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Use of ionic liquids in SECM experiments to distinguish effects of temperature and water in organic coating swelling D. TRINH, C. VOSGIEN-LACOMBRE, G. BOUVET, S. MALLARINO, S. TOUZAIN* Laboratoire des Sciences de l'Ingénieur pour l'Environnement, LaSIE UMR 7356 CNRS, Université de La Rochelle, Avenue Michel Crépeau, 17042 La Rochelle France.

8

9 Abstract

During hygrothermal ageing of organic coatings, water and temperature lead to a coating swelling which can be in situ monitored by scanning electrochemical microscopy (SECM). However, it is difficult to separate the respective influence of water and temperature when ageing is performed in aqueous solution. In order to overcome this problem, room temperature ionic liquids can be a solution.

In this work, a model DGEBA/DAMP polyepoxide resin, with or without pigments (TiO₂) was applied onto steel Q-panels, with a thickness about 100 μm, completely cross-linked, and was aged in a 3wt.% NaCl aqueous solution. The swelling was measured by SECM for different ageing temperatures in the saline solution. The same epoxy systems were placed in RTIL (1-Ethyl-3-methylimidiazolium ethyl sulfate) and the swelling was measured by SECM at different temperatures.

A typical procedure was applied in order to analyze SECM results obtained in RTIL. The results allowed to evaluate the respective contribution of water uptake and temperature to the global coating swelling. The swelling due to temperature was 0.5%/10°C for unpigmented coatings and 0.3%/10°C for pigmented coatings while the total swelling was respectively about 5% and 4%, which is higher than the water uptake at saturation. It was then proposed that the swelling excess (about 2% and 1% for unpigmented coating and pigmented coatings respectively) was related to the internal stress relaxation of the polymer network during immersion.

27 Keywords

28 Organic coatings, water uptake, SECM, EIS, swelling, RTIL.

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32 I. Introduction

33 The durability of organic coatings can be estimated through different parameters as the water 34 uptake, the wet adhesion and the evolution of their physico-chemical and mechanical properties 35 during natural or artificial ageings [1-10]. In the latter case, hygrothermal tests are usually realized 36 and the water uptake is measured by gravimetry or electrochemical impedance spectroscopy (EIS). 37 But when water penetrates a polymeric network, dimensional changes are also evidenced [11-14]. 38 These dimensional changes as swelling can induce an evolution of mechanical properties of the 39 organic coatings, as well as composites and joint adhesives and hence, can modify the durability of 40 these systems. It is usually believed [14, 15] that water diffuses within the epoxy network and breaks the initial interchain Van der Waals (VdW) forces between hydrophilic groups. Then, water molecules 41 42 form new VdW bounds with these polar groups and this allow an increase of the chain segment mobility and so, the swelling. This has paid however little attention with organic coatings, maybe 43 44 because of their low thickness with regards to bulk polymers.

The swelling of bulk polymers can be easily measured using micrometers [14] or more complex techniques as photoelastic stress analysis (PSA) [16], digital image correlation [17] or fibre Bragg grating (FBG) sensors [18]. To our knowledge, the first work relating the swelling of organic coatings was published by Souto and al. [19]. In this work, the authors evidenced the swelling of polyester paints onto galvanized steel using scanning electrochemical microscopy (SECM). Thanks to this electrochemical technique, a mapping of the organic coating surface revealed a global modification of the thickness but the swelling was not quantified.

52 In recent works [20-22], we proposed an experimental protocol using SECM to measure in situ the 53 organic coating swelling during immersion in NaCl 3wt.% aqueous solution with the addition of a 10 54 mM potassium ferrocyanide (K_4 [Fe(CN)]₆) as a redox specie. The current of the tip was measured 55 during approaching the tip towards the substrate in the z-direction (approach curve) with a very slow velocity 0.5 μ m/s. When the tip is positioned far away from the substrate (z = 0), the tip current is 56 57 constant. When the tip is moved towards the organic coating surface, the tip current decreases 58 because the diffusion of the redox mediator is blocked by the insulating coating (negative feedback mode). The touching position d₀ at t=0 is determined by fitting the experimental approach curve with 59 60 the analytical negative feedback curve equation (Eq. 1) [23] :

$$I_{norm} = \frac{\frac{2.08}{RG^{0.358}} \left(L - \frac{0.145}{RG} \right) + 1.585}{\frac{2.08}{RG^{0.358}} \left(L + 0.0023RG \right) + 1.57 + \frac{\ln RG}{L} + \frac{2}{\pi RG} \ln \left(1 + \frac{\pi RG}{2L} \right)}$$
Equation 1

62 Where $I_{norm} = \frac{I_{tip}}{I_{ss}}$ is the normalized tip current, $RG = \frac{Rg}{a}$ is the normalized outer tip radius 63 and $L = \frac{d}{a}$ is the normalized tip- coated substrate distance. Other parameters are: I_{tip} the tip 64 current, I_{ss} the steady state current when the tip is far from the coated substrate, Rg the outer tip 65 radius and a the tip radius.

- This measurement is repeated during the immersion (and swelling) of the organic coating and the evolution of the touching position d(t) at immersion time t is monitored, keeping always the same initial position (z=0) for the tip. Finally, the difference $d(t)-d_0$ allows to get the coating thickness increase and the coating thickness evolution which is defined as $[d(t)-d_0]/h_0$ where h_0 is the initial coating thickness. It can be considered that the coating can only swell along the normal direction because of the adhesion to the substrate so the swelling $\Delta V/V_0$ is equal to $[d(t)-d_0]/h_0$.
- 72 In our last work (Figure 1, [22]), the swelling curves were plotted versus the reduced time au= $\sqrt{time/thickness}$. The swelling of unpigmented epoxy during immersion in NaCl 3wt.% aqueous 73 74 solution for ageing temperatures between 30°C and 50°C systems was between 5% and 6% while it 75 was only between 3.7% and 4.3% for pigmented coatings. In the same time, the volume water uptake 76 $\chi_{v_{r}}$ measured thanks to electrochemical impedance spectroscopy (EIS) and the modified Brasher and 77 Kingsbury equation [21], was calculated for unpigmented and pigmented coatings (Figure 2) during 78 immersion in NaCl 3wt.% aqueous solution. In Figure 2, $\chi_{\rm V}$ is related to the initial polymer volume 79 which means that for 20wt.% TiO₂ pigmented coatings (corresponding to a pigment volume fraction 80 equal to 7 vol.%), only 93% of the coating volume was considered. As it can be seen, the volume 81 water uptake at saturation is close to 3% whatever the temperature is. Indeed, these water uptake 82 curves were corrected by the swelling curves that are temperature dependent (Fig. 1). Finally, the 83 modified volume water uptake curves are not temperature dependent.

84 If different swelling values between unpigmented and pigmented coatings can be explained by 85 additional internal stresses that develop in presence of pigments [24], the swelling values higher than 86 the volume water uptake raise question.

87





Figure 1: Coating swelling curves obtained from SECM experiments for unpigmented and pigmented
 coatings during hygrothermal ageing in NaCl 3wt.% aqueous solution at different temperatures [22].





Figure 2: Volume water uptake obtained from EIS measurements in NaCl 3wt.% aqueous solution for
 unpigmented and pigmented coatings during hygrothermal ageings at different temperatures [22].

98 According to Adamson [11], the swelling process in polymers (free films) is composed by three stages

99 (Figure 3).



100



102

103 During stage I (Region I, Fig. 3), the swelling is lower than the absorbed water volume. The water 104 absorption is controlled by diffusion and water fills free volume of the polymer network and there is 105 no swelling. Then water begins to form hydrogen bonds with the polymer network and swelling 106 begins. For stage 2 (Region II, Fig. 3), the swelling is equal to the absorbed water volume: the 107 experimental curve is parallel to the water swelling efficiency curve. It means that diffusion 108 equilibrium is obtained and free water in free volumes links to the polymer while other molecules 109 arrive. Then comes the stage 3 (Region III, Fig. 3) where all free volumes are occupied and water 110 diffuses to micelles or clusters where swelling is lower. Finally, the difference between the 111 experimental and theoretical curves is related to the free volume.

112 The ageing temperature can also play a role in the swelling process and to identify this role, it is 113 necessary to remove the water influence. The work presented in this paper aims then to distinguish effects of temperature and water in organic coating swelling by performing SECM experiments, using
 room temperature ionic liquid as a conductive medium to get the sole temperature effect.

116

117 II. Experimental part

The epoxy resin was prepared from diglycidylether of bisphenol A (DGEBA from Aldrich, D.E.R.[™] 332) 118 119 cured with methylpentanediamine (DAMP from Aldrich, 99% Assay). All materials were used as 120 received without further purification. A stoichiometric amount of DGEBA was added to the amine 121 hardener and mixed at room temperature. For pigmented free films, titanium dioxide (DUPONT TS-6200) was inserted into the mixture at a rate of 20 wt.%. The size of the particles were about 0.39 122 123 μm. The mixtures were deposited onto steel Q-panels and coated panels were inserted between to 124 aluminum plates covered by a Teflon sheet and separated by 120µm thick spacers. The details of 125 curing conditions can be found elsewhere [24]. The dry film thickness was about $120 \pm 6 \mu m$ for all 126 coatings (measured by an Elcometer 311 Gauge Thickness).

127 The swelling of coated samples was measured using SECM (Biologic M470) according to the 128 procedure described elsewhere [20]. In order to measure the temperature induced swelling, the 129 coated substrate was immersed in 1-Ethyl-3-methylimidiazolium ethyl sulfate RTIL with the addition 130 of a 1 mM potassium ferrocyanide (K4[Fe(CN)]6) as a redox specie at 20°C in a thermally controlled 131 cell. A first SECM experiment was done at t20°C then the temperature wsa increased at 30°C. After 132 30 min, a new SECM experiment was recorded. Then the T was increased to 40°C to get the third 133 SECM results. 30°C and 40°C. We avoid measuring at 50°C due to the security reasons since the RTIL is rather volatile and carcinogen. The viscosity of the RTIL is 98 mm²/s at 25°C. When the 134 135 temperature increases, the tip current increases due to the lower viscosity which increases the diffusion coefficient, as it can be seen in Figure 4. 136

Prior to SECM experiments, it was verified that no chemical interaction exists between the organic coating and RTIL. Three different coatings were detached from the metallic surface and immersed in RTIL at ambient temperature. After 48h of immersion in RTIL, the coatings were removed from the bath, rinsed with water and dried at 70°C in an oven for 24h. Gravimetric and FTIR-ATR experiments were realized before and after immersion in RTIL. No mass variation nor modifications of IR absorption bands were recorded.

143 A microelectrode of 10 μ m was used as a tip. The current of the tip was measured during 144 approaching the tip towards the substrate in the z-direction (approach curve) with a continuous 145 mode and an approach rate of 1 μ m/s. During immersion of the coated panels in NaCl 3wt.% aqueous solution, EIS measurements were performed with a Gamry REF600 at the free corrosion potential using a 30 mV r.m.s perturbation (11pts/decade) in the oven acting as a Faraday cage. From these measurements, the high frequency film capacitance (C_{HF}) was determined using the real Re(Z) and imaginary Im(Z) parts of the impedance at high frequency (f =10 kHz) using Equation 2 [25]:

151
$$C_{HF} = \frac{-Im(Z)}{2\pi f(Re(Z)^2 + Im(Z)^2)}$$
 Equation 2

Finally, the volume water uptake was calculated using the modified Brasher and Kingsbury equation
that includes the thickness evolution, obtained from SECM experiments in NaCl 3wt.% aqueous
solution, as previously described [21].

155

156 III. Results and discussion

157 Typical approach curves obtained by SECM for unpigmented coatings are presented in Figure 4a and 158 the three different approach curves obtained by SECM for pigmented coatings are presented in 159 Figure 4b. These curves are quite different from those usually obtained in aqueous solutions with 160 organic coatings (negative feedback mode where the tip current decreases when approaching the tip towards the non-conductive surface) or with metallic surfaces (positive feedback mode where the tip 161 162 current increases when approaching the tip towards the conductive surface). The experimental 163 curves present a first part where the tip current increases (positive feedback) and then a second part 164 where the tip current decreases (negative feedback). This behavior was already observed and 165 explained by Nkuku and LeSuer [26]. When the microelectrode goes down to the coating, the tip 166 carries viscous RTIL molecules which induces an artificial concentration increase of the redox species 167 and leads to a current increase. But when the tip is very close to the coating surface, a normal 168 negative feedback is recovered where the diffusion of redox species is blocked: all molecules are 169 consumed and the tip current decreases. Finally, when the tip touches the surface, the current is constant and tends to zero and the touching position d_0 can be graphically determined. Three 170 171 different experiments were performed for each temperature in RTIL medium. As it can be seen from 172 Fig. 4b, very good reproducibility was obtained with pigmented coatings and the same result was 173 verified with unpigmented coatings.

The touching position at 20°C, obtained for pigmented and non-pigmented coatings (Figure 4), corresponds to the reference swelling measurement. SECM experiments performed at 30°C and 40°C allowed to estimate higher swelling values than that obtained at 20°C so relative swelling values

- 177 (d₀@30°C-d₀@20°C)/h₀ and (d₀@40°C-d₀@20°C)/h₀ can be deduced and plotted versus temperature
- 178 (Figure 5). In RTIL, there is no water so the swelling is only due to the thermal expansion. Therefore,
- 179 we measured the thermal expansion in the range of 20°C to 40°C. We did not perform measure at
- 180 50°C due to security reasons because the RTIL is rather volatile and carcinogen. However, it can be
- 181 reasonably supposed that the thermal expansion is linear till 50°C in RTIL, which is the higher ageing
- 182 temperature in aqueous solutions. As it can be seen in Figure 5, the swelling increase is about +0.5%
- 183 for every 10°C interval for unpigmented coatings (Figure 5a) and is about 0.3% for every 10°C interval
- 184 for pigmented coatings (Figure 5b). These results are in good agreement with swelling curves
- obtained in aqueous solution between 30° and 50°C (Figure 1). Then, it appears clear that with higher
- temperatures, the polymer network expands quite linearly with temperature in this temperature
- 187 range.





Figure 4: Typical approach curves obtained by SECM in RTIL medium at different temperatures for a)
 unpigmented coatings and b) pigmented coatings.



Figure 5: Influence of temperature on a) unpigmented coatings swelling b) pigmented coatings
 swelling in RTIL medium.

From Figure 2, where only the initial polymer volume in the coatings is considered, it can be seen that the volume water uptake is about 3.3% and no clear influence of temperature can be drawn. Indeed, as these volume water uptake values were obtained from electrochemical data that where corrected from the thickness evolution for each ageing temperature, it means that the influence of temperature was removed.

205 It is then now interesting to plot the swelling curves obtained in NaCl 3wt.% aqueous solution versus 206 the volume water uptake obtained in NaCl 3wt.% aqueous solution, in the same way that Adamson 207 did with bulk epoxy networks (Figure 3). For each ageing temperature, the swelling curves from 208 Figure 1 were fitted for the three different samples and a mean curve was obtained versus the 209 reduced time $\tau = \sqrt{time}/thickness$. The same procedure was applied to the water uptake curves from Figure 2. Finally, the mean swelling curve can be plotted versus the mean water uptake curve 210 211 for a given reduced time for each ageing temperature (Figure 6). The water swelling efficiency curve 212 (straight line) is the curve corresponding to a swelling that equals the water uptake.

The first interesting result is that all experimental curves (points) present a positive deviation from the water swelling efficiency curve while a negative deviation was observed by Adamson. This means that pigmented and unpigmented coatings swell more than the water volume absorbed: water is then not responsible for this additional swelling. Moreover, as the volume water uptake χ_v is not temperature



Figure 6: Swelling vs. volume water uptake for unpigmented (left) and pigmented (right) coatings during hygrothermal ageing at different temperatures.

dependent, as seen above (Figure 2), it means that thermal expansion is not responsible for the additional swelling either.

227 The second finding is that the maximum swelling value in NaCl 3wt.% aqueous solution is about 2% 228 higher than the maximum volume water uptake value for unpigmented coatings for all ageing 229 temperatures while it is only about 1% for pigmented coatings. The presence of pigments seems to 230 have an effect that lowers the global swelling. This results was previously observed with global 231 swelling of pigmented coatings (Figure 1) and the pigment influence was interpreted as additional 232 internal stresses that develop within the pigmented coating. It can be then supposed that when 233 water penetrates the polymer network, water molecules fill in the free volume but also allow 234 plasticization and the relaxation of internal stresses due to curing, pigments, fillers, ... Finally, it can 235 be proposed that the additional swelling is due to the relaxation of internal stresses within the 236 coating, which is lower in the case of pigmented coating because of the filler reinforcement effect.

237

238 IV. Conclusions

239 SECM experiments in RTIL allowed to measure the effect of temperature onto the swelling of organic coatings. Different temperature induced swelling values were found between pigmented 240 241 and unpigmented coatings and it was proposed that compressive internal stresses due the 242 presence of pigment are responsible for this lower swelling values. The temperature induced 243 swelling in RTIL was found to be much lower than the swelling measured by SECM during 244 hygrothermal ageing in NaCl 3wt.% aqueous solution. It means that water that fills the free 245 volumes of the polymer network has the major effect. However, when comparing the 246 hygrothermal swelling to the volume water uptake, it appeared that the swelling values are 247 higher than the maximum absorbed water volume. This means that an additional swelling occurs 248 that is not related to temperature and/or water. It was proposed that this additional swelling is 249 due to a relaxation of internal stresses within the polymer network during the plasticization process during hygrothermal ageing. 250

251

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