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The influence of the exposure conditions on the chemical and physical changes of polyester–urethane coatings during photodegradation

Koen N.S. Adema [a, b], Hesam Makki [a, b], Elias A.J.F. Peters [a], Jozua Laven [a],
Leendert G.J. van der Ven [a], Rolf A.T.M. van Benthem [a], Gijsbertus de With [a, *]

[a] *Eindhoven University of Technology, Laboratory of Materials and Interface Chemistry, Department of Chemical Engineering and Chemistry, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands*

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ABSTRACT

The influence of the conditions of artificial degradation experiments on the photodegradation process of polyester–urethane clearcoats has been studied by comparing three types of exposure experiments with different conditions regarding the spectral power distribution (SPD), the exposure atmosphere (aerobic and anaerobic) and the presence of water. The presence of short wavelengths ($\lambda < 295$ nm) in the SPD largely influences the depth-inhomogeneity of degradation with respect to the optical properties and the chemical composition of the coating. The availability of oxygen in the exposure atmosphere determines the degradation pathway that is followed, such as to what extent the photo-oxidative breakage of urethane bonds or the formation of yellow chromophores due to aromatic crosslinking reactions occurs. Indentations at the surfaces of virgin and degraded coatings showed an increase in Young's modulus and hardness when degraded under aerobic conditions, while degradation under anaerobic conditions did not lead to significant changes. The presence of water is responsible for increasing the surface roughness of the coating during degradation, which directly influences the coating's gloss retention. Several time-independent correlations between the changes in chemical, optical and mechanical properties of coatings resulting from different exposure experiments have been established.

1. Introduction

Weathering research largely deals with the question how the performance of a material evolves under the circumstances that this material experiences during its service life. The (literally) most natural approach to address this question experimentally is via so-called field exposure: a situation in which a material is exposed to its intended (outdoors) service environment and therefore, by default, experiences the conditions that match exactly those that the material would experience upon application in the field [1]. Although often perceived as the most reliable form of weathering experiments, field exposure suffers from several disadvantages, including the long exposure times that are generally required, the cost of those prolonged experiments and the lack of control and reproducibility. Even though the parameters of changing weather can be monitored and therefore included into later analyses, the fact that the weather cannot be controlled makes it difficult to understand the influence of individual degradation factors on the weathering process.

In order to avoid most of these disadvantages, researchers in the weathering field have since a long time been conducting laboratory exposure studies besides field exposure. Laboratory exposure, also called artificial exposure, is characterised by a large amount of control on the degradation conditions and allows for the design of weathering experiments that include a specific set of desired degradation factors. Depending on the application of interest, the number of factors that can influence a material's photodegradation process can be very large. For the sake of conciseness, only a few factors that play an important role for most applications will be discussed here.

As the term "photodegradation" already suggests, irradiance by (UV) photons is always of importance. The wavelength-dependent intensity of the irradiation source, generally denoted as the spectral power distribution (SPD), may influence both the rate and the nature of photodegradation [2]. Its influence on the rate of

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* Corresponding author.
E-mail address: G.deWith@tue.nl (G. de With).

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photodegradation is primarily through the absorption properties of the material: only radiation that is absorbed can cause photodegradation. For the same reason, a photon's wavelength determines where this photon is absorbed (via its penetration depth) and may therefore introduce a thickness-dependency of degradation, as also discussed in a previous publication [3]. Absorbed photons with shorter wavelengths have higher energy and therefore have higher potential to break chemical bonds and generate radicals [2]. For very short wavelength radiation (down to ≈ 255 nm), the photons may be able to break bonds that cannot be broken by any photon present in the terrestrial solar spectrum ($\lambda > 295$ nm). Examples of photodegradation processes in which the nature of degradation is altered due to such very short wavelength radiation [4] and in which it is not affected [5], are both known. An increase of the intensity of the SPD without a change in the spectral composition is generally believed to only influence the rate of degradation, but not to distort the weathering chemistry [6]. The validity of extrapolating very high radiant flux results to in-service flux levels, based on the principle of reciprocity in polymer photodegradation [7], has not often been shown experimentally and this issue should thus be approached with care.

The temperature during exposure is of importance for the simple fact that photodegradation reactions are chemical reactions and the associated reaction rates are well known to depend on the temperature [1,8]. Next to this general temperature dependency, there is another, more specific effect of temperature since we are interested in polymer coatings with a glass transition temperature of typically 60 °C. Thus, situations of weathering below T_g (e.g., during winter) as well as close to or above T_g (e.g., a car parked in the sun on a summer day) are realistic and relevant. Apart from a difference in molecular mobility and therefore reaction conditions in both situations, in exposure periods below T_g, degradation is also influenced by physical ageing, which is the (spontaneous) relaxation process of the coating material that occurs in its glassy state resulting from its non-equilibrium state [9]. Physical ageing has been demonstrated to play a role in the weathering process of common coating systems, for example, by influencing the mechanical properties and the build-up of stresses in the coating [10,11].

The composition of the atmosphere in which the degrading material is situated has a large influence on the degradation process, for example, via the amount of oxygen it contains. In an aerobic atmosphere, polymer photodegradation mainly follows oxidative pathways, which involve the generation of peroxy radicals due to reactions between oxygen and light-induced radicals in the polymer. Under anaerobic conditions (e.g., nitrogen atmosphere or vacuum), the radicals react with other species instead and the degradation process is often found to be dominated by crosslinking reactions, as opposed to the photo-oxidative chain-breaking reactions that often dominate under aerobic conditions [2]. Similar to the penetration depth effect of photons, the availability of oxygen at different coating depths may also add to the thickness-dependency of photodegradation [12], a process known as diffusion limited oxidation (DLO) [8]. The importance of oxygen diffusion in the photodegradation process has been demonstrated in a previous publication on the simulation of coating degradation [13]. The oxygen permeability of a material is also influenced by degradation reactions [14] and is therefore, similar to the optical absorptivity discussed in a previous publication [3], a quantity of which the change during initial degradation influences degradation at a later stage. Additionally, the oxygen permeability may be influenced by physical ageing [15] and by deformation of the coating during exposure [16].

Finally, the presence of water in either liquid (rain) or gaseous (humidity) form affects the degradation process of most polymers. Water has been shown to act as a plasticiser, decreasing both the T_g and the modulus of a coating, and it may cause hydrolysis of the (virgin) coating binder and/or of degradation products [17]. Such processes have been shown to influence the apparent quantum efficiency of photodegradation [18] and to be responsible for the hydrolytic generation of UV chromophores that accelerate further photo-oxidation [19]. Furthermore, water can disrupt the adhesion of coatings by adsorption at the coating/substrate interface and the presence of liquid water causes washing of the coating surface, leading to surface erosion and to extraction of loosely bound or water-soluble material [17]. This washing effect, together with the role of water as a hydrolytic agent [20], is largely responsible for the formation of roughness and/or pits during weathering.

In order to study the influence of the exposure conditions on the photodegradation process of the polyester–urethane coatings, three types of exposure experiments with different conditions were performed. To be able to make a useful comparison between these experiments, some conditions, most notably the black standard temperature, are kept constant. Other exposure conditions, such as the SPD, the degradation atmosphere and the presence of water, are varied to study their influence on photodegradation.

2. Materials and methods

2.1. Preparation of virgin coatings

Poly(neopentylisophthalate) or PNI (sample kindly provided by DSM Resins, Zwolle) with a hydroxyl value of 100 (theoretical molecular mass 1144 g mol^{-1}, degree of polymerisation 4.4) was dissolved in 1,3-dioxolane at 70 °C. For preparing the UV–VIS samples, depending on the desired layer thickness, solutions with polymer concentrations between 20 and 38 m% were prepared. After cooling down to room temperature, hexamethyldiisocyanurate trimer or HDT (sample kindly provided by Perstorp) was added to the solution at an NCO:OH ratio of 1.05. For the UV–VIS samples, substrates of fused silica (CGQ, Chemglass Life Sciences, Bedfordshire) were cleaned by UV-ozone treatment (Novascan PSD-UVT) and coated with the solution by spin coating (Laurell WS-650SX-6NPP/LITE). For all other characterisation purposes, panels of aluminium alloy AA3003 (Q-Lab Corporation) were degreased with acetone, dried with nitrogen gas and coated with the solution by doctor blade application, using a 160 μm gap height. After application, coatings were dried and cured in a convection oven at 120 °C for 1 h. The dry coating thickness ranged from 5 to 10 μm for the UV–VIS samples and was approximately 30 μm for the coatings on the metal panels. The glass transition temperature of the polyester–urethane is 62 °C, as measured with modulated DSC (TA Q800) using a heating rate of 3 °C/min and a modulation period and amplitude of 30 s and 0.5 °C, respectively.

2.2. Artificial weathering

One set of samples was exposed in a Ci65A Weather-Ometer, or WOM (Atlas MTS), for artificial weathering, equipped with xenon arc lamps and borosilicate inner and outer filters. Exposure was done at a black standard temperature (BST) of 65 °C and an irradiance of approximately 57 W m^{-2} (300–400 nm), and with a total cycle time of 2 h, 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 sample degraded in the WOM is defined by the moment at which it is removed from the equipment. WOM-exposed samples were not re-exposed after removal.

Two other sets of samples were exposed in a Suntest XXL+ (Atlas MTS) for artificial weathering, equipped with xenon arc lamps and Coated Quartz inner/Daylight outer filters. Two custom