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Influence of pigment on the degradation of anticorrosion polymer coatings using a thermodynamic analysis of electrochemical impedance spectroscopy data

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ABSTRACT

As commercial paints have a complex composition, this work was carried out on a model epoxy system (DGEBA/DAMP) with or without pigment (TiO_2). Firstly, physico-chemical properties of the composites free films were studied by using DSC and DMA and compared to those of the sole resin. Then, composites films were applied onto steel panels and were immersed in 3 wt.% NaCl solution at different temperatures (30, 40, 50 and 60 °C). The water uptake and diffusion processes were followed by Electrochemical Impedance Spectroscopy (EIS). Using a thermodynamic approach, it was shown that the diffusion process is accelerated in presence of pigments due to internal stresses that develop in composite systems. However, these stresses are relaxed by water sorption during ageing. Finally, it appears that the monitoring of water sorption by EIS allows to characterize the mechanical effects at the coating/substrate interface during immersion.

1. Introduction

Epoxy coatings are widely used for corrosion control of metallic substrates because of their low cost and their efficiency in corrosive environments such as seawater. However, many environmental factors (water, temperature, UV, oxygen, . . .) cause degradation and thus affect the durability of the coated systems. Many studies have been done in order to evaluate their performances under natural or artificial ageing [1–6].

The water uptake in organic coatings and the wet adhesion are key parameters to better evaluate the coating durability [7–9]. However, commercial paint formulations are complex because they are a mixture of the binder, the solvent, the fillers, the pigments and the additives and it is difficult to evaluate only the answer of the polymeric material when the coating is aged. In our previous studies, we proposed to study a model epoxy system in order to obtain a comprehensive understanding of the influence of the macromolecular structure onto water sorption processes [10,11]. It was shown that the microstructural specificities of the polymer networks had a significant influence on the water diffusion and the solubility, especially due to the interactions of water molecules with the polar groups of the binder. These systems, however, were non-pigmented and consequently, the influence of pigments onto water uptake has not been evaluated.

For pigmented paints, the water transport is dependent of the pigment volume concentration (PVC) and of the quality of pigment dispersion [12]. This can be explained by the creation of an interphase around the pigment particle, which can play an important role on pigmented system properties [12,13]. Moreover, long range internal stresses are developed in the binder due to curing and the presence of pigments [12,14] and their evolution with ageing could be a new explanation of the coating degradation.

In this work, we studied the ageing of a pigmented epoxy coating using the same model epoxy system as in previous studies [11,15]. Then, the influence of the pigments on the water sorption characteristics can be easily found by comparing with previous results.

2. Experimental

2.1. Materials and ageing conditions

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

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stoichiometric mixture of the DGEBA and the amine hardener was mixed at room temperature and degassed under vacuum. For pigmented free films, titanium dioxide (DUPONT TS-6200) was inserted into the mixture at a rate of 20 wt.% (which corresponds to 7 vol.%). The size of the particles was about 0.39 μm. After stirring at room temperature, the pigmented and unpigmented systems were degassed under vacuum for 10 minutes.

In order to create free films, the mixture was transferred between two Teflon sheets, which were separated by a spacer of about 120 μm thick. For coated steel panels, the mixture was deposited onto steel Q-Panels which were thoroughly rinsed with acetone before coating. A controlled curing protocol was used to create a homogeneous fully cured network, as explained elsewhere [11]. The systems were heated for 7 h at 30 °C, then heated for 3 h at 60 °C, then heated for 3 h at 80 °C, then heated for 3 h at 100 °C, then heated for 3 h at 120 °C, with a final postcure period for 1 h at 130 °C. Finally, Scanning Electron Microscopy (SEM) was used to observe the microstructure of the composite. The pigment was found to be homogeneously dispersed in the binder as it can be observed on the cross-section of a pigmented free film obtained by cryofracture (Fig. 1).

The fully cured specimens (free films and coatings) were stored in a desiccator containing silica gel desiccant to prevent moisture absorption before immersion. The dry thicknesses were between 100 and 140 μm for free films and coatings (measured by an Elcometer 311 Gauge Thickness).

2.2. Physico-chemical characterization of the polymer systems

Fourier transform infrared (FT-IR) analyses of cured materials were carried out by Thermo-Nicolet Magna IR 760 spectrometer equipped with a Smart MIRacle ATR accessory with a diamond crystal. Spectra were collected over a range 600–4000 cm^{-1} with a resolution of 8 cm^{-1}. Each spectrum was produced by coaddition of 128 scans.

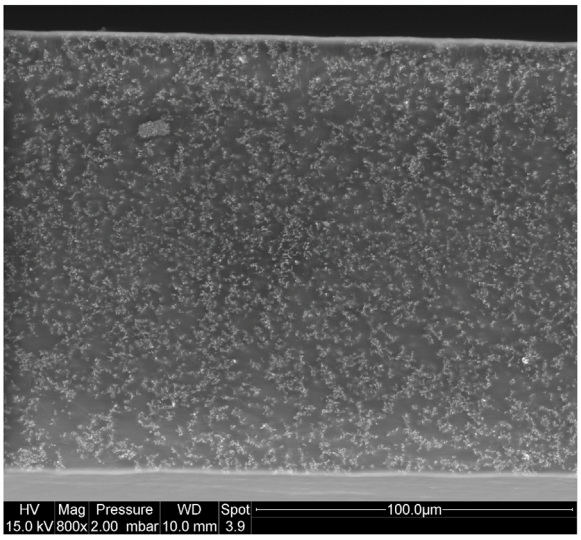

Fig. 1. SEM micrograph of the cross-section of a 20 wt.% TiO_2 free film.

Glass transition temperature (Tg) measurements were performed by Differential Scanning Calorimetry (DSC) with a TA Instruments Q100. The epoxy resins were scanned from 20 to 200 °C at 10 °C.min^{-1} under nitrogen flow. The glass transition temperature Tg is taken at the half height of the change in heat capacity (middle of transition).

Dynamic Mechanical Thermal Analyzer (DMTA) – tensile mode (Q800 TA Instruments) was used to investigate the dynamic mechanical properties of resins. Rectangular samples (15 mm × 5

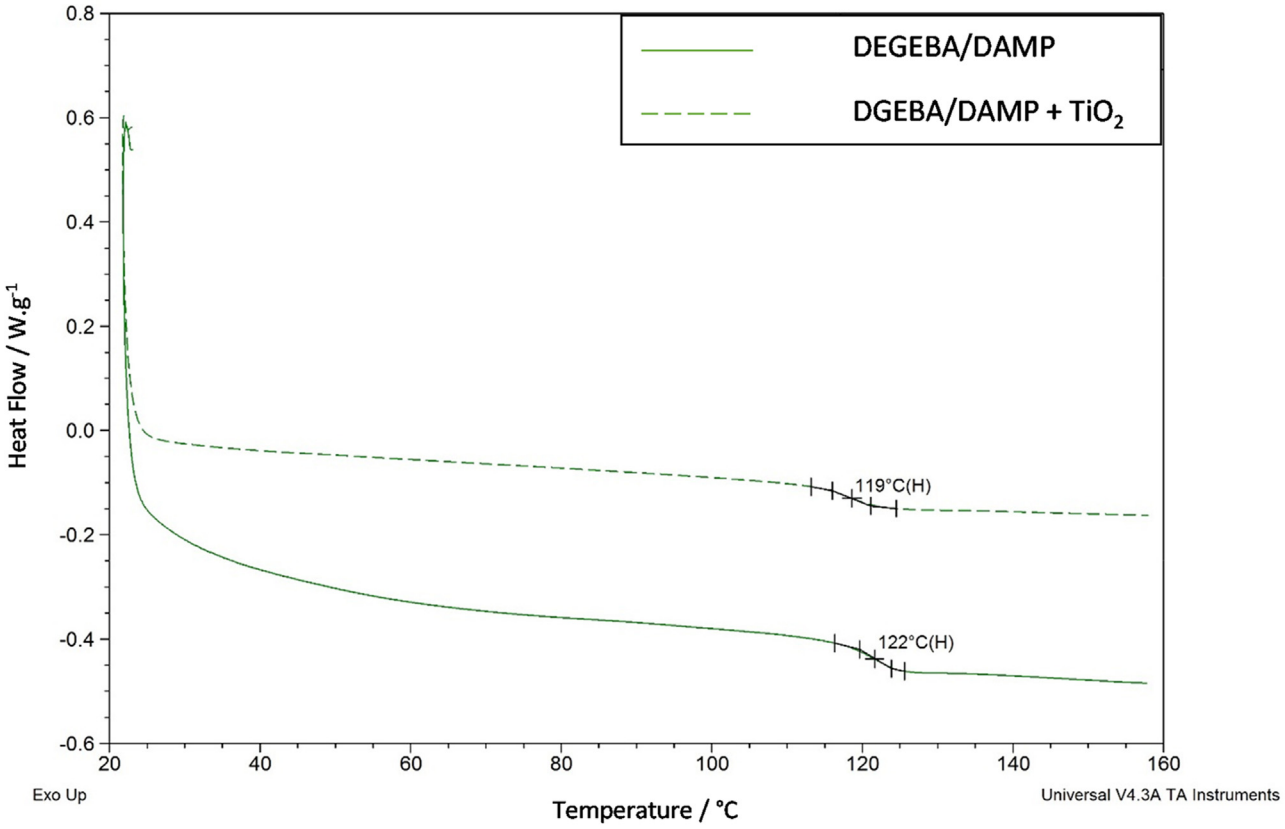

Fig. 2. DSC thermograms (second scan) for the unpigmented and pigmented systems.