PVDF 0.45 μm, where the frequency analysis show, that with increasing frequency first a rising and then a decrease in desorption peak size. This could be explained by the fact that the material is made hydrophilic, resulting in a frequency dependency with water. Also no electrode polarization occurred because the pore sizes are between porous PE/cotton linter and PTFE/nitro cellulose.

Clearly DSA is a powerful technique for measuring vapor sorption rates in a wide range of polymer materials and filters. For films with defects (pinholes, etc.) the DSA technique can be useful. Also, due to the possibility of frequency analysis, more complicated water sorption processes can be investigated in some detail as is demonstrated for PA6.6, and the porous filter materials, where ''bulk'' and absorbed water contribute to the response.

To establish the potential of the new technique in the field of nondestructive coating inspection and early warning testing, future work will be done on other types of polymer films. In addition UV degradation will be inflicted on epoxy coatings to determine the sensitivity of the DSA to detect chemical surface changes.

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