

Multi-scale simulation of degradation of polymer coatings: Thermo-mechanical simulations



Hesam Makki ^{a, b}, Koen N.S. Adema ^{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, c}, Gijsbertus de With ^{a, *}

^a Laboratory of Materials and Interface Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5612, AZ, Eindhoven, The Netherlands

^b Dutch Polymer Institute (DPI), P.O. Box 902, 5600, AX, Eindhoven, The Netherlands

^c DSM Ahead Performance Materials BV, P.O. Box 18, 6160, MD, Geleen, The Netherlands

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ABSTRACT

In this work we simulate the full sequence of steps that are also typically performed in an experimental approach when studying photo-degradation of a polymer coating, namely, i) sample preparation, ii) photo-degradation and iii) thermo-mechanical analysis of the material during photo-degradation. In the current paper, we focus on performing several molecular dynamics simulations to study the thermo-mechanical properties of a virgin thermoset coating as well as degraded ones. Using an atomistic structure that is obtained by fine-graining the mesoscopic structure, we obtain consistent correlations between the simulated thermo-mechanical properties of the material and those measured experimentally. In addition, it is shown that by using oscillatory strain fields in MD - instead of the commonly applied linear tensile/compression strain fields - one can acquire greater knowledge on the structure-property relation of polymeric materials. Eventually, we show that our simulation approach gives rise to a remarkable insight into the mechanism of the photo-degradation process.

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1. Introduction

Polymeric coatings are designed for different demands and, accordingly, have to fulfill different requirements. Among these, preserving their functionality during the service life of these coatings is of a great importance. Exposure to the environmental stress factors, i.e., photons, elevated temperature, oxygen and water, for prolonged time leads to macroscopic failure of these coatings, such as (micro) cracks. Accordingly, a keen interest exists in understanding the long-term performance of these coatings, and sophisticated experimental methods such as FTIR [1] and UV-vis spectroscopy [2], ESR [3] and mass spectroscopy [4] techniques are used to characterize their degradation processes.

Due to the fact that organic coatings, particularly 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 mimic real outdoor conditions with higher intensity of the stress factors are used, although there is always a fear of deviation from

the chemical pathways of degradation for natural exposure because “relatively small variations in weathering performance can lead to significant variations in failure rates at a given time in service” [5]. Moreover, due to the complex chemistry of the photo-degradation processes, in which several stress factors influence the process at the same time, it is difficult to distinguish the effect of each parameter separately.

Although these type of measurements give a wealth of information, a great deal of interpretation is needed to deduce reaction pathways or failure mechanisms. In this respect high quality molecular simulations can provide a more direct view. In addition, simulations offer much more elements of control than experiments. For example, one can artificially allow one possible mechanism to play its role in a degradation simulation, to clarify its role. Finally, by combining experiments and simulation, a deeper mechanistic understanding can be developed. However, there are only a few simulation studies on this topic available in the literature [6–8] despite the extensive experimental investigations on the photo-degradation of polymeric coatings [9–14].

There are generally two approaches for simulation studies on photo-degradation processes in the literature, namely the stochastic approach [5] and mechanistic modeling [7]. Both types of

* Corresponding author.

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

simulation give insight into changes in the *macroscopic* properties of a coating during the degradation process. In order to assess the *microscopic* aspects of the photo-degradation process via simulation, as required to obtain insight into the structure-property relations of these coatings, one needs to think about the wide time spectrum of different degradation events taking place in the material [8]. This means that the spectrum of time scales in such a simulation should range from picoseconds – the typical time scale of chemical reactions – to years – the time scale before mechanical failure of the material is observable. No single molecular simulation method can cover such a wide spectrum in time; therefore, a multi-scale approach is necessary. The focus of this paper is to justify our multi-scale approach. We also show that our approach is capable of providing the relation between the mechanisms involved and the changes in material's properties.

The material used (Fig. 1) and the conditions for the photo-degradation (under dry nitrogen) employed for our simulations are the same as in a preceding paper [8]. Here, after a brief overview of our multi-scale simulation approach [8] (Section 2), we introduce the additional simulation methods, not covered in the previous paper, that enable us to compute the physical and mechanical properties of the material during the photo-degradation process (Section 3). Thereafter we discuss the results of our study (Sections 4 and 5).

2. The methodology of photo-degradation simulation

Our multi-scale simulation approach consists of four major steps: 1) Building up the cross-linked structure of the virgin material by a coarse-grained method, where molecules are composed of beads that represent groups of atoms [15], 2) performing the photo-degradation simulation, 3) reverse mapping from the coarse-grained (CG) structure to the corresponding atomistic structure of the material, and 4) computing the properties of the degraded material by atomistic methods.

2.1. Network formation

The first step of our approach is constructing a cross-linked polymer network. This is hardly feasible in an atomistically detailed Molecular Dynamics (MD) simulation, due to the large time scale of the cross-linking process in polymers as compared to the time scales that can be attained in MD simulations; therefore, we used a CG method, i.e., Dissipative Particle Dynamics (DPD) [16]. For our study we used a polyester resin with an isocyanurate cross-

linker based on hexamethylenediisocyanate. The coarse-graining as used in the DPD method is shown in Fig. 1. Note that we used 5 different beads and 4 different bonds, as such detail is required for the subsequent Kinetic Monte Carlo (KMC) simulations from which the degraded structures are obtained.

2.2. Photodegradation

For the second step, namely, “photo-degradation simulation”, the spectrum of time scales is so large that no time-driven molecular simulation method is able to capture the whole spectrum (from reaction times of typically a few picosecond to the final stage of degradation after several years). Consequently, we developed an event-driven simulation method based on a Kinetic Monte Carlo (KMC) algorithm to capture the chemical pathways of the photo-degradation process. We also showed that it is necessary to couple our event-driven method to a time-driven method in order to allow for structural relaxation of the network during the photo-degradation process [8]. Therefore, we connected our photo-degradation simulation to a DPD simulation to fulfill the structural relaxation requirement of the material [8].

During the photo-degradation simulation, according to the chemical reactions involved (see Fig. 2), different beads and bonds can form. As shown in Fig. 1, the virgin material (the cross-linked polyester at zero degradation time) consists of five different CG beads (from A to E) and four different CG bonds (A–B, B–C, C–D and D–E). As a result of photo-degradation, five other beads (A', B, C, β and β') and two other types of bonds (A–A' and β–β') can form. Fig. 3 shows a summary of new CG beads and bonds that can evolve during a photo-degradation simulation.

In case study II of a previous paper [8], the reaction rate constants for each set of reactions, i.e., initiation, propagation and termination, were set at 1 dt^{-1} , where for the ‘degradation time’ $\text{dt} = 1 \text{ s}$ was chosen as unit of time. Because the structure was fully relaxed in between subsequent degradation events, the time evolution expressed in dt units will be the same, irrespective of the absolute value of dt . Real differences occur only if rates are changed relative to each other. In this paper, we discuss the results for independently generated samples of the material obtained at four moments in time during the photo-degradation simulation process, namely, 0, 0.1, 3 and 5 dt , with conditions similar to case II of the previous paper. Fig. 2 shows the list of reactions and the corresponding rate constants.

2.3. Reverse mapping

Computing the physical and mechanical properties for polymer glasses can be done either by atomistically detailed or by CG simulation methods. The results obtained in the past ten years show that nowadays MD simulations are mature enough to address several physical and mechanical properties, in spite of the obvious limitation in time and length scales [17]. CG methods, on the other hand, so far cannot provide quantitatively accurate predictions. Therefore, after some degradation time, we reverse map our (degraded) CG structure to a fine-grained (FG) one, as the third step of our simulation scheme.

2.4. Property calculations

In the fourth stage, we perform several MD simulations on the FG structure to obtain material properties. We briefly reviewed the first two steps of our multi-scale approach in the previous sections. In the following section, we will elaborate on the fine graining and MD methods employed in steps three and four of our multi-scale simulation approach.

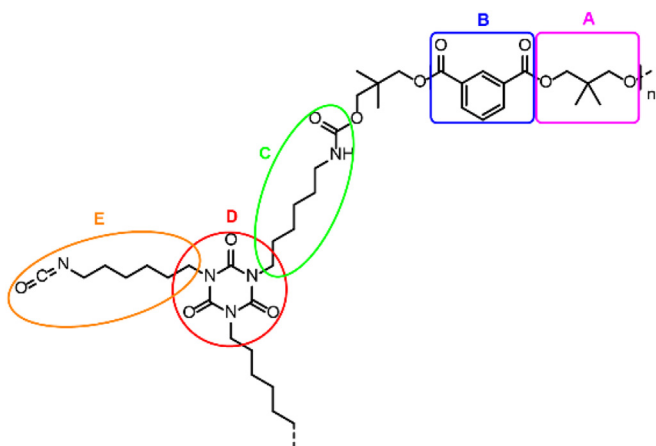


Fig. 1. The atomistic and the corresponding coarse-grained chemical structure of the cross-linked polyester network.

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