Use of ionic liquids in SECM experiments to distinguish effects of temperature and water in organic coating swelling

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Use of ionic liquids in SECM experiments to distinguish effects of temperature and water in organic coating swelling

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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 (TiO_2) 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.

Keywords

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

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I. Introduction

The durability of organic coatings can be estimated through different parameters as the water uptake, the wet adhesion and the evolution of their physico-chemical and mechanical properties during natural or artificial ageings [1-10]. In the latter case, hygrothermal tests are usually realized and the water uptake is measured by gravimetry or electrochemical impedance spectroscopy (EIS). But when water penetrates a polymeric network, dimensional changes are also evidenced [11-14]. These dimensional changes as swelling can induce an evolution of mechanical properties of the organic coatings, as well as composites and joint adhesives and hence, can modify the durability of 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 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 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.

In recent works [20-22], we proposed an experimental protocol using SECM to measure in situ the organic coating swelling during immersion in NaCl 3wt.% aqueous solution with the addition of a 10 mM potassium ferrocyanide ($K_4[Fe(CN)]_6$) as a redox specie. The current of the tip was measured during approaching the tip towards the substrate in the z-direction (approach curve) with a very slow velocity 0.5 µm/s. When the tip is positioned far away from the substrate (z = 0), the tip current is constant. When the tip is moved towards the organic coating surface, the tip current decreases because the diffusion of the redox mediator is blocked by the insulating coating (negative feedback mode). The touching position d_0 at t=0 is determined by fitting the experimental approach curve with the analytical negative feedback curve equation (Eq. 1) [23] :

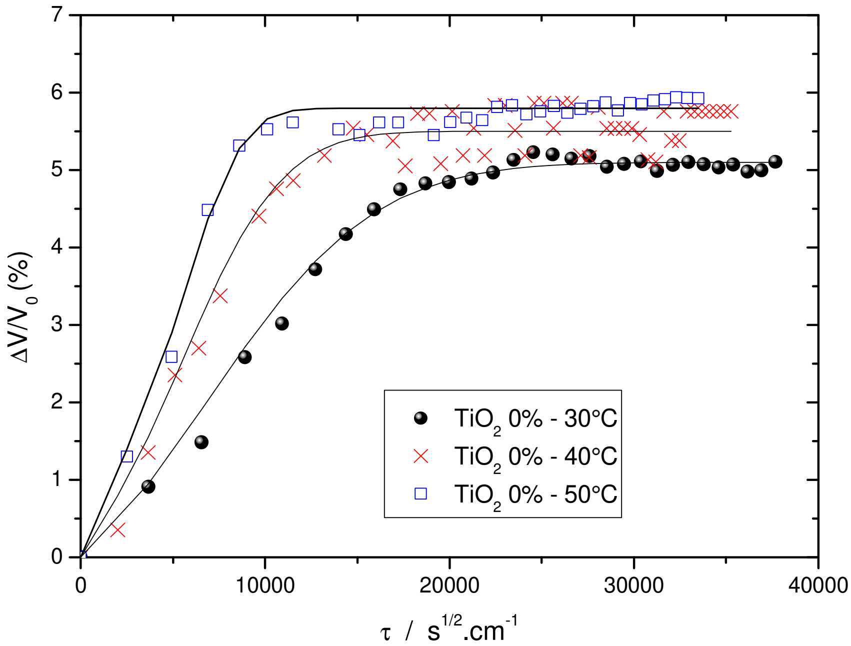
$$I_{norm} = \frac{\frac{2.08}{RG^{0.358}}\left(L - \frac{0.145}{RG}\right) + 1.585}{\frac{2.08}{RG^{0.358}}\left(L + 0.0023RG\right) + 1.57 + \frac{\ln RG}{L} + \frac{2}{\pi RG}\ln\left(1 + \frac{\pi RG}{2L}\right)} \qquad \text{Equation 1}$$

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

In our last work (Figure 1, [22]), the swelling curves were plotted versus the reduced time $\tau = \sqrt{time}/thickness$. The swelling of unpigmented epoxy during immersion in NaCl 3wt.% aqueous solution for ageing temperatures between 30°C and 50°C systems was between 5% and 6% while it was only between 3.7% and 4.3% for pigmented coatings. In the same time, the volume water uptake χ_V, measured thanks to electrochemical impedance spectroscopy (EIS) and the modified Brasher and Kingsbury equation [21], was calculated for unpigmented and pigmented coatings (Figure 2) during immersion in NaCl 3wt.% aqueous solution. In Figure 2, χ_V is related to the initial polymer volume which means that for 20wt.% TiO_2 pigmented coatings (corresponding to a pigment volume fraction equal to 7 vol.%), only 93% of the coating volume was considered. As it can be seen, the volume water uptake at saturation is close to 3% whatever the temperature is. Indeed, these water uptake curves were corrected by the swelling curves that are temperature dependent (Fig. 1). Finally, the modified volume water uptake curves are not temperature dependent.

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



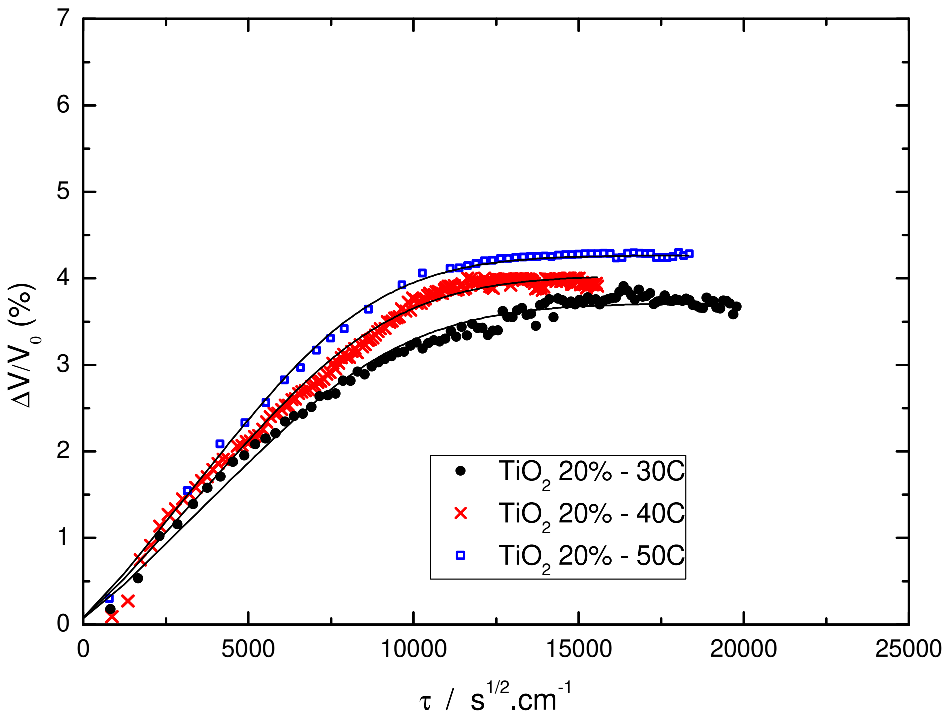
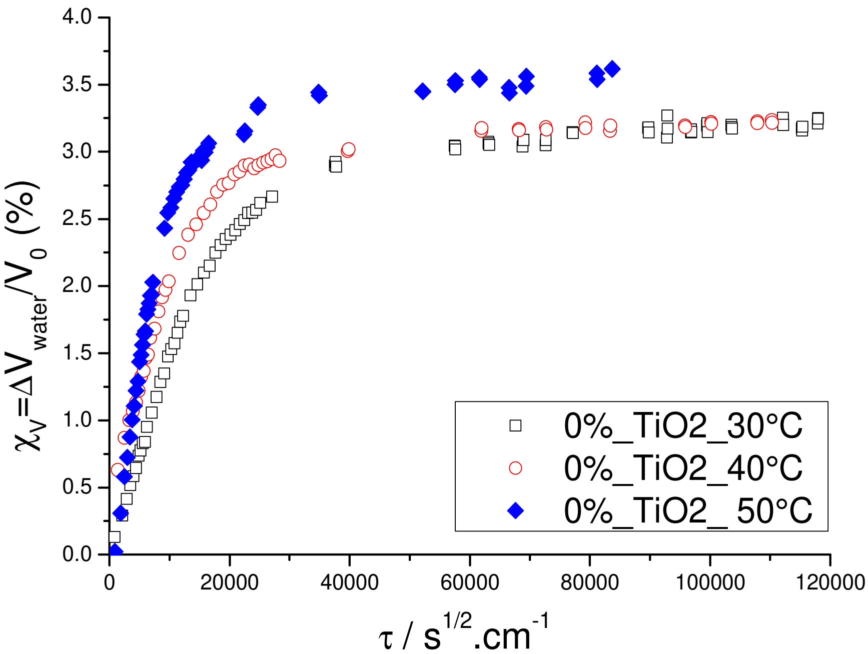


Figure 1: Coating swelling curves obtained from SECM experiments for unpigmented and pigmented coatings during hygrothermal ageing in NaCl 3wt.% aqueous solution at different temperatures [22].



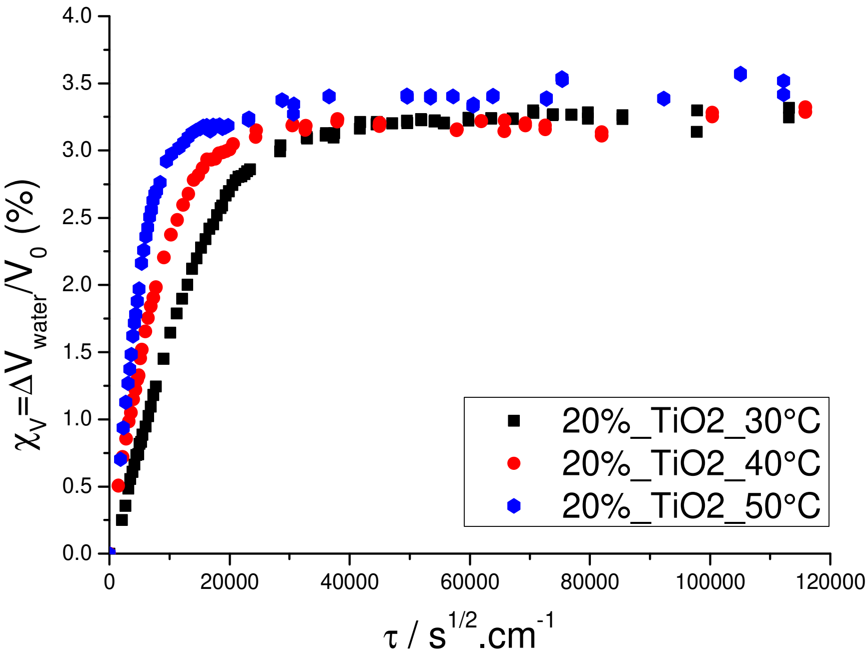


Figure 2: Volume water uptake obtained from EIS measurements in NaCl 3wt.% aqueous solution for unpigmented and pigmented coatings during hygrothermal ageings at different temperatures [22].

According to Adamson [11], the swelling process in polymers (free films) is composed by three stages (Figure 3).

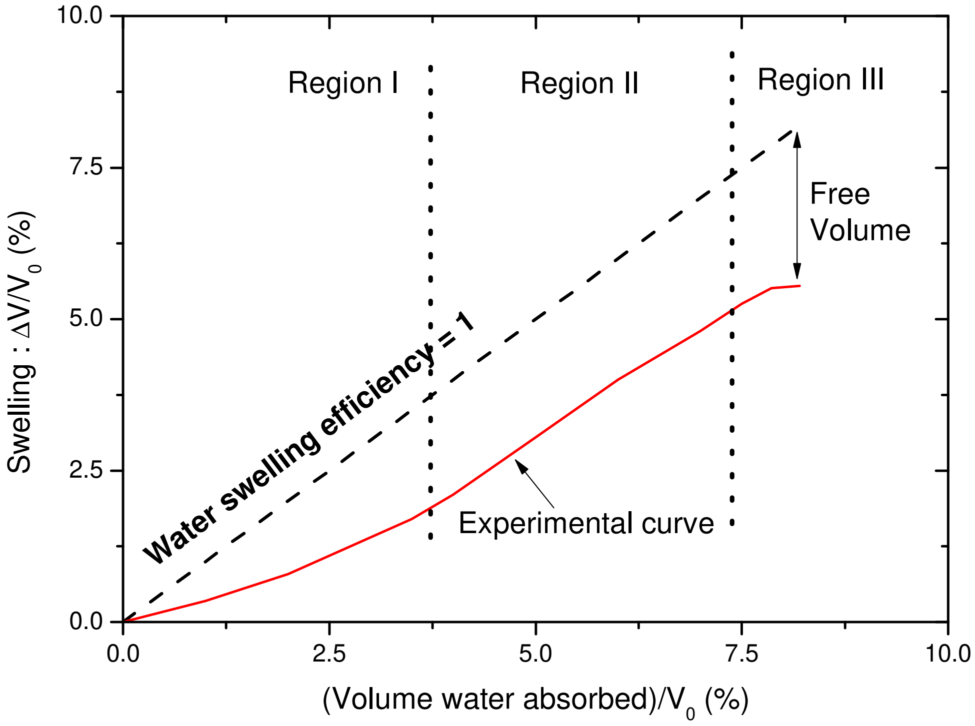


Figure 3 : Schematic representation of Adamson's figure given in [11].

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

The ageing temperature can also play a role in the swelling process and to identify this role, it is 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.

II. Experimental part

The epoxy resin was prepared from diglycidylether of bisphenol A (DGEBA from Aldrich, D.E.R.™ 332) cured with methylpentanediamine (DAMP from Aldrich, 99% Assay). All materials were used as received without further purification. A stoichiometric amount of DGEBA was added to the amine 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 µm. The mixtures were deposited onto steel Q-panels and coated panels were inserted between to aluminum plates covered by a Teflon sheet and separated by 120µm thick spacers. The details of curing conditions can be found elsewhere [24]. The dry film thickness was about 120 ± 6 µm for all coatings (measured by an Elcometer 311 Gauge Thickness).

The swelling of coated samples was measured using SECM (Biologic M470) according to the procedure described elsewhere [20]. In order to measure the temperature induced swelling, the coated substrate was immersed in 1-Ethyl-3-methylimidiazolium ethyl sulfate RTIL with the addition of a 1 mM potassium ferrocyanide (K4[Fe(CN)]6) as a redox specie at 20°C in a thermally controlled cell. A first SECM experiment was done at t20°C then the temperature wsa increased at 30°C. After 30 min, a new SECM experiment was recorded. Then the T was increased to 40°C to get the third 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 mm^2/s at 25°C. When the temperature increases, the tip current increases due to the lower viscosity which increases the diffusion coefficient, as it can be seen in Figure 4.

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.

A microelectrode of 10 µm was used as a tip. The current of the tip was measured during approaching the tip towards the substrate in the z-direction (approach curve) with a continuous mode and an approach rate of 1 µm/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]:

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

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].

III. Results and discussion

Typical approach curves obtained by SECM for unpigmented coatings are presented in Figure 4a and the three different approach curves obtained by SECM for pigmented coatings are presented in Figure 4b. These curves are quite different from those usually obtained in aqueous solutions with 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 current increases when approaching the tip towards the conductive surface). The experimental curves present a first part where the tip current increases (positive feedback) and then a second part where the tip current decreases (negative feedback). This behavior was already observed and explained by Nkuku and LeSuer [26]. When the microelectrode goes down to the coating, the tip carries viscous RTIL molecules which induces an artificial concentration increase of the redox species and leads to a current increase. But when the tip is very close to the coating surface, a normal negative feedback is recovered where the diffusion of redox species is blocked: all molecules are 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 different experiments were performed for each temperature in RTIL medium. As it can be seen from Fig. 4b, very good reproducibility was obtained with pigmented coatings and the same result was 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

(d_0@30°C-d_0@20°C)/h_0 and (d_0@40°C-d_0@20°C)/h_0 can be deduced and plotted versus temperature (Figure 5). In RTIL, there is no water so the swelling is only due to the thermal expansion. Therefore, we measured the thermal expansion in the range of 20°C to 40°C. We did not perform measure at 50°C due to security reasons because the RTIL is rather volatile and carcinogen. However, it can be reasonably supposed that the thermal expansion is linear till 50°C in RTIL, which is the higher ageing temperature in aqueous solutions. As it can be seen in Figure 5, the swelling increase is about +0.5% for every 10°C interval for unpigmented coatings (Figure 5a) and is about 0.3% for every 10°C interval 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 range.

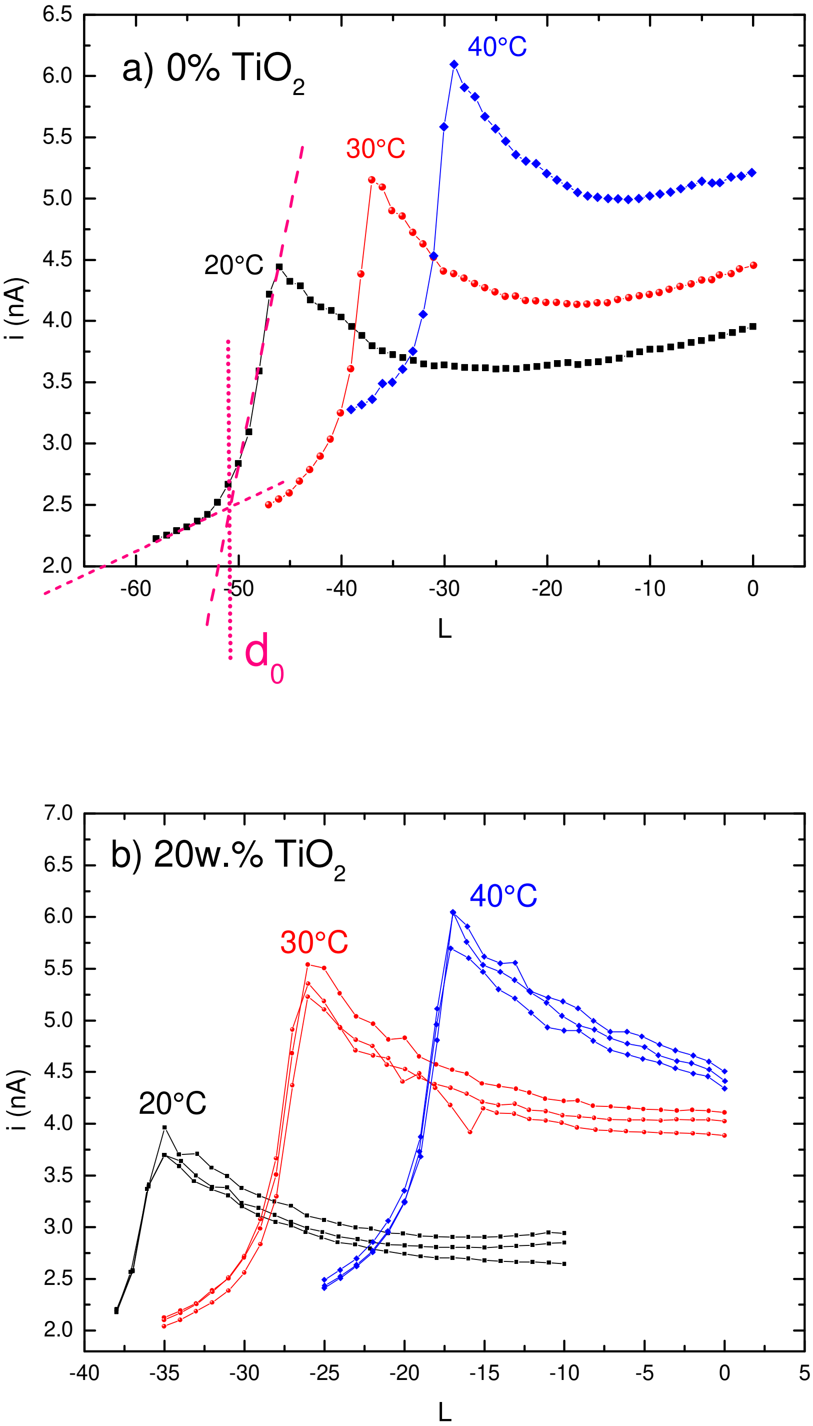


Figure 4: Typical approach curves obtained by SECM in RTIL medium at different temperatures for a) unpigmented coatings and b) pigmented coatings.

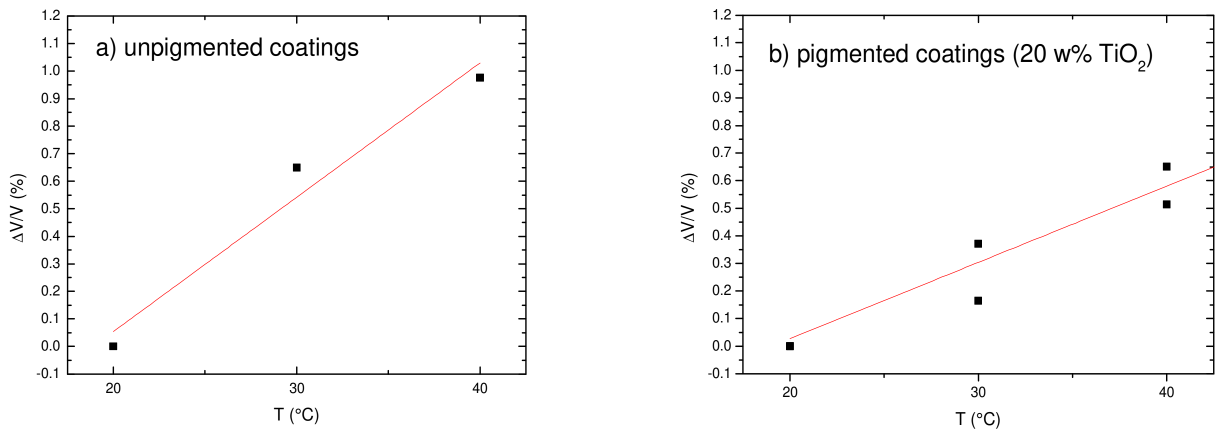


Figure 5: Influence of temperature on a) unpigmented coatings swelling b) pigmented coatings swelling in RTIL medium.

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.

It is then now interesting to plot the swelling curves obtained in NaCl 3wt.% aqueous solution versus the volume water uptake obtained in NaCl 3wt.% aqueous solution, in the same way that Adamson did with bulk epoxy networks (Figure 3). For each ageing temperature, the swelling curves from Figure 1 were fitted for the three different samples and a mean curve was obtained versus the 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 for a given reduced time for each ageing temperature (Figure 6). The water swelling efficiency curve (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

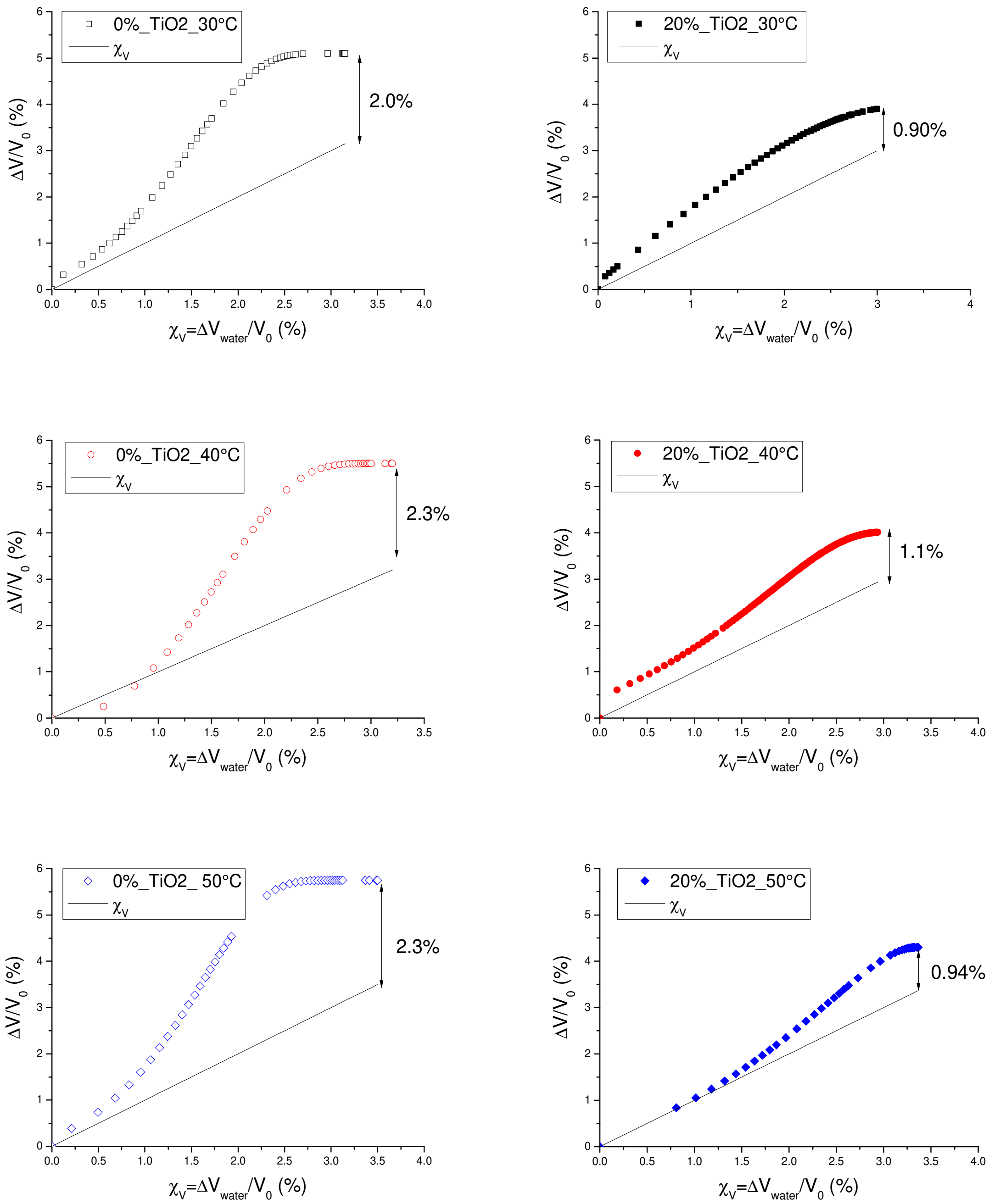


Figure 6: Swelling vs. volume water uptake for unpigmented (left) and pigmented (right) coatings during hygrothermal ageing at different temperatures.

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

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

IV. Conclusions

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 and unpigmented coatings and it was proposed that compressive internal stresses due the presence of pigment are responsible for this lower swelling values. The temperature induced swelling in RTIL was found to be much lower than the swelling measured by SECM during hygrothermal ageing in NaCl 3wt.% aqueous solution. It means that water that fills the free volumes of the polymer network has the major effect. However, when comparing the hygrothermal swelling to the volume water uptake, it appeared that the swelling values are higher than the maximum absorbed water volume. This means that an additional swelling occurs that is not related to temperature and/or water. It was proposed that this additional swelling is due to a relaxation of internal stresses within the polymer network during the plasticization process during hygrothermal ageing.

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