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Water sorption in UV degraded clear and pigmented epoxy coatings assessed by dielectric sorption analysis

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Abstract

Degraded clear and pigmented epoxy coatings were investigated by dielectric sorption analysis (DSA). Differences in dynamics of absorption, due to increased hydrophilicity, crosslinking and porosity, were found between UV degraded and undegraded epoxy coatings. Desorption was observed for longer degradation times, caused by swelling of the coating, squeezing out the excess of water. Model system measurements of pigmented coatings with various filters on top reproduced the desorption behaviour. Due to crack formation during DSA measurements, clear coatings showed fluctuating results, a result of release of tension of the UV degraded clear coating by humidified nitrogen. Pigmented coatings did not show this behaviour, resulting in an increasing water absorption trend with increasing degradation times. Larger desorption peaks were found for lower frequencies, indicating that either polarization takes place or water-hydrophilic interaction. Based on these results, DSA is suitable for non-destructive investigation of degraded coatings and paints.

Keywords: Epoxy coating; UV degradation; Dielectric measurement; Water (de-) sorption; Organic coating

1. Introduction

Life time prediction of organic coatings plays an important role in today's world. From around 1950–1960 scientists and industries started to bring more coherence in coating degradation [1–11], and tried to find methods to estimate when their coating or paint should be replaced. Also the consumer expects a ranking or indication from the paint industry of how good their coating is in comparison to their competitors (clearly the paint industry also would like to know this). For this, accelerated test facilities, like the weather-o-meter, QUV, salt spray test and others [12] have been built to speed up degradation and get fast results, dependent on the conditions the coating is likely to experience. Of course the traditional long term exposures in exotic places like (the most famous one) in Florida, Australia, and nowadays all over the world [13–16] are also still performed. After extensive trials to compare the accelerated degraded coatings with the naturally degraded coatings [17–24], it became clear that most likely due to nature's irreproducibility (and laboratory's reproducibility), the link between both is very difficult to make. Still, in order to give an indication of the coating quality, and to keep paint development going, the paint industry uses accelerated weathering tests on large scale in combination with natural weathering tests.

Besides various ways of degrading the coating naturally or accelerated, numerous methods of analysing the degree of degradation (involving different fields of expertise: chemists, mathematicians, physicists, material scientists, mechanical engineers etc.) have been performed over time. There is gloss, hardness, rheometric, UV–VIS, WAXS, DSC, FTIR, AFM, SEM, DRS, etc. [25–31]. Unfortunately all these results have been obtained separately on different coatings, resulting in a scattered whole. Following the trend of articles though, it becomes clear that the degradation should be detected at an

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earlier level, and therefore more sensitive equipment is used (like the AFM and micro ATR-FTIR).

Previous articles [32,33] have shown that the dielectric sorption analyser is suitable for measuring sorption curves for various organic coatings and filters. UV degraded clear and pigmented coatings were chosen to investigate sorption differences. From the results in this paper it will follow that the DSA shows clear trends with increasing degradation times. Also a desorption mechanism is found that occurs after a certain amount of degradation time. This desorption phenomenon has already been shown for DSA measurements on filters [33], and will be extended with model systems in this paper. A dielectric frequency sweep with DSA measurements resulted in a higher sensitivity at lower frequencies. It will become clear that the advantage of DSA over most other measurements' devices is the non-destructive aspect and the fact that both the surface and the whole coating are measured (in time).

2. Experimental

2.1. Materials

An epoxy clear coating (resin) and a fully commercial pigmented epoxy coating, both received from Akzo Nobel, have been used for UV degradation. The clear coating contains only surfactant and defoamer as additives. The pigmented coating is chemically similar to the clear coating, but it is in a commercial state (which means more additives and pigments added); and is used as a marine protective coating.

Both coatings were air sprayed on glass plates, cured at ambient conditions, and end cured for 30 min at 110 °C. DSC measurements were done to make sure the coatings were fully cured. The coatings are then released from the glass and dried under a dry nitrogen flow. The clear coatings had an average thickness of 100 μm and the pigmented coatings 60 μm.

2.2. DSA set-up

An extensive description involving the principles of the dielectric sorption analysis can be found in a previous article [32]. The main advantage of this technique involves the possibility of measuring in real time the change in dielectric properties of the coating during moisture uptake.

Gaseous nitrogen (2%RH at 27 °C) represents the dry flow and the "wet" flow is humidified gaseous nitrogen (86% RH at 27 °C), with a flow rate of 7 ml/s.

Gaseous nitrogen (dry or wet) absorption by the sample is achieved by a porous top electrode and a solid bottom electrode; the whole is place in a closed compartment.

The dielectric analysers used for these experiments are an Andeen Hagerling (high precision 1 kHz bridge, type 2500A) and a Hewlett Packard (HP 4284A precision LCR meter) frequency analyser with a frequency range from 20 Hz to 1 MHz.

2.3. Degradation set up

A closed system was built, to degrade the coatings under controlled parameters. Basically it is a closed box with a quartz window for UV degradation; a heating element is used to adjust the temperature, and the medium is dry air (<25 vpm). The UV source is a Philips PL lamp, of which the difference in spectrum and intensity becomes clear in Fig. 1, when compared to the sun (direct and indirect). The indirect spectrum is measured by exposing the spectrometer at such an small angle to the sun, that the CCD of the meter was no longer over saturated; and is just shown as comparison.

The clear coatings were UV degraded in two ways. For the first method one coating was degraded cumulatively for 0, 1, 2, 4, 8 and 16 days. In the second method a new clear coating was used for each separate degradation (0, 2, 4, 14, 20 and 40 days). The pigmented coatings were degraded for 0, 2, 4 and 40 days (a fresh coating for each degradation).

3. Results and discussion

3.1. DSA measurements on degraded samples

3.1.1. Clear coating

The DSA result for the cumulative degraded clear coating is shown in Fig. 2. Fig. 2(a) shows the difference $\Delta C'$ ($C_t' - C_{sat}'$), which is the capacitative part of the signal; and Fig. 2(b) the difference $\Delta C''$ ($C_t'' - C_{sat}''$), which is the resistive part of the signal.

Interestingly, the differences in $\Delta C'$ in Fig. 2(a) between 0, 2 and 4 days are not significant. A difference can be seen for 1 day degraded, which is characterized by a higher water uptake. Increased hydrophilic behaviour is caused by scission (and oxidation) of bonds in the polymer, which could explain this higher water uptake. In comparison with the undegraded coating degradation times between 2 and 4 days causes similar water uptake. Most likely crosslinking dominates the process (despite the hydrophilic surface), keeping the water uptake the same due to a decrease in free volume. Longer degradation times show a clear difference in the shape of a bend (for 8 days) and a bump (for 16 days). Compared to the undegraded

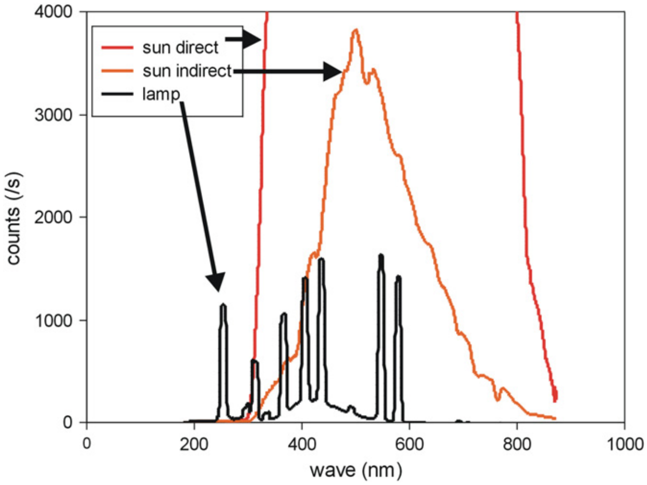

Fig. 1. Spectrum of UV source used for degradation, compared with sunlight.

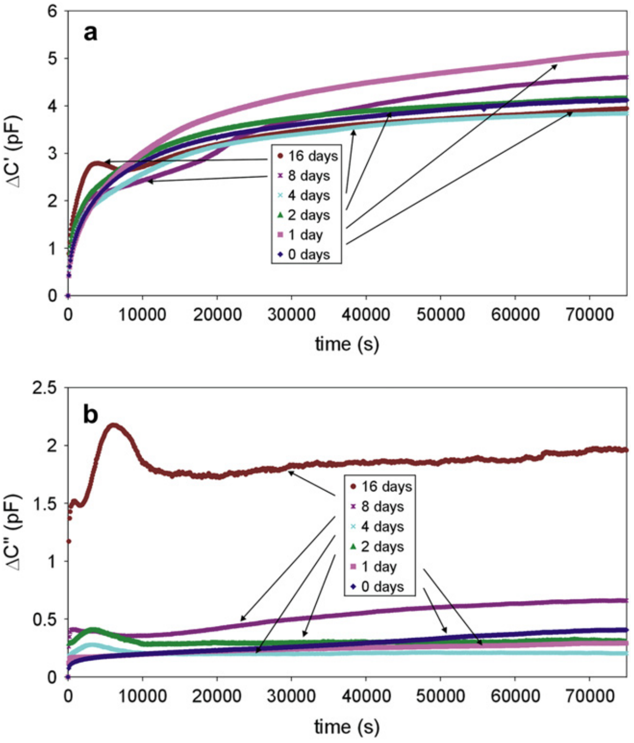

Fig. 2. Cumulative degraded clear coating (a) $\Delta C'$ vs. time and (b) $\Delta C''$ vs. time.

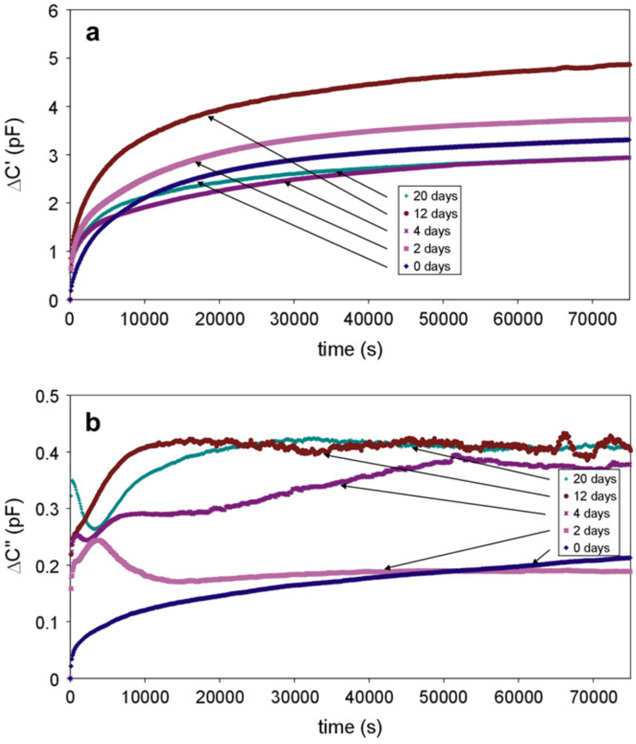

Fig. 3. Non-cumulative degraded clear coating (a) $\Delta C'$ vs. time and (b) $\Delta C''$ vs. time.

coating, longer degradation times do not result in a significant higher water uptake.

Although $\Delta C'$ does not show any difference for the 2 and 4 days, $\Delta C''$ clearly displays a bump. A large signal difference in $\Delta C''$ can be seen for 8 and 16 days UV degradation, but also for 1, 2 and 4 days a bump appears in the first 10.000 s, which makes it possible to discriminate it from the undegraded coating. These results show that it is more interesting to use $\Delta C''$ to detect changes in coatings during uptake of water vapour, since the largest change can be found there. This emphasizes that the resistivity ($\Delta C''$) is more affected during degradation than the capacitative ($\Delta C'$) part of the coating, by movements of polar groups and water in the polymer matrix.

Instead of cumulative degradation with one sample, for comparison non-cumulative (a fresh sample for every degradation) was also performed. The result is shown in Fig. 3. In Fig. 3(a) the $\Delta C'$ is plotted against time and no clear trend for increasing degradation time and water sorption can be observed. Degradation for 2 and 12 days shows a higher signal than 4, 20 and 40 days, implying that the water uptake is lower than an undegraded sample assuming that the capacitative part $\Delta C''$ is directly related to weight [32,33]. Similar to the cumulative curves in Fig. 2(b), plotting $\Delta C''$ (Fig. 3(b)) shows that there are clear differences between the curves. Looking at the saturation level the trend is from low to high, 0, 2, 4, 12 and 20 days; and for the peak height in the first 10.000 s the trend is from low to high, 0, 2, 4, 12 and 20 days. Also in the non-cumulative case it is clear that the resistive dielectric signal gives a more clear trend than the capacitative signal.

Comparing cumulative and non-cumulative degraded samples it can be seen that the capacitative signal shows the same trend for both coatings in the saturation area. A different trend is shown for 8 and 16 days cumulative, compared with 12 and 20 days non-cumulative; where the cumulative coating shows a depression at 8 days and a bump after 16 days degradation. When the samples were investigated with a microscope (Fig. 4), the undegraded coatings were undamaged, which was also the case after degradation (Fig. 4(a)), but after the DSA measurements the coatings showed cracks at the surface (Fig. 4(b)). Unfortunately the cumulatively degraded coatings were not monitored consistently with the microscope, but it is clear that when cracks are present in the coating further cumulative UV degradation and measurements with the DSA gives results which are different than when the cracks are not yet present.

Crack formation after DSA measurements is a result of stresses present at the surface of the coating on UV degradation, which are released after humidifying it during the DSA measurement. Humidity causes the coating to swell and lowers its T_g [34–39]. During swelling the degraded part of the coating swells more than the bottom part, due to higher porosity and hydrophilicity. It is not expected that the cracks are being formed during swelling, but during the drying cycle, since the top layer releases the water more quickly causing a higher shrinkage, and most likely cracking, of the top layer. Also the fact that the top electrode is pressed on the coating surface may facilitate crack formation.

In Fig. 3(b) it can be seen that the cumulative 16 days degraded sample shows a much higher signal than Fig. 4(b) the 20 days degraded sample, suggesting that due to the fact the cracks are already present in the cumulative sample the

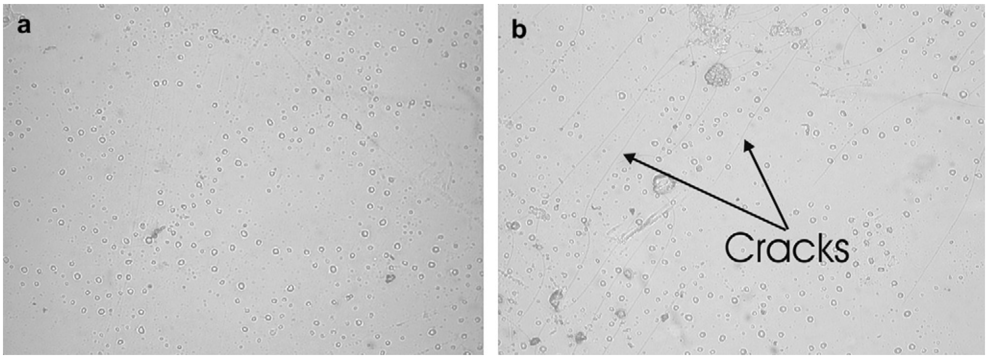

Fig. 4. (a) Degraded coating, before DSA measurement. (b) Degraded coating (cracked), after DSA measurement.

resistive part of the coating increases more than when the cracks are not yet present, as is the case for the non-cumulative samples.

The stresses at the surface followed by crack formations of the clear coatings cause fluctuations in the DSA measurements.

The peaks that appear in both cumulative and non-cumulative measurements are the result of desorption of water due to crack closure or stress relaxation by swelling of the degraded coating. Desorption has been discussed in a previous paper [33], and crack closure due to swelling has been described by Lundgren and Gudmundson [40].

3.1.2. Pigmented coating

In Fig. 5 the non-cumulative undegraded and degraded (Fig. 5(a) and (b)) pigmented coatings are shown for 0, 2, 4 and 40 days. Compared to the undegraded clear coatings (Fig. 3(a) and (b)), a lower value is expected for saturation $\Delta C'$ and $\Delta C''$ for the pigmented coating (Fig. 5(a) and (b)), since the pigments do not contribute to the water sorption. Instead a higher value is found and this can be attributed to the thickness difference between clear coating (about 100 μm) and the pigmented coating (about 50 μm); A thinner coating results in a higher $\Delta C'$ and $\Delta C''$ difference. For both $\Delta C'$ and $\Delta C''$ an increasing peak is observed for longer degradation times as shown in Fig. 5(a) and (b); similar to the degraded clear coatings, but more profound. Likely the pigments contribute to a better stress distribution inside the degraded resin, resulting in reproducible measurements of the DSA. No cracks were found before or after degradation and after the DSA measurements, supporting the assumption of a better stress distribution mentioned before. Therefore in the case of pigmented coatings there cannot be a crack closure mechanism causing desorption of water. Still during UV degradation scission of polymer chains causes a higher permeability of the resin. In a previous article it was shown that membranes with different porosities causes different desorption peaks during DSA measurements, due to pore closing as a result of swelling [33], which can also be the case for degraded pigmented coatings.

Considering that only the top layer of both coatings degrades, the pigmented coating gives a better resolution for the DSA measurements because of its lower thickness. Unfortunately a lower thickness could not be achieved with the clear coatings, due to dewetting and break up of the film.

3.1.3. Diffusion coefficient of undegraded clear and pigmented coating

The undegraded clear and pigmented coating can be compared to find out what effect pigments and fillers have on the sorption rate of water vapour. Both coatings cannot be compared directly since the thicknesses are not the same, therefore the diffusion coefficients will be calculated and compared to each other.

The validation and explanation for the calculation of diffusion coefficients for DSA measurements is discussed in a previous article [33], therefore it suffices only to show Eq. (1).

$$\frac{M_\mathrm{t}}{M_\mathrm{sat}} = \Phi\left(1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\left(2n+1^2\right)\frac{\pi^2 Dt}{4d^2}\right)\right) + (1-\Phi)[1-\exp(-kt)] \quad (1)$$

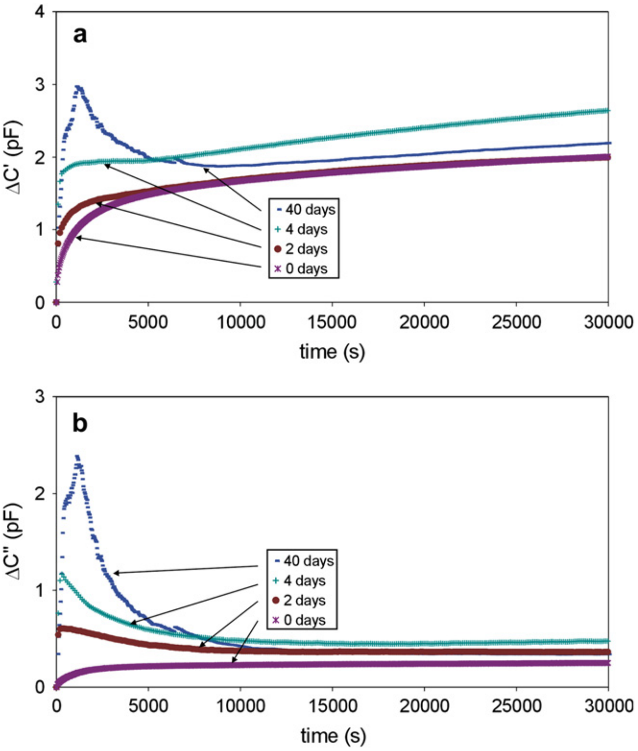

Fig. 5. Degraded pigmented coating (a) $\Delta C'$ vs. time and (b) $\Delta C''$ vs. time.

M_t is the weight increase in time, M_{sat} the weight increase at saturation, d the half thickness [m], D the diffusion coefficient [$m^2\,s^{-1}$], t the time [s], Φ the equilibrium ratio constant which represents the ratio of the equilibriums of the first stage to that of the second stage in the sorption, and k the rate constant of the relaxation process [s^{-1}].

For a clear coating the diffusion coefficient is $3.1 \times 10^{-12}\,m^2/s$ and for a pigmented coating $8.9 \times 10^{-13}\,m^2/s$. The lower diffusion coefficient for the pigmented coating indicates that the presence of pigment and filler material slows the sorption of water into the resin, probably due to the platelet shape of the filler material.

3.1.4. Comparison between clear and pigmented coatings

Instead of the AH 1 kHz dielectric bridge, a HP dielectric bridge was used, which is capable of frequency sweeps between 20 Hz and 1 MHz.

An undegraded and degraded (40 days UV) clear and pigmented coatings were measured with the DSA and the results are shown in Fig. 6(a)–(d). To compare the signal heights of the clear coatings with the pigmented ones, $\Delta\varepsilon'$ and $\Delta\varepsilon''$ have been plotted against time, instead of $\Delta C'$ and $\Delta C''$. $\varepsilon' = C'd/\varepsilon_0 A$, where ε' is the dielectric permittivity, C' the capacitative part of the signal, d the thickness [m], ε_0 the permittivity of vacuum [$J^{-1}\,C^2\,m^{-1}$] and A the measured area [m^2], $\Delta\varepsilon' = \varepsilon'_t - \varepsilon'_0$, where ε'_t is the permittivity at time t, and ε'_0 the permittivity in the dry state. ε'' and $\Delta\varepsilon''$ are found in the same way, where ε'' represents the loss of signal.

For the clear and pigmented undegraded coating the normalized sweeps $|\varepsilon'|$ are shown in Fig. 7(a) and (c) and $|\varepsilon''|$ in Fig. 7(b) and (d). A similar result in Fig. 7(a) has been discussed in a previous paper, showing that the frequency overlap is a result of water penetrating the coating without interacting with the resin. Fig. 7(b) shows the same result for $|\varepsilon''|$. For the pigmented samples it can be seen in Fig. 7(c) and (d) that at frequencies 100 kHz and 1 MHz the curve deviates slightly from all other frequencies. This minor deviation might be the result of chemical or physical interaction of water with the pigments.

The frequency dependence is very prominent in Fig. 7(a)–(d), which is not the case for undegraded samples. Furthermore, the maximum for clear and pigmented samples are both around 1200 s, which is also expected since the resins are the same.

Maximum peak height ($\Delta\varepsilon'$ and $\Delta\varepsilon''$) is obtained at low frequencies and decreases (even tends to disappear) at high frequencies for clear and pigmented samples. A high dielectric signal at lower frequencies could indicate hydrogen bonding of water with (degraded/oxidized) hydrophilic parts of the coating. Also, due to higher water uptake close to the surface of the coating, (electrode) polarization might be an issue at lower frequencies. The fact that the peak disappears with time suggests that another mechanisms are present. Water binds to the hydrophilic parts of the coating, causing a higher

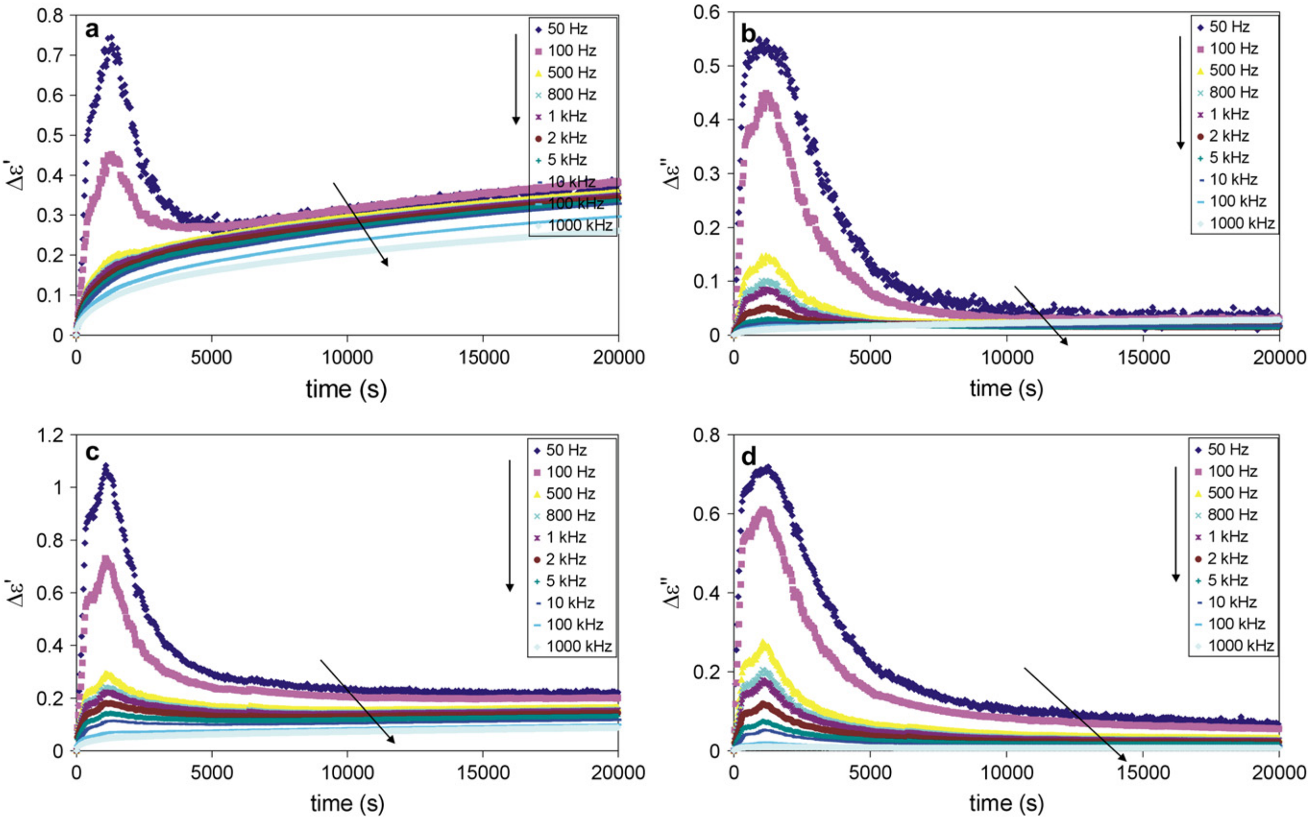

Fig. 6. Frequency sweep (50 Hz to 1 MHz) for a 40 days UV degraded clear coating (a) $\Delta\varepsilon'$ vs. time and (b) $\Delta\varepsilon''$ vs. time. Frequency sweep (50 Hz to 1 MHz) for a 40 days UV degraded pigmented coating (c) $\Delta\varepsilon'$ vs. time and (d) $\Delta\varepsilon''$ vs. time.

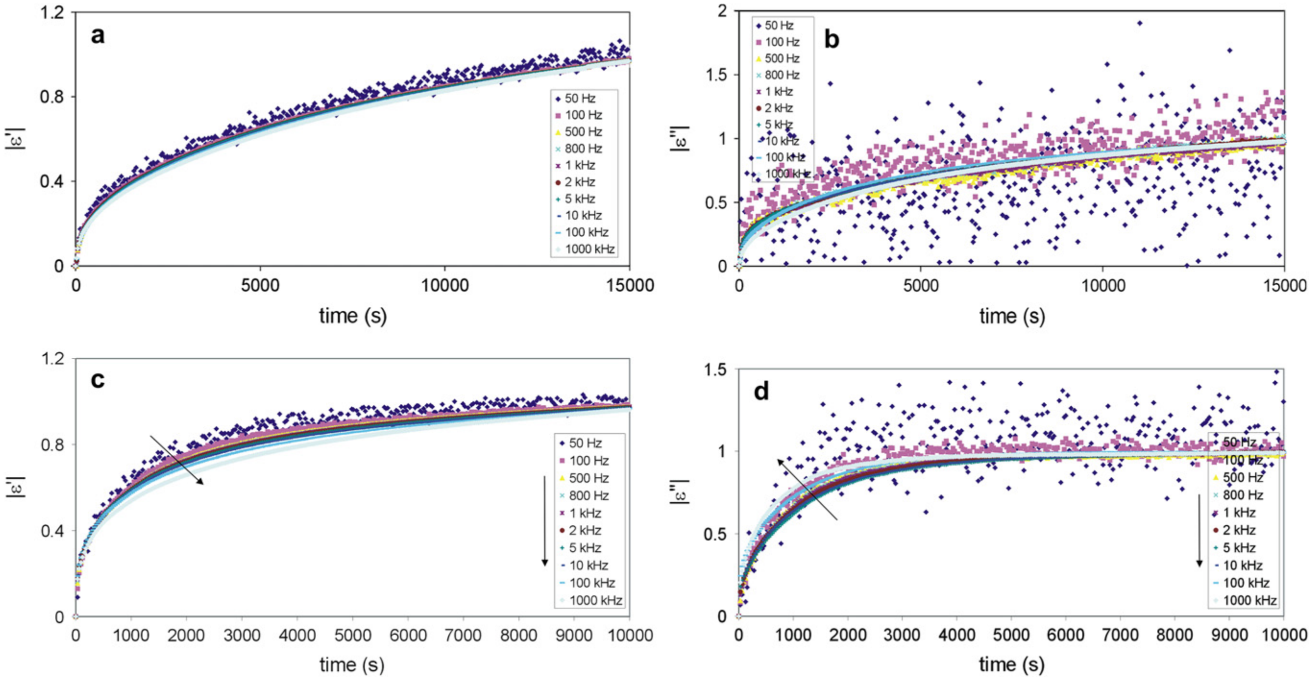

Fig. 7. Normalized frequency sweep (50 Hz to 1 MHz) for an undegraded clear coating(a) $|\varepsilon'|$ vs. time and (b) $|\varepsilon''|$ vs. time. Normalized frequency sweep (50 Hz to 1 MHz) for an undegraded pigmented coating (c) $|\varepsilon'|$ vs. time and (d) $|\varepsilon''|$ vs. time.

peak for lower frequencies, followed by desorption due to swelling of the coating. As already mentioned, the rise of the peak could be created due to polarization of water in large cavities/pores, and fall after desorption of water due to swelling of the resin. One thing remains clear that lower frequencies give better resolution for water uptake in degraded coatings, indicating that slow processes dominate the movements inside the polymer resin (with water) caused by the electric field.

3.1.5. Simulation of data – pigmented coatings

To investigate whether the peak can be reproduced, several model systems have been chosen where an undegraded pigmented coating with a filter on top has been measured with the DSA. This way a simulation is created, where the filter on top of the pigmented coating artificially includes pores.

The filters used are porous polyethylene [porous PE] (porous PE Solupor Solupor:3p07A from DSM), cotton linters (cotton linters from Schleicher & Schell Gmbh 595) and nitrocellulose (nitrocellulose 0.05 μm type VM from Millipore). These filters were already measured separately in a previous study [33]. Nitrocellulose has very small pores (0.05 μm) and is semihydrophilic, porous PE has a very open structure (3 g/m^2) and is hydrophobic; cotton linters have an open structure (78 g/m^2) and are hydrophilic. SEM pictures of these filters can be seen in Fig. 8(a)–(c).

In Fig. 9(a)–(f) the DSA measurements are shown for the three model systems.

For the pigmented coating with nitrocellulose (Fig. 9(a) ($\Delta C'$)), desorption is not observed. In Fig. 9(b) ($\Delta C''$) a small peak can be found, indicating desorption, which is more pronounced at lower frequencies. No peak can be found for either $\Delta C'$ or $\Delta C''$, for the model system pigmented with porous PE, as shown in Fig. 9(c) and (d). Finally for the pigmented coating with cotton linters, for both $\Delta C'$ and $\Delta C''$, clear peaks can be found (Fig. 9(e) and (f)).

From these results it can be deduced that the peaks found in the degraded samples are most likely the result of increasing hydrophilicity and porosity due to UV degradation. Since porous PE (Fig. 9(c) and (d)) does not show desorption, either the size of the pores has influence on desorption (Fig. 8(a)), or the hydrophilicity, or both. The last option seems to be the most likely one, since hydrophilicity alone is not enough to cause high water uptake and eventually squeeze out enough water to cause a significant decrease of signal (otherwise it should already have been found for example for nylon, which is quite hydrophilic [41]). Also for a highly porous system that is very hydrophobic, water is not contained in high quantities and clustering does not occur; and therefore swelling is not likely to take place in order to squeeze out the water; as shown for porous PE. The amount of pores also seems to have an influence on the effect of desorption. Nitro cellulose has a low amount of pores, as shown in the SEM picture, Fig. 8(b), and has only little desorption, whereas cotton linter shows a higher desorption due to higher porosity inside the cotton linters, Fig. 8(c). To obtain more clarity on this, more research should be done on different pore sizes, pore densities and various levels of hydrophilicity.

4. Conclusions

The DSA is clearly capable of detecting differences between undegraded and degraded coatings, which makes

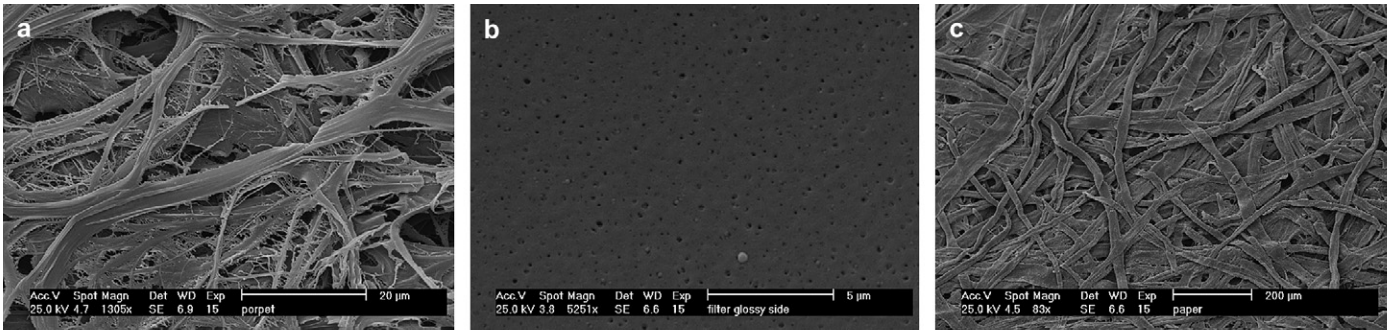

Fig. 8. SEM picture of (a) porous PE, (b) nitro cellulose and (c) cotton linter.

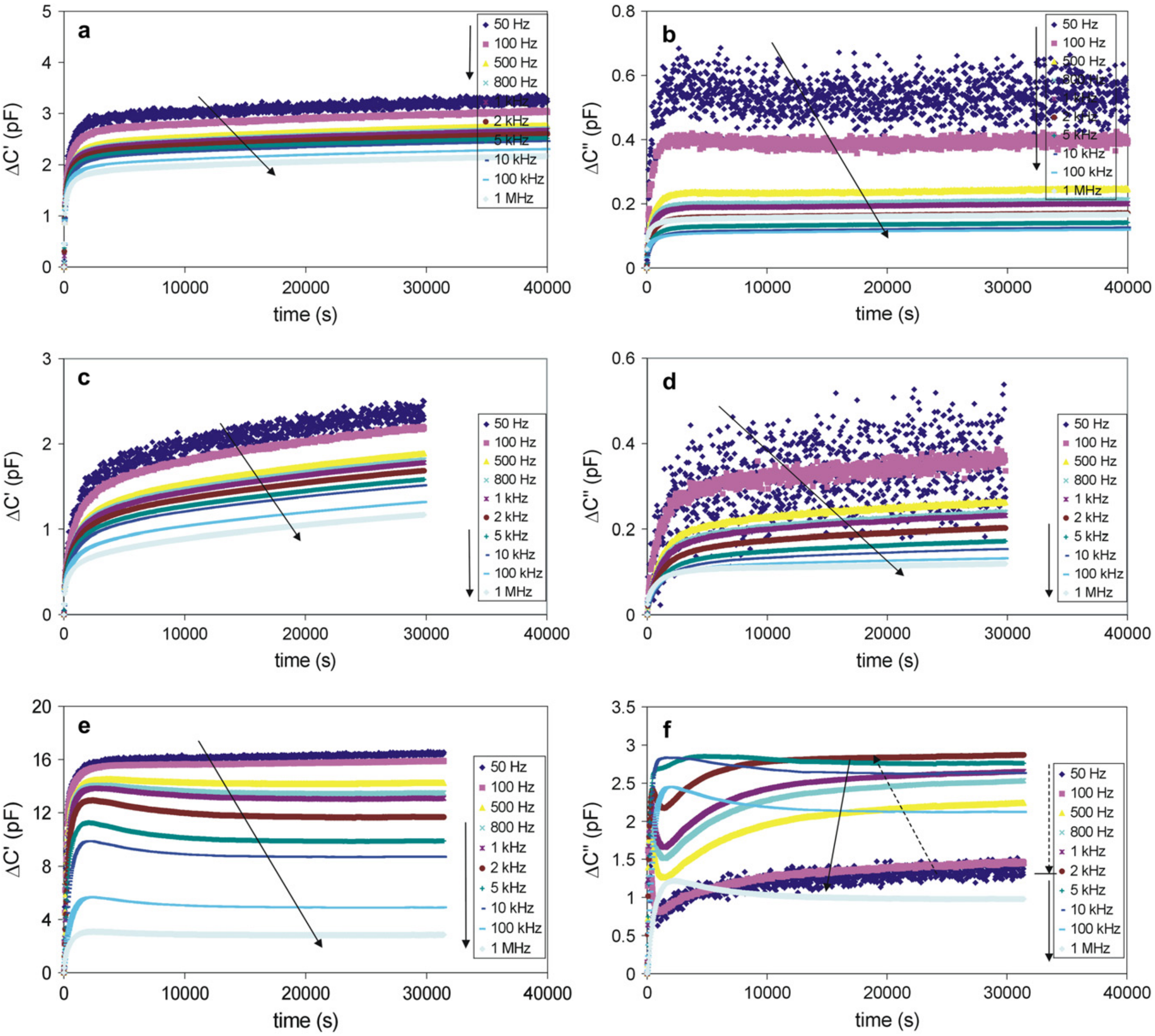

Fig. 9. Frequency sweep (50 Hz to 1 MHz) of model system undegraded pigmented coating with nitro cellulose (a) $\Delta C'$ vs. time and (b) $\Delta C''$ vs. time. Frequency sweep (50 Hz to 1 MHz) of model system undegraded pigmented coating with porous PE (c) $\Delta C'$ vs. time and (d) $\Delta C''$ vs. time. Frequency sweep (50 Hz to 1 MHz) of model system undegraded pigmented coating with cotton linter (e) $\Delta C'$ vs. time and (f) $\Delta C''$ vs. time.

this device useful as a non-destructive, in depth profiling, instrument for such purposes.

Degradation of clear and pigmented coatings affects the water sorption into these coatings, due to increased porosity and hydrophilicity. Also data fluctuations are found for UV degraded clear coatings which are caused by crosslinking, resulting in surface stress and eventually cracking during DSA measurements; this is not the case for UV degraded pigmented coatings. Furthermore, the resistive part of the DSA signal is more sensitive to changes in water sorption of degraded coatings, instead of the capacitative part of the DSA signal.

DSA measurements on UV degraded clear and pigmented coatings show a desorption profile. Desorption is likely to occur due swelling of the coating, causing pores to shrink and water to be squeezed out. Higher porosity and hydrophilic regions, are induced by UV degradation.

Measurements at different frequencies show that lower frequencies results in higher peaks, indicating that either polarization occurs at the electrodes or a water-hydrophilic interaction takes place.

Covering an undegraded pigmented coating with various (porous) filters supports the idea that porosity combined with the presence of hydrophilic regions are the cause of the peak that appears for DSA measurements on degraded samples. Porosity size and level of hydrophilicity are parameters that are responsible for the amount of desorption and are interesting for further investigation.

Acknowledgements

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References

[1] Adams CH, Taylor JR. Rubber World 1954;131(1):239–43.

[2] Brand BG, Nowacki LJ, Mirick W, Mueller ER. J Paint Technol 1968;62:37–42.

[3] Vachon RN, Rebenfeld L, Taylor HS. Textile Res J 1968;38:716–28.

[4] Blum GW, Shelton JR, Winn H. Ind Eng Chem 1951;43:464–71.

[5] Clark FG. Ind Eng Chem 1952;44:2697–709.

[6] Dubois P, Hennicker J. Plastics 1960;428–30.

[7] Dubois P, Hennicker J. Plastics 1960;474–8.

[8] Reinhart FW, Mutchler MK. Am Soc Test Mater Bull 1956;45–51.

[9] Roxburgh CM. J Soc Dyers and Colourists 1968;84:518–9.

[10] Tamblyn JW, Armstrong GM. Anal Chem 1953;25:460–5.

[11] Feller RL, Bailie CW. Bull Am Group 1966;6(1) [pages not numbered].

[12] Sherbondy VD. In: Koleske JV, editor. Paint and corrosion testing manual; 1995. p. 643–53.

[13] Hicks LS, Crewdson MJ. In: Koleske JV, editor. Paint and corrosion testing manual; 1995. p. 619–42.

[14] Biggs S, Lukey CA, Spinks GM, You S-T. Prog Org Coat 2001;42: 49–58.

[15] Tidjani A. Polym Degrad Stab 2000;68:465–9.

[16] Gijsman P, Sampers J. Die Angew Makromol Chem 1998;261/262:77–82.

[17] Hardcastle K, Searle ND. In: Rijntz RA, editor. Plastics & coatings; 2001. p. 189–240.

[18] Martin JW, Nguyen T, Byrd E, Dickens B, Embree N. Polym Degrad Stab 2002;75:193–210.

[19] Nguyen T, Martin J, Byrd E, Embree E. Polym Degrad Stab 2002;77:1–16.

[20] Bauer DR. J Coat Technol 2002;74:33–8.

[21] Bauer DR. Polym Degrad Stab 2000;69:297–306.

[22] Mallon PE, Li Y, Chen H, Zhang R, Zhang J, Wu YC, et al. Appl Surf Sci 2002;194:176–81.

[23] Jacques LFE. Prog Polym Sci 2000;25:1337–62.

[24] Martin JW. Proc Corros 97 Res Topical Symp 1997;235–58.

[25] Rabek JF. Polym Photodegradation 1995;433–598.

[26] MacQueen RC, Granata RD. Prog Org Coat 1996;28:97–112.

[27] Armstrong RD, Jenkins ATA, Johnson BW. Corros Sci 1995; 37:1615–25.

[28] Perrin FX, Irigoyen M, Aragon E, Vernet JL. Polym Degrad Stab 2000;70:469–75.

[29] Sugura M, Mitsuoka T, Murase A. Polym J 2001;33:617–20.

[30] Delobelle P, Guillot L, Dubois C, Monney L. Polym Degrad Stab 2002;77:465–75.

[31] Lukey CA. Prog Org Coat 2001;41:129–34.

[32] Giacomelli Penon M, Picken SJ, Wübbenhorst M, de Vos G, van Turnhout J Rev Sci Instrum 2006;77:115107–(1–6).

[33] Giacomelli Penon M, Picken SJ, Wübbenhorst M, van Turnhout J. J Appl Polym Sci, in press.

[34] Barrie JA. In: Crank J, Park GS, editors. Diffusion in polymers; 1968 [Chapter 8].

[35] Adhikari B, Majumdar S. Prog Polym Sci 2004;29:699–766.

[36] Kondratowicz B, Narayanaswamy R, Persaud KC. Sens Actuators B 2001;74:138–44.

[37] Buchold R, Nakladal A, Gerlach G, Herold M, Gauglitz G, Sahre K, et al. Thin Solid Films 1999;350:178–85.

[38] Pradas MM, Ribelles JLG, Aroca AS, Ferrer GG, Anton JS, Pissis P. Colloid Polym Sci 2001;279:323–30.

[39] Turner DT. Polymer 1982;23:197–202.

[40] Lundgren JE, Gudmundson P. Compos Sci Technol 1999;59: 1983–91.

[41] Khanna YP, Han PK, Day ED. Polym Eng Sci 1996;36:1745–54.