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Influence of internal stresses on the physicochemical and mechanical properties evolution of pigmented epoxy systems during hygrothermal ageing

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ABSTRACT

This study focused on the influence of a pigment (titanium dioxide at rates of 10 wt% and 20 wt%) on the hygrothermal ageing of a model epoxy polymer resin (DGEBA-DAMP). Firstly, FT-IR, DSC, DMTA and mechanical tests were carried out in order to obtain thermal, physicochemical and mechanical properties. Specific mechanical tests performed under DMA were developed to determine the internal stresses (type II and III) present within these systems and linked to microstructural heterogeneities. Results of the pigmented free films were compared to those of the resin alone to better understand the impact of the titanium dioxide. They show that the addition of titanium dioxide does not influence the physicochemical properties while the mechanical properties are modified. Then, free films were immersed in pure water at 30 °C to investigate water influence on the system behaviors through measurements of the properties at each step of ageing. In the wet state, the physicochemical and mechanical properties of the pure resin show a plasticization of the system by absorption of water. Concerning pigmented samples, a decrease in Tg is observed whereas Young's modulus is not modified and internal stresses increase. Indeed the evolution of Young's modulus is modified by presence of titanium dioxide. This is due to the presence of the additional internal stresses of type II. The latter are therefore predominant on plasticization effect onto the evolution of mechanical properties. After a desorption step, the results of thermal properties show that plasticization seems to be reversible. This result is in contradiction with the fact that additional internal stresses induced by water ingress are not recovered during the desorption step. This suggests that plasticization is not totally reversible. Finally swelling of free films during hygrothermal ageing is modified because of internal stresses due to introduction of titanium dioxide.

1. Introduction

The excellent chemical resistance and adhesion to metals of epoxy resins allow to obtain very durable anticorrosive coatings in many aggressive media such as seawater. Commercial paints are then a mixture of the epoxy binder with pigments, fillers and other additives [1]. In order to evaluate the durability of such coatings, natural or accelerated ageing tests are performed but the complex formulation of these systems makes difficult the evaluation of the behavior of each component. This is particularly important for highly pigmented/filled paints where the pigment volume concentration (PVC) can be up to 85 wt% [1]. The PVC and the quality of pigment dispersion are then key parameters [2] for the coating performances.

However, the presence of pigments/fillers induces internal stresses within the binder [2] which are added to those created by the curing [3]. All these internal stresses affect the coating behavior and it seems then interesting to evaluate them in epoxy systems before and during a hygrothermal ageing.

In a recent work [4] dealing with model epoxy coatings, it was proposed that three scales of internal stresses can be identified, similarly to electrodeposits [5] (Fig. 1). Internal stresses of type I are due to the difference of properties at the interface between the substrate and the coating. Internal stresses of type II come from the presence of different phases inside the coating (e.g. fillers in a polymer resin). Finally internal stresses of type III are caused by the repartition of crosslinking nodes in the polymeric matrix which can be not perfectly homogeneous.

In this previous work [4], it was shown that the presence of pigment induce internal stresses within the binder which modify the water sorption mechanism when compared to an unpigmented resin one. However, internal stresses were not directly measured during ageing.

In the present study, we propose to evaluate the internal stresses of

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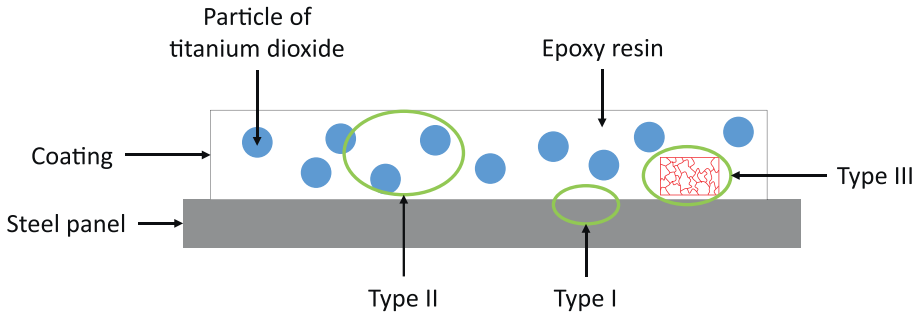

Fig. 1. Different scales of internal stresses.

model pigmented epoxy systems before and during hygrothermal ageing in order to assess their effects onto the epoxy system properties. In a first approach, this work considered only free films to avoid the effect of the substrate (adhesion) and to focus onto the influence of pigments on internal stresses of type II and III.

2. Experimental

2.1. Materials and sample preparation

Free films were composed of an epoxy resin and titanium dioxide particles. The epoxy resin was prepared from Diglycidyl Ether of Bisphenol A (DGEBA, supplied by Aldrich™, D.E.R. 332) cured with methylpentanediamine (DAMP, from Aldrich, 99% assay). Titanium dioxide was supplied by Dupont (TS-6200). Particle diameter was around 0.39 µm. Tested TiO_2 amounts were 0 wt% (pure DGEBA-DAMP matrix), 10 wt% (corresponding to 3.2 vol%) and 20 wt% (corresponding to 6.9 vol%). All products were used as received without further purification.

Desired amount of titanium dioxide was added to DGEBA and mixed at room temperature. Then the amine was incorporated to obtain a stoichiometric epoxy resin. For the pure resin, this amount was 15.1 wt % while it was adjusted at 14.5 wt% and 13.8 wt% for pigmented systems at 10 wt% and 20 wt% of TiO_2 respectively. The final mixture was mixed at room temperature and degassed under vacuum. To create free films, this blend was placed in a mold which is composed of two Teflon sheets. In order to control free film thickness, both sides of the mold were separated by a spacer. Thickness of unpigmented free films was about 120 µm and about 150 µm for pigmented free films. A curing protocol was applied to achieve homogeneous and fully cured networks, as previously reported [6]. Finally, SEM analysis was performed to verify the distribution of TiO_2 pigments within the binder, after cryofracture of the samples (Fig. 2a and b). SEM micrographs revealed that TiO_2 pigments are homogeneously distributed within the binder, even if agglomerates are rarely observed. Numeric analysis (ImageJ software) of the SEM pictures showed that the mean size of the particles was about 0.4 ± 0.05 µm for both pigmented systems (Fig. 2c and d). This result is consistent with the size given by the supplier (0.39 µm).

2.2. Hygrothermal ageing protocol

Free films were initially placed in an oven at 30 °C for the temperature control during 24 h to avoid the presence of humidity. The initial mass was then recorded with a balance PRECISIA with a precision of 10^{-5} g. For each titanium dioxide amount, three free films were submitted to an ageing cycle composed of a sorption and a desorption step. Samples were immersed in deionized water at 30 °C during 15 weeks. Then, they were placed in a desiccator under vacuum for a desorption step during 4 weeks. Water uptake was achieved by regular weighing and through Eq. (1).

$$\chi_{m_c}(t)(\%) = 100 \cdot \frac{m_t - m_0}{m_0} \quad (1)$$

where

$\chi_{m_c}(t)(\%)$: water content at time t (%).

m_t: samples mass at time t.

m_0: initial mass of samples.

All the results were presented as function of the reduced time $\tau = \sqrt{time}/_{thickness}$ ($s^{1/2} \cdot cm^{-1}$) in order to remove the thickness effect [7].

2.3. Physicochemical properties

Fourier Transform Infrared (FT-IR) analyses were carried out on free films with Nicolet iS50 spectrometer with the ATR mode. Spectra covered a range of 540–4000 cm^{-1} with a resolution of 8 cm^{-1}. For each sample, seven spectra were achieved and each one resulted from the coaddition of 128 scans.

Differential Scanning Calorimetry (DSC) experiments were carried out with TA Instruments Q100 apparatus to measure glass transition temperature (Tg) of fully cured free films. Samples were heated from 20 °C to 180 °C at a rate of 10 °C/min. Tg was taken at half height of the change in heat capacity (middle of glass transition). Three samples were tested for reproducibility. Measurements at initial state were carried out in aluminum crucibles. To avoid water evaporation, measurements during hygrothermal ageing were performed in hermetic crucibles.

Structural relaxations and free volume fraction were achieved with Dynamic Mechanical Thermal Analyzer (DMTA) Q800 from TA Instruments in tensile mode. On one hand free films were heated from − 100 °C to 180 °C at a rate of 3 °C/min. Tests were performed on three samples at a frequency of 1 Hz to obtain tan δ evolution. Free volume fraction was measured through multi-frequency sweeps (at 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 5, 10, 20, 30, 50 Hz) and using the William-Landel-Ferry (WLF) theory [8].

2.4. Mechanical properties and internal stresses measured by DMTA

To measure mechanical properties of free films, loading-unloading-recovery experiments were carried out with DMTA Q800 from TA Instruments at a rate of 10 MPa/min to obtain mechanical domains as reported previously [9]. The Young's modulus and apparent internal stresses were obtained from different parts of the curves. First the Young's modulus was taken as the slope of linear part of loading curves. Indicated values corresponded to the average of five measurements.

Internal stresses of types II and III can be measured by a specific mechanical loading-unloading process. Traditionally, measurement of internal stresses arising to this specific mechanical test are associated to crystalline materials [5] but Dupend-Brusselle et al. and Yakimets-Pilot et al. adapted Cottrell method modified by Hanfield and Dickson to semi-crystalline polymers [10–14]. In the present work, this method was adapted to non-crystalline epoxy free films. The different steps of this procedure are described in Fig. 3. The fundamental idea of this approach is based on the fact that long-range internal stresses, which arise to different plastic stain incompatibilities, induce a translation of viscoelastic domain in stress space. Thus to determine apparent internal stresses, a sequence of loading-unloading steps are performed for different level of strain. For each step, the curves of unloading in