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Quantitative analysis of photoinitiated coating degradation at constant artificial exposure conditions

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Abstract

This work concerns the development of simulation tools for mapping of degradation phenomena and estimation of mass loss and ablation rates during weathering tests of thermoset coatings. A novel mathematical model, which includes photoinitiated oxidation reactions, intrafilm oxygen permeability, water absorption and diffusion, reduction of crosslink density, and development of a thin surface oxidation zone, was recently developed. The model has been validated against three previous experimental data series with two-component epoxy-amine coatings at constant exposure conditions. One data series includes the effect of nano-particles (SiO₂ and multi-walled carbon nano-tubes) on the rate of degradation. In this presentation, a concise introduction to the model and some of the simulation results are provided. Further development of the simulation tool to commercial coatings and dynamic exposure conditions will be shortly discussed.

Introduction

Degradation of coatings exposed to solar ultraviolet (UV) radiation, heat, moisture and other environmental stresses is termed weathering [1]. For thermodynamic reasons, all organic coatings are prone to weathering eventually, at least in principle, converting the organic components to the stable end products CO₂ and water [1]. However, the rate at which this happens is strongly dependent on the binders and other coating materials used and the conditions of exposure. For modern high-performance coatings, weathering is usually a slow process typically taking five years or longer before a critical performance property can be said to have failed [2]. New products are continuously developed by the coatings industry and there is a constant need for accelerated weathering tests. Accelerated testing can be done in laboratory exposure equipment, using high radiation intensity and/or high temperature and relative humidity, or outdoor in climatically stable regions such as the very sunny reference climates in Miami, Florida, where the relative humidity is high, and Phoenix, Arizona, where the air is very dry [1]. However, it is essential that the exposure strategies developed allow valid extrapolations to in-service exposure conditions [2]. To analyse and improve the correlations between laboratory and field data and increase the understanding of coating behavior during accelerated exposure conditions it is of relevance to quantify the underlying physical and chemical mechanisms and develop modeling tools. In this work a mathematical model, which quantifies coating degradation of a thermoset coating, at constant exposure conditions, is briefly presented and some important results discussed.

Mathematical coating degradation model

The mathematical model was presented and verified against experimental data for epoxy-amine coatings in a recent publication [3] and here will only be given a concise, equation-free introduction. Epoxy-amine coatings are rarely used in the heavy-duty sector without a UV radiation resistant top coat [4] and therefore serves here only as a reference system for which a significant amount of experimental data has accumulated in the open literature.

A closed-loop mechanism, including photoinitiation, radical oxidation, and termination reactions, was used to describe the degradation chemistry. The process that takes place when a densely crosslinked epoxy-amine coating is exposed to conditions of constant UV radiation, humidity and temperature in an accelerated exposure device is schematically shown in Fig. 1. From the onset of exposure, photoinitiated reactions take place, which slowly degrade the top layer of the coating. Simultaneously, if the coating, prior to exposure, has been stored at another value of relative humidity than that in the exposure chamber, moisture is absorbed (or desorbed depending on the relative humidity in the chamber), and starts to penetrate the coating. At the surface, an oxidation front begins to move into the coating.

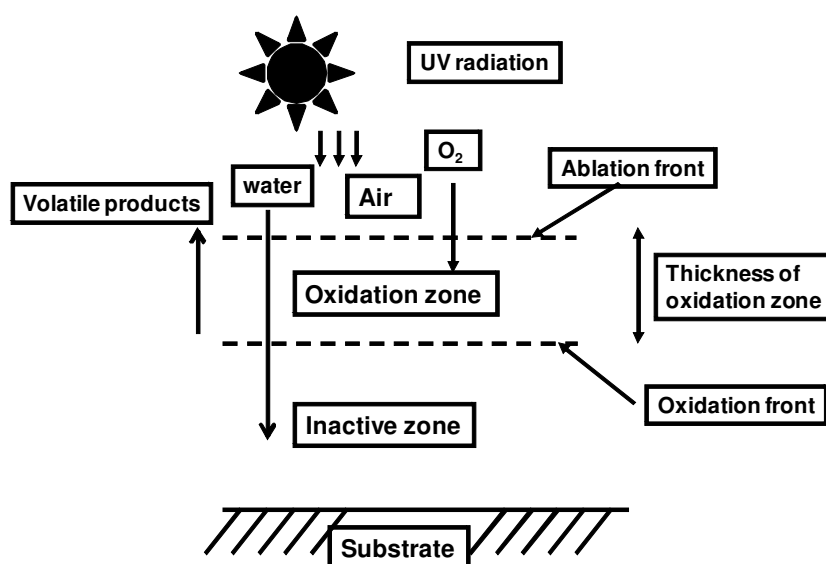


Figure 1: Schematic illustration (cross-section view) of epoxy-amine coating during exposure to ultraviolet radiation and humidity. On the surface of the coating, a thin oxidation zone is formed, where the degradation takes place. Figure is not to scale, in reality the oxidation zone is much thinner than the initial coating thickness. After Kiil [3].

The rates of chemical oxidations, the solubility of oxygen in the coating, and the rate of diffusion of oxygen into the coating determine the rate of movement of this front. At the point in time where a critical fraction of the original network chains (termed $X_{CL,max}$) has been broken at the coating surface, the ablative front (i.e. the coating surface) begins to move and the thickness of the coating is reduced. At some point, the rate of movement of the oxidation and ablative fronts can become equal and a stable oxidation zone thickness is established (see Fig. 1 and [3]). This stable surface zone has been observed in practice for densely crosslinked epoxy-amine coatings and estimated by various analytical methods to be about $2 \mu\text{m}$ [3]. In the inner, much wider and oxygen-free zone, no degradation takes place despite the fact that radiation penetrates. When radicals are formed in this zone, they rapidly recombine and no damage occurs. In the stable oxidation zone, concentration gradients are established, the original matrix structure is partly lost, and oxidation products are present. As evidenced by Nguyen et al. [5], about 80 % of the original benzene rings in the epoxy structure can disappear from the outer part of the oxidation zone and the presence of carbonyl and amide groups increase rapidly.

In summary, the model includes the following rate-influencing phenomena: photoinitiated oxidation reactions, intrafilm oxygen permeation, water absorption and diffusion, reduction of crosslink density, and development of a thin surface oxidation zone. The overall purpose of the model is to quantify the rates of ablation and mass loss and estimate the ablation lag time (defined as the initial time lag before the crosslink density at the coating surface has been sufficiently reduced for ablation to begin).

Results and Discussion

The model developed is relevant for industrial protective coatings and therefore does not include a direct description of how the gloss develops, but rather focuses on prediction of mass loss and ablation rates (thickness reduction). As discussed in Kiil [3], the simple epoxy-amine coatings used for model verification and the constant exposure conditions (with no dark cycles and no water spray) applied leads to very thin surface oxidation zones of just a few microns. This situation is expected to be quite different for commercial coatings containing UV absorbers, radical scavengers, and more UV radiation stable binders at dynamic exposure conditions. In those more realistic exposure scenarios, oxygen diffusion is most likely not the main factor determining the thickness of the oxidation zone, but rather UV radiation absorption [3]. So, the present model is the first step towards simulations under realistic exposure conditions.

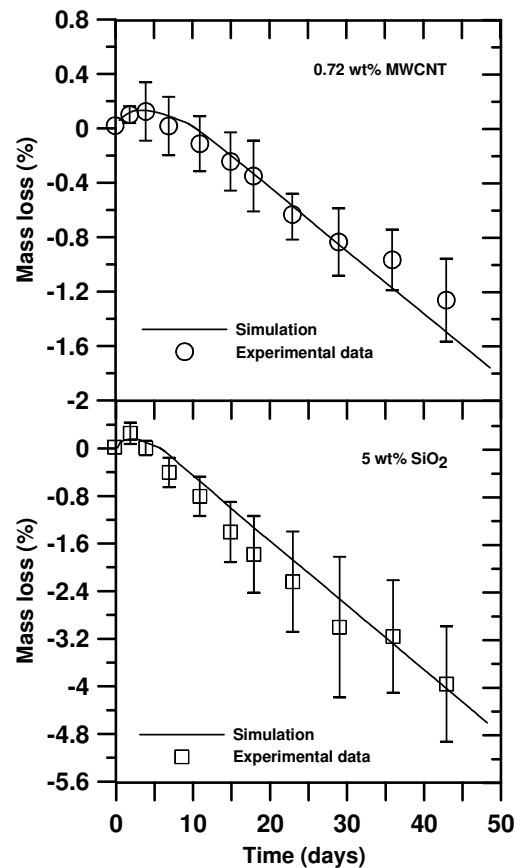


Figure 2: Comparison of model simulations (lines) with experimental mass loss data (symbols) of an epoxy-amine coating containing either 0.72 wt% multi-walled carbon nanotubes (MWCNT) or 5 wt% nano-SiO₂ particles. Conditions: 50 °C, relative humidity 75 %, and 480 W/m² (295-400 nm). The experimental data were taken from Nguyen et al. [5] and the figure reproduced from Kiil [3] (open access publication). Model parameters are available in [3].

Simulations with the model for densely crosslinked epoxy-amine coatings have been compared to three experimental data series (artificial UV exposure). As an example, in this short communication, the transient mass loss for two coatings containing nano-particles will be reviewed (see the original reference [3] for details).

In Fig. 2 a comparison of simulations and experimental data from [5] for two low-pigmented coatings are shown. One of the coatings contains 0.72 wt% multi-walled carbon nano-tubes (MWCNT) and the other 5 wt % nano-SiO₂. A good agreement between simulations and experimental data is evident (for a list of and discussion of the parameter values used see [3]). Initially, the mass increases due to absorption of moisture. Later, ablation of the coating surface becomes important and the rate of mass loss increases significantly and finally attains a constant value. For the coating containing nano-SiO₂, all adjustable parameters were the same as for the same pigment-free coating and the difference (not shown) in the relative mass loss (and associated ablation rates) can be attributed entirely to a difference in the initial dry film thickness. So, there is no effect of adding 5 wt% nano-SiO₂ to these simple coatings. On the other hand, the rate of mass loss for the coating containing MWCNT is smaller than that of the clear coat. The constant rate of ablation (not shown) is reduced by 36 % when the coating contains as little as 0.72 wt % MWCNT. The effect of MWCNT is thought to be mechanical though the material can most likely also absorb some UV radiation. This was verified by the fact that increasing $X_{CL,max}$ from 0.4 (the value used for the pigment-free coating) to 0.6 resulted in the very good fit shown in Fig. 2 suggesting that the effect of MWCNT is mostly mechanical (an increase in $X_{CL,max}$ means that more bonds must be broken at the coating surface before ablation sets in). Many other simulations and experimental data series are available in Kiil [3] showing, for instance, the effect of changing the relative humidity in the exposure chamber.

The next step in the model development will be to consider dynamic conditions and thereby provide simulations of coating behaviour in various cyclic exposure scenarios being used in accelerated testing equipment. Subsequently, conditions of natural weathering should be considered. In addition, it may be investigated how the effects of e.g. UV radiation absorbers and light stabilizers can be included in the model. The model approach can be extended to other coating systems provided experimental data and observations are available for calibration of the model and a closed-loop mechanism for the degradation chemistry can be established. Simultaneous measurements of rates of mass loss, ablation, and formation of photoproducts, as well as oxidation zone thickness measurements, on the same well-characterized coatings, at controlled exposure conditions, would be very useful.

Conclusions

The mathematical model developed is able to simulate experimental data available for simple densely crosslinked epoxy-amine coatings under constant exposure conditions. The phenomena influencing the rate of degradation have been mapped. In the presentation a range of simulations with the model will be shown and discussed. Future work with the model involves extension to dynamic exposure conditions and more industrially relevant coatings.

Acknowledgement

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