



## The influence of the exposure conditions on the simulated photodegradation process of polyester-urethane coatings



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

<sup>a</sup> 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

<sup>b</sup> Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX, Eindhoven, The Netherlands

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### ABSTRACT

A kinetic Monte Carlo method to simulate photodegradation of a polymer coating is applied to the weathering process of a polyester-urethane clearcoat during artificial exposure under different conditions. Firstly, the optimised simulation parameters that yield the best match with experimentally measured results on the depth-resolved ester and urethane bond fractions are determined and compared for two different aerobic exposure experiments (one in a Weather-Ometer (WOM) and one in a Suntest equipment). Secondly, several other quantities that are obtained from the simulations, but cannot be determined experimentally, are compared, such as the fraction of newly formed crosslink bonds, absorptivity states, oxidised states, the fraction of radicals, the concentration of oxygen and the total amount of remaining material. Depth-inhomogeneity of the rate of photon absorption leads to the formation of distinct depth gradients in the WOM simulation, while a much more homogeneous evolution is obtained for the Suntest-air simulation. Photo-oxidative damage in the WOM simulation is more concentrated on the upper layer of the coating, resulting in the extensive evaporation of highly oxidised material, whereas degradation in the Suntest-air simulation is more spread out over the entire coating thickness, resulting in less material loss.

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### 1. Introduction

One of the key questions that researchers in the field of polymer photodegradation try to answer is how the performance of a polymer application is influenced by the circumstances that the material is subjected to during its service life. In a previous publication [1] the influence of the conditions of different artificial exposure experiments on the photodegradation process of a model polyester-urethane clearcoat has been studied experimentally. Amongst other insights, this experimental study showed that the spectral power distribution and the type of atmosphere in which degradation occurs (aerobic or anaerobic) largely influence the depth-resolved evolution of the chemical composition of a degrading coating, in terms of both the type of degradation reactions (“degradation pathway”) and the rates of these reactions at different coating depths (“depth-inhomogeneity”).

In the present article a similar study is conducted, following the approach of coarse-grained computer simulations based on a kinetic Monte Carlo (KMC) method that has been introduced in previous work [2]. In that article, depth-resolved coating degradation was simulated by modelling the depth-dependency of physical processes that occur in the coating, such as the absorption of photons and the diffusion of oxygen, together with a procedure to simulate individual degradation reactions based on a rate-weighted KMC algorithm. By matching the simulated chemical depth gradients to their experimental counterparts, the numerical values of several kinetic and physical parameters, such as various reaction rate constants, can be obtained via this method.

The number of simulation studies in the field of polymer photodegradation, in which a similar attempt was made, is very limited. Among these few studies, three types of approaches can be distinguished if one considers the extent to which the specific chemistry of the degrading material is taken into account. Studies in which the chemistry is completely disregarded include earlier attempts to simulate changes in surface topography [3] and a

\* Corresponding author.

E-mail address: [G.deWith@tue.nl](mailto:G.deWith@tue.nl) (G. de With).

statistical approach [4,5]. Such a statistical approach to degradation is based on the notion that the time it takes for a coating to fail can differ dramatically in different climatological conditions. When a combination of climate and consumer/population distribution is taken into account, together with process variability during coating manufacture, the probability of failure can be assessed for any location with known climatological parameters [5]. The practical value of such an approach will be clear, but due to its generality, it is not very insightful for learning how degradation processes are influenced by specific factors causing degradation.

A second type of simulation approach involves a rather general consideration of the coating chemistry, without specification of the precise chemical structure and degradation mechanisms. Such an approach has been used for Monte Carlo simulations of coating degradation with a focus on the evolution of the surface topography and its relation to various physical characteristics [6,7]. The change of the coating chemistry during degradation was modelled as “hardening” or “sensitising”, that is, a decreased or increased vulnerability of coating material near the location at which photon-induced damage occurred [6]. Besides this artificial incorporation of the chemistry, the influence of specific degradation factors on weathering was not considered.

The third type of approach involves a much more detailed specification of the coating chemistry. An early example of such a specific study was published by Martin, who developed a stochastic model to predict the degradation process of PMMA [8]. More recent examples deal with the photo-oxidative degradation of polypropylene [9] and epoxy-amine coatings with high and low glass transition temperatures [10,11]. These latter studies use a formalism of reaction rate equations based on the specific degradation chemistry and then simulate the evolution during exposure by solving a system of differential equations. In addition, physical processes such as light attenuation and mass transport of oxygen and water are included and the depth-dependence of degradation is taken into account as well. Our previous simulation work on polyester-urethane coatings also followed this last type of approach and includes, in addition to the KMC simulations already mentioned, Dissipative Particle Dynamics (DPD) simulations [12] and Molecular Dynamics (MD) simulations to determine physical properties of degraded networks after a fine-graining procedure [13].

In addition to studying the effect of the exposure conditions on quantities that have also been determined experimentally before [1,14], several quantities that can only be observed in the simulations will also be determined for the different exposure conditions. Although the simulated evolution of these quantities cannot be directly verified, some interesting insights into degradation processes and pathways can be obtained from such a study.

## 2. Modelling and simulation setup

### 2.1. Polyester-urethane model system

The material of study consists of the hydroxyl-functional polyester of isophthalic acid (IPA) and neopentylglycol (NPG) that is crosslinked with the trimer of hexamethyldiisocyanate (HDT). The chemical structure of the virgin polyester-urethane is represented by four types of coarse-grained beads (clusters of atoms which are grouped together into a single entity) [2]. The polyester part is composed of two bead types, that is, the IPA residue, denoted as “aromatic bead” and the NPG residue, called “aliphatic bead”. The HDT crosslinker is also composed of two types of beads: the isocyanurate ring, or “crosslinker body” (one per crosslinker molecule), and the isocyanate residue tail, or “crosslinker arm” (three per crosslinker molecule). Two types of bonds interconnecting the

beads are modelled explicitly: the urethane bond (connecting crosslinker arm and aliphatic bead) and the ester bond (connecting aliphatic bead and aromatic bead). These bonds can be broken as a consequence of photodegradation reactions. In addition, new bonds may form due to, for example, radical recombination reactions. These “new crosslinks” (interconnecting two aromatic beads or two aliphatic beads) are also modelled explicitly.

Different properties are assigned to individual beads by a numerical coding system that reflects the internal state of a bead [2]. This internal state may change as a consequence of photodegradation reactions. Some of the defined properties are relevant for all different bead types (for example, the number and type of connecting bonds, the number of radicals on the bead) whereas other properties are only relevant for a specific type (for example, the characteristic related to the absorption of UV photons is only relevant for the aromatic bead type). This specificity also determines in which reaction mechanisms a bead may or may not participate in order to simulate the evolution of the system with progressing degradation [2].

The introduction of a coarse-grained representation already leads to a significant reduction in the number of entities to handle during the simulation, but for a large simulated volume, further simplification is required. This simplification is achieved by converting the chemical network with topology into a compositional representation of the network, without topology. In short, this step involves discarding all the connections between beads in the coarse-grained network representation, so that it is no longer known which individual beads are mutually connected, but instead the number of beads with a certain connection type is tracked [2].

The direct output of the simulations is the depth-resolved time evolution of the (coarse-grained) chemical composition, that is, of the number of all the different beads with different internal states. All the other chemical and physical output that is discussed in the remainder of this article, can be derived from the direct output by post-simulation analyses.

### 2.2. Simulated exposure experiments

One set of simulations aimed at representing experimental exposure in a Ci65A Weather-Ometer, or WOM (Atlas MTS), equipped with xenon arc lamps and borosilicate inner and outer filters [14]. This WOM exposure experiment was performed at a black standard temperature (BST) of 65 °C and an irradiance of approximately 57 Wm<sup>-2</sup> (300–400 nm), and with a total cycle time of 2 h, composed of a 102 min dry cycle at 40–60% relative humidity and an 18 min wet cycle with water spray. Since the effect of water is not explicitly incorporated into the degradation model used for the simulations, the (wet/dry) cycling is not taken into account in the simulation of WOM exposure. The results of these simulations have been published previously [2].

Two other sets of simulations aimed at representing experimental exposure in a Suntest XXL + (Atlas MTS), equipped with xenon arc lamps and Coated Quartz inner/Daylight outer filters [1]. Two custom made exposure cells were installed inside the Suntest to control atmospheric conditions during exposure. One cell was continuously purged with dry air (“air-exposed samples”) and the other with dry nitrogen (“nitrogen-exposed samples”). Non-cyclic exposure was performed at an irradiance set to 48 ± 2 Wm<sup>-2</sup> (300–400 nm) as measured by the sensors outside the exposure cells. The settings were determined in such a way that during stationary operation, the resulting BST as measured inside the exposure cells was approximately equal to 65 °C, which is equal to the BST from WOM exposure.

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