Progress in Organic Coatings 76 (2013) 1197–1202

Contents lists available at SciVerse ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Natural versus accelerated weathering: Understanding water kinetics in bilayer coatings

Viktor Baukh[a], Hendrik P. Huinink[a,*], Olaf C.G. Adan[a,b], Leendert G.J. van der Ven[c]

[a] Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, NL-5600MB Eindhoven, The Netherlands
[b] TNO, Delft, The Netherlands
[c] AkzoNobel Automotive & Aerospace Coatings, Sassenheim, The Netherlands

ARTICLE INFO

Article history:
Received 22 November 2012
Received in revised form 18 March 2013
Accepted 27 March 2013
Available online 7 May 2013

Keywords:
Accelerated weathering
Water kinetics
Multilayer coatings

ABSTRACT

Exposure to water is a key issue in the performance of multilayer coatings. It may take place in different forms, i.e. as rainfall, dew and humidity variation. Consequently, coatings will experience time-dependent water activity fluctuations. In industrial practice, coatings are subjected to artificial water activity fluctuations in weathering tests. Little is known about the connection between these tests and the reality experience by a coating.

This article presents a theoretical investigation of the response of multilayer coatings to water activity fluctuations. This investigation is performed on the basis of a validated model for water transport in hydrophilic base coat/hydrophobic top coat systems. The study aims to understand how permeability and sorption properties determine the overall coating response to fluctuations.

It is concluded that present accelerated weathering tests do not mimic natural weathering due to the response time of the considered systems, which are insensitive to rapid fluctuations.

1. Introduction

Coatings are frequently applied in multiple layers with distinct properties to meet required specifications. Usually, primers are applied to provide adhesion and corrosion protection, base coats give color and top coats deliver protection against environment.

During their service life, these systems are exposed to UV light, humidity and heat, resulting in weathering and reduction of their lifetime [1,2]. The failure of systems due to weathering occurs as a result of a complex interplay of UV exposure, temperature and humidity. Water, which can be present in the form of water vapor or liquid, can promote deterioration of coatings, both as a single factor and in combination with UV light and heat. Carfagna et al. [3] showed how hygrothermal aging affects mechanical properties of epoxy-based coatings. Martin et al. [4] and Nguyen et al. [5–7] concluded that water damages acrylic melamine coatings both alone and in combination with UV light and heat during artificial and natural weathering.

Natural and accelerated artificial weathering exposures are standard durability benchmarks for polymeric materials [1,2,8]. Natural weathering means that samples are subjected to natural conditions, i.e. direct sunlight, ambient outdoor temperature and moisture. Accelerated artificial weathering is applied to perform durability tests in a shorter time span than in natural weathering tests, see Table 1. Accelerated weathering can be performed via two routes. The first one is done outdoor, like natural weathering tests, with sole difference is that the timescale of exposure is accelerated by concentrating natural sunlight and by applying heating and cooling, wetting and drying of the samples. The second route is accelerated weathering in laboratory conditions, which is performed through exposure of samples to artificial UV light, heat and water. Natural weathering includes a broad range of timescales. For example, rainfall and day/night cycles introduce typical timescales in the order of hours and days, while humidity variations due to seasonal change have timescales in the order of months. In accelerated artificial weathering, typical timescales are in the order of hours [2,9]. Shi et al. [10] pointed out that results from accelerated tests may differ from natural weathering, if wet/dry cycles become shorter durations of uptake or drying. In such case, water exposure in accelerated test will not mimic natural weathering. As timescales in wet/dry cycles play an important role in weathering of coatings, understanding the influence of timescales of ambient humidity fluctuations on water migration in multilayer coatings becomes crucial.

In our previous work, we investigated water transport in hydrophilic base coat/hydrophobic top coat systems, which are representative for automotive coatings [11–13]. It was found that the transport rate is limited by penetration through the top coat and

* Corresponding author. Tel.: +31 4 0247 5375.
E-mail address: h.p.huinink@tue.nl (H.P. Huinink).

0300-9440/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.porgcoat.2013.03.029

Table 1
Water activity ranges and related timescales for different weathering tests. Florida and Arizona are typical locations for natural weathering tests. The humidity is rather high in Florida and low in Arizona and its fluctuations comprise various timescales, i.e. from hours to months. Artificial and accelerated weatherings include wet/dry cycles, implemented with water spraying. Typically, the duration of a cycle is a few hours.

	Activity range	Typical timescales
Florida humidity	0.6–0.95	Hours–months
Arizona humidity	0.2–0.5	Hours–months
Artificial/accelerated weathering	0–1	Few hours

that most of water accumulated in the base coat. Water in the base coat caused significant swelling of the layer [11]. Furthermore, it was found that hydrophilic polymeric dispersants in the base coat play a key role in promoting water uptake [12].

Moreover, a theoretical model was introduced and validated for this type of multilayer coatings [13]. It was shown that transport could be described on the sole basis of the top coat permeability and the base coat sorption isotherm. The top coat permeability determines the typical timescale of water transport and the sorption isotherm defines the precise process kinetics. The validity of the model to predict water transport on the basis of the top coat permeability and the base coat sorption isotherm was proven. Consequently, this theoretical model may serve as a tool for investigating the response of the two-layered coatings to time-dependent humidity fluctuations.

The present paper aims to gain insight in the influence of the layer properties on the response of such base coat/top coat systems to humidity fluctuations. Fig. 1 shows a schematic picture of such systems. A basic description of the fluctuations is introduced in the model, in which the fluctuations are considered as harmonic oscillations of water activity. Special attention is paid to the influence of the shape of the base coat sorption isotherm on the response to fluctuations. In order to understand the physics of the response, a linear model is discussed, which is applicable in case of a linear sorption isotherm or small humidity fluctuations. As a second step, systems with non-linear sorption isotherms are considered and the influence of the shape of the isotherm on the response time is studied. Finally, this paper shows how the response of a real system depends on the humidity range and fluctuations timescale.

2. Theory

2.1. Model

The aim of this section is to formulate a model for water transport in 2-layered coatings with hydrophilic base coats and hydrophobic top coats that are subjected to time-dependent humidity fluctuations. In these systems water redistributes much faster in the base coat than in the top coat, and that water permeates through the top coat via Fickian diffusion with a constant diffusion coefficient [11,13]. Time dependency of water content of the base coat $\theta \equiv n/n_{max}$ is considered, where n [mol] and n_{max} [mol] are the actual amount of water in the base coat and the water uptake capacity of the base coat, respectively. In this case, the rate of change of the water content in the base coat can be connected with the difference in water activity in the environment a_{ex} and in the base coat a_{BC}, see [13]

$$\frac{d\theta}{dt} = \frac{1}{\tau}[a_{ex} - a_{BC}(\theta)]\,, \tag{1}$$

where $a_{BC}(\theta)$ is the inverse sorption isotherm of the base. Note that in case that the environment consist of air a_e = RH/100% (RH is the relative humidity). The timescale of water transport τ reads

$$\tau = \frac{n_{max}L}{AD\rho_S} \tag{2}$$

where L [m] is the thickness of the top coat, A [m^2] is area of water penetration and $D\rho_S$ [mol m^{-1}s^{-1}] is the permeability to water of the top coat (D [m^2/s] is a diffusion constant of water in the top coat and ρ_S [mol m^{-3}] is the maximal water concentration in the top coat).

The time-dependency of the water activity is taken into account by making a_{ex} in Eq. (1) time dependent: $a_{ex} = a_{ex}(t)$.

In this study, the fluctuations of the water activity in the environment are modeled as harmonic oscillations with an amplitude $\triangle a$ and radial frequency ω.

$$a_{ex}(t) = a_0 + \triangle a \sin \omega t\,, \tag{3}$$

where a_0 is the average external water activity. The parameters are restricted: $\triangle a \le a_0$ and $\triangle a \le 1 - a_0$, because the activity varies by definition between 0 and 1. Thus, fluctuations in the water activity can be characterized by the average water activity a_0, the activity range $2\triangle a$ and their period $T \equiv 2\pi/\omega$. Finally, it has to be mentioned that every fluctuation can be decomposed in harmonic functions of the type of Eq. (3), which makes the outcomes of this study applicable to a wide range of fluctuation types.

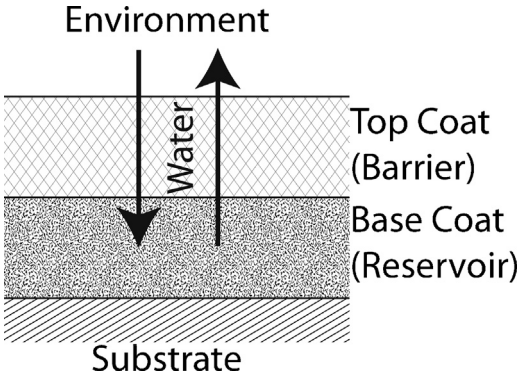

Fig. 1. A schematic picture of the multilayer coatings, considered in this paper. The top coat acts as a barrier from the environment, whereas the base coat is hydrophilic and is a reservoir for water. Environment is represented by time dependent variations of water activity.

2.2. Role of the timescale of humidity fluctuations

First, to understand the physics of the response to the activity fluctuations, we consider systems with linear sorption isotherms. Linearizing the problem allows to obtain an analytical solution for the water content of the base coat during fluctuations. In this section the role of the timescale of fluctuations is studied with analysis of the solution. A relationship between the layers properties and the response to the fluctuations is investigated.

A linear sorption isotherm can be written as follows:

$$\theta = c + ka_{BC}\,, \tag{4}$$

where k is the solubility of water in the base coat and c is a constant. Obviously, in the case of Henry's law $c = 0$. By substitution Eq. (1) the external water activity a_{ex} with Eq. (3) and taking into account linear dependency between water activity in the base coat and water content $a_{BC} = (\theta - c)/k$ (Eq. (4)) an equation for water content oscillations was obtained. The integration of this equation resulted in the following expression for the water content variation in the base coat

$$\theta(t) = \theta_0 + \frac{k\triangle a}{\sqrt{1+\omega^2\tau^2k^2}} \sin(\omega t - \arctan \omega\tau k) \tag{5}$$

where $\theta_0 \equiv c + ka_0$ is the water content, when the system is in equilibrium with the average water activity a_0. The water content