



## Quantitative spectroscopic analysis of weathering of polyester-urethane coatings



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### ABSTRACT

Transmission FTIR analysis of polyester-urethane coatings (PUC), that were degraded under different accelerated laboratory weathering conditions, are compared. The aim of this comparison is to deepen our insight into the chemical pathways of weathering of polyester-urethane coatings. We monitored the chemical changes for different environments, such as aerobic or anaerobic conditions as well as wet or dry conditions, in order to increase our insight into the effect of each individual stress factor, i.e., photons, oxygen, temperature and water, on the chemical pathways of weathering.

We showed that the degradation of urethane groups proceeds via photo-oxidative pathways and that the ester groups mainly degrade via photolytic reactions. The ester bond scission accelerates after an initially-slow-rate stage of weathering in the presence of urethane groups. This is due to an increase in the optical absorptivity of the coating as a result of degradation under anaerobic conditions, as shown before. By means of a kinetic analysis using a combination of FTIR and UV–Vis spectroscopy results (obtained before), we found that a first-order kinetic model can perfectly describe the rate of ester bond scission during the weathering and that the increase in the rate of reaction is due to the increase in the light absorptivity of the coating as a result of degradation. Finally, using the interference fringes of FTIR spectra, we showed that evaporation and water-caused removal of degraded material cause a particularly pronounced decay in the thickness of the coating. In the absence of water spray, the material loss takes place in the same period as urethane groups decompose and stops afterwards, even though the ester bond scission proceeds with higher rates. This supports the hypothesis of photo-oxidative pathways for the urethane group decomposition and photolytic mechanisms for ester bond scission. Dark experiments showed that PUC coatings are highly resistant to hydrolysis and thermal degradation.

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## 1. Introduction

Polymeric coatings are designed for different applications and, accordingly, have to fulfill different requirements. Among these, clearcoats, the external layers of automotive and aerospace coatings, are designed to be resistant against environmental stress factors, i.e., UV light, oxygen, temperature and water [2]. Exposure to these stress factors for prolonged time leads to macroscopic failure of these coatings, such as cracks. Accordingly, a keen interest

exists in understanding the long-term performance of these coatings. Sophisticated experimental methods such as FTIR and UV–Vis spectroscopy [3–8], ESR [9] and mass spectroscopy [10,11] techniques are used to chemically characterize the degradation processes involved [12–18]. In addition to the experimental techniques, simulation methods are also employed to study chemical evolution of coatings as a result of degradation [19,20].

Chemical changes in the coating due to the weathering, such as chain scission, cross-linking and oxidation, lead to changes in physical properties of the coating, i.e.,  $T_g$ , moduli, hardness and oxygen and water diffusivities. The changes in these properties have been investigated at macro- [21,22] and micro-scales [23–25] for different systems. Weathering builds up internal stresses in the

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coatings which eventually lead to (micro) cracks and mechanical failure [26]. Therefore, understanding the mechanisms of weathering is the key factor to understand the relation between chemical and physical changes of the coating due to weathering.

Due to the fact that clearcoats are designed to be highly resistant to environmental stress factors, outdoor experimental degradation tests are rather time-consuming. Therefore, faster artificial degradation setups, which are designed to mimic real outdoor conditions with higher intensity of the stress factors, are used.

Considering that each stress factor in photo-degradation triggers specific changes in the material, applying all stress factors at the same time, significantly complicates studying the mechanisms of weathering [27]. However, in order to mimic the real outdoor condition one needs to expose the material to all of them at the same time. So, to keep this study as close as possible to the real outdoor condition and at the same time, to be able to identify the role played by each stress factor (light, temperature, oxygen and water), we first conducted an artificial weathering experiment which has water (spray), oxygen and daylight, all together. Thereafter, a set of controlled experiments was conducted in which individual stress factors come into play in a systematic way, e.g., dark hydrolysis and dry anaerobic or aerobic weathering conditions.

## 2. Experimental

### 2.1. Material

A model OH-functional polyester poly (neopentylisophthalate) or PNI (provided by DSM Resins) with a hydroxyl value of 100 (theoretical molecular mass 1144 g/mol, degree of polymerization 4.4), non-cross-linked or cross-linked with hexamethylenediisocyanurate trimer or HDT (provided by Perstorp), are used in this study, see Fig. 1.

### 2.2. Coating preparation

Polyester-urethane coatings (PUC) were prepared using solution coating application. PNI is dissolved in 1,3-dioxolane at 70 °C, after cooling down to room temperature, HDT was added to the solution at an NCO:OH ratio of 1.05 and then stirred for 5 min at room temperature before application using spin coating. Thereafter, coatings were dried and cured in a convection oven at 120 °C for 1 h.

In order to perform transmission FTIR measurements, an IR-transparent substrate is needed. We used silicon wafers (p-doped, Anadis Instruments Benelux B.V., Almere, The Netherlands), cleaned by UV-ozone treatment (Novascan PSD-UVT) and coated

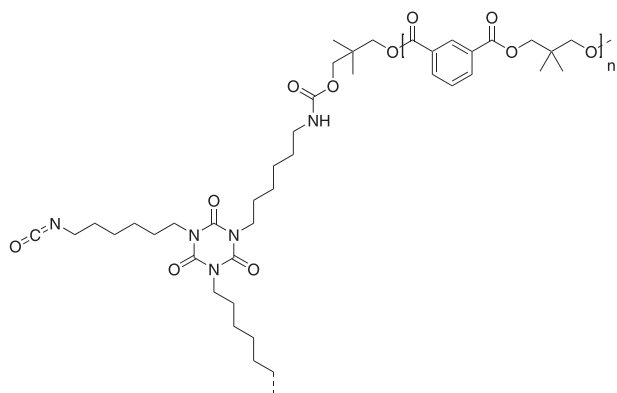


Fig. 1. Chemical structure of the cross-linked PNI.

with our solution (30 m% of PNI) by spin coating (Laurell WS-650SX-6NPP/LITE) for 30 s, at 4000 or 2000 rpm depending on the desired thickness.

### 2.3. Artificial weathering

A Ci65A Weather-Ometer (Atlas MTS), equipped with xenon arc lamps and borosilicate inner and outer filters, was used as the first artificial weathering machine. Exposure was carried out at a black standard temperature (BST) of 65 °C, with a total cycle time of 2 h that was composed of a 102 min dry cycle at 40–60% relative humidity (ISO 11341, cycle-A with daylight filters) and an 18 min wet cycle with water spray (ISO 4892-2, cycle 2). The exposure time of each weathered sample is defined by the moment at which it is removed from the equipment. Samples were not re-exposed after removal.

A Suntest XXL+ (Atlas MTS), equipped with xenon lamps (NXe1700) and daylight inner and outer filters was used, as the second artificial weathering machine. Two exposure cells were made (Equipment and Prototype Center at TU/e, Eindhoven) in order to have two exposure conditions in a single run of the Suntest XXL+, see Fig. 2. Cells were made of aluminum alloy with a top window of fused silica which has been sealed by a silicon rubber O-ring. Each cell had an inlet and an outlet tube to purge it by a desired gas. One cell was constantly purged by dry air and the other one by dry nitrogen during exposure. The BST was set to 45 °C outside the cells, which approximately corresponded to a BST of 65 °C inside the cells. Samples made for transmission FTIR measurements were re-exposed after removal. Samples were reshuffled every 500 h in order to provide a uniform irradiance of light for all of them.

Dark experiments were performed to rule out the effects of hydrolysis and thermal degradation in the absence of light. Samples were placed in a dark oven and other samples soaked in demi-water in the same oven at 60 °C. The exposure times of the samples was set to be the same as the accumulative time of samples in the WOM exposed to dry and wet cycles, respectively. Samples were dried in a convection oven for 3 h prior to each measurement and re-exposed after each measurement. Table 1 summarizes the information about all weathering tests.

### 2.4. Analytical methods

UV–Vis spectra were studied using an Ocean Optics USB4000 spectrometer. This spectrometer was calibrated for measuring absolute values of photon fluxes. For this purpose, a cosine corrector was placed next to the samples in the weathering machines and the collected light was transferred to the spectrometer using an optic

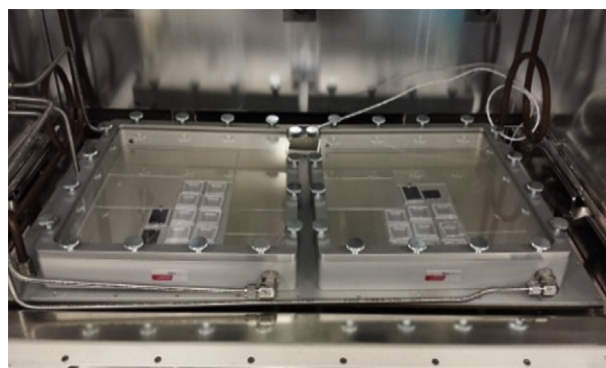


Fig. 2. Suntest air and nitrogen cells.

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