



Short communication

Process control for thin organic coatings using fluorescence dyes



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ABSTRACT

The fluorescence dyes rhodamine B and auramine O were added to a coating material based on hybrid polymers (ORMOCER[®]s) in concentrations of 10 ppm each. The fluorescence intensity of the auramine depends on the curing state of the lacquer while rhodamine is almost insensitive to this variation of the molecular environment. With the combination of both these dyes, the curing state as well as the thickness of the coating can be measured.

Due to the low concentration the dyes do not degrade the properties of the lacquer coating.

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1. Introduction

Coatings of materials are in wide spread use in industry to adjust the surface properties [1]. In particular, lacquer coatings have a long tradition.

While typical coating materials have a thickness >10 μm, many functional coatings and primers are applied much thinner (<3 μm). Especially, if an organic coating is applied on a polymer the quality control can be difficult. One example of a thin functional coating is the hybrid-polymer-based coating in an ultra-barrier coating stack. Such multilayer coatings are used to reduce the permeation of oxygen and water vapor through polymer films by many orders of magnitude [2] and they are meant to be applied as flexible encapsulation materials for organic electronic devices as organic light emitting diodes (OLEDs). In the Fraunhofer POLO[®] approach to ultra-barrier coatings [3] a layer of a hybrid-polymer is applied between two sputtered metal oxide layers. This intermediate coating is supposed to decouple defects in the two inorganic coatings. The targeted thickness is well below 1 μm. Since all the coatings are supposed to be produced in roll-to-roll processes there is a demand for a process control technology for the hybrid polymer lacquer coating process.

This situation led to the idea to use fluorescent dyes to determine the thickness of very thin organic coatings on organic materials such as polymer films. Meanwhile a paper has been published in

which the authors have shown that fluorescent dyes can be used to monitor the homogeneity of the deposition of atmospheric pressure plasma polymers [4]. In the present paper we will show how this technique can be improved to obtain additional information.

Many organic materials fluoresce, i.e., if they are irradiated with light of a particular wavelength they absorb this light and emit light with a longer wavelength. Some dyes show a fluorescence effect which depends on the environment of the dye molecules. The surrounding molecules influence the intensity and the wavelength of the fluorescence light. For example, the fluorescence may depend on the pH or the ionic strength of the medium. Other dyes are influenced by the viscosity of the matrix. They show a stronger fluorescence in a solid than in a solution or a stronger fluorescence in a highly cross-linked resin than in a less cross-linked one.

These properties can be used to tag materials and coatings. For this purpose a dye is used showing special fluorescence bands which depend on the chemical and the physical properties of the material where it is added to. The fluorescence depends, for example, on the exact chemical composition as determined by the ratio of components that form the material. The degree of curing or the cross-linking density of a resin may influence the fluorescence, too. If two or more dyes are added to the material which differ in their fluorescence response when interacting with the coating compounds, a coating can be prepared which is extremely difficult to imitate. This feature can be utilized for counterfeit protection.

Fluorescence can be detected with an extremely high sensitivity. Thus, a very small concentration is sufficient for the identification. For example, up-to-date equipment can record spectra of femtomolar solutions of fluorescein. If we assume a sampling thickness

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analyzed by the spectrometer in the order of 1 mm, we can estimate that in a 1 μm thick coating a dye concentration well below 1 ppb (parts per billion) would be detectable.

In the current paper we will show how the addition of fluorescence dyes to a lacquer can be used to follow the thickness and curing state of a coating at the same time.

2. Materials and methods

Poly(vinyl alcohol) PVA (Fluka, Mw = 72 000 g/mol), rhodamine B (CAS Number 81-88-9, Sigma–Aldrich, >95%), auramine O (CAS Number 2465-27-2, Sigma–Aldrich, >80%) were used as received. Polypropylene PP (Sabic PP412MN40) was mixed with rhodamine B in several steps to obtain a material with 20 ppb of the dye. This material was used for injection molding of sheets (diameter 25 mm, thickness 2 mm). ETFE film (Nowoflon ET 6235) was supplied by NOWOFOL Kunststoffprodukte GmbH (Germany).

Barrier coatings based on hybrid-polymers: All solvents and chemical substances were used as received from the market. The educts for the ORMOCER[®] lacquers were aluminum-sec-butylate (AsB, Sasol), ethyl acetoacetate (EAA, Sigma–Aldrich), (3-glycidoxypropyl)trimethoxysilane (GLYMO, Brenntag) and tetramethoxysilane (TMOS, Brenntag).

A fluorescence spectrometer Fluorolog 122 (Yobin-Yvon, France) was used which was equipped with a Xenon Lamp, a single stage excitation monochromator, a two stage emission monochromator, and an electron multiplier detector.

The water vapor transmission rate (WVTR) and the oxygen transmission rate (OTR) were determined using AQUATRAN and OX-TRAN instruments (Mocon, USA), respectively.

3. Results

We chose a model system in order to demonstrate the mechanisms of detection we intended to use. Poly(vinyl alcohol) (PVA) is a water soluble polymer. The fluorescence dyes rhodamine B and auramine O were added to a 2.5% solution of PVA in water. In a particular example their concentration in the solution was 4.8 and 3.2 ppm, respectively.

In Fig. 1 the fluorescence of the solution is shown for an excitation at 400 nm. The fluorescence maximum of the auramine is observed at 490 nm while that of the rhodamine appears at 581 nm. Then the solution was cast on a siliconized glass plate and the water was evaporated to obtain a film of the PVA containing the dyes.

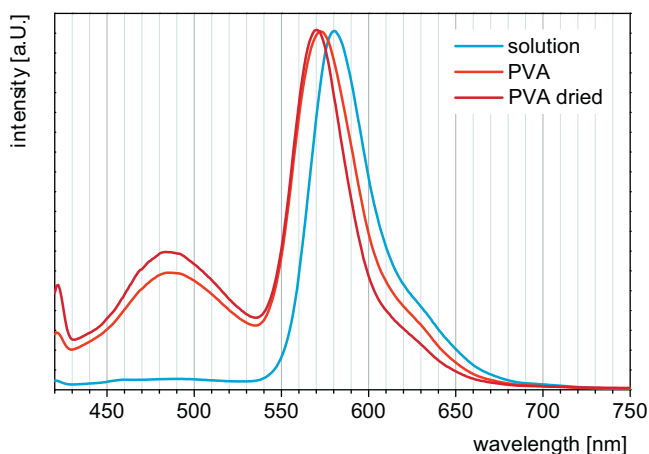


Fig. 1. Normalized fluorescence spectra of a 2.5% PVA solution and PVA films in an air dried (PVA) and a vacuum dried (PVA dried) state. All contain the fluorescence dyes rhodamine and auramine (solution concentrations: 4.8 mg/l rhodamine, 3.2 mg/l auramine, 2.5% PVA; 1 h 60 °C vacuum dried).

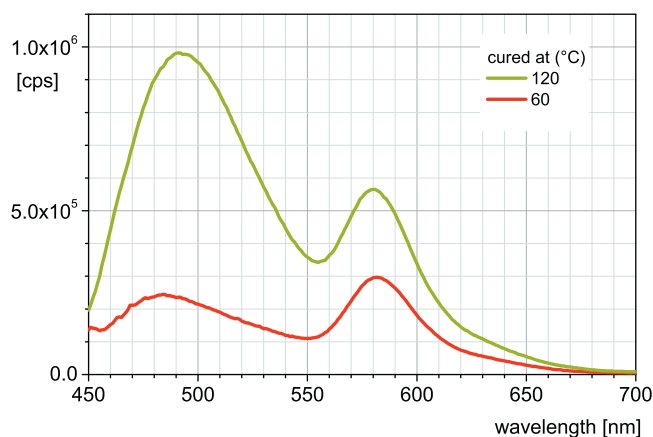


Fig. 2. Fluorescence dye contained in ORMOCER[®] lacquer coated on a Nowoflon ET 6235 film (10 mg/l rhodamine 10 mg/l, auramine).

The concentration of the dyes was 192 ppm for rhodamine and 128 ppm for auramine. The air dried film was used to record a fluorescence spectrum which is also shown in Fig. 1. All spectra were normalized in a way that the intensity at 750 nm was set to zero and the maximum intensity of the rhodamine fluorescence was set to 1. Compared to the solution fluorescence, the intensity of the auramine in PVA was higher by a factor 10.7 and the maximum is shifted slightly to 487 nm. The rhodamine fluorescence maximum was found shifted to 572 nm.

The air dried PVA film still contains some percent of water which acts as a plasticizer. In order to reduce the water concentration of the film, it was dried in vacuum at 60 °C for 1 h. In this dried film the auramine fluorescence maximum appears at 483 nm with a relative intensity 12.6 times higher than in solution and 1.17 times higher than in the air dried film. The rhodamine fluorescence maximum was found being shifted further to 570 nm.

Comparing the spectra it is apparent that the fluorescence properties of the auramine depend much more on the molecular environment of the dye molecules than the rhodamine does. The more the ability to conformational alterations is hindered in the case of auramine the more efficient the incoming radiation is released by fluorescence instead of being dissipated as heat. Therefore, the higher viscosity of the matrix results in a higher fluorescence intensity. This situation suggests that it might be possible to use this dye as a probe for the curing state of a lacquer. Since the fluorescence of rhodamine does react much less on the viscosity of the matrix the combination of the two dyes gives the opportunity to detect the thickness of a coating and its curing state at the same time.

In order to test such an approach, both dyes were added to an ORMOCER[®] lacquer in a concentration of 10 ppm each. Then the lacquer was coated onto an ETFE film which was corona treated before. With a rotogravure technique we were able to produce a homogeneous coating [3] with a thickness of about 1 μm . The coating was cured at 60 °C and at 120 °C, respectively. There is

Table 1

Oxygen permeation of a SiO₂-PET film (M401) which was coated with an ORMOCER[®] which contained 100 ppm of fluorescein in the liquid (detection limit: 0.05 cm³/(m² d bar)).

Thickness (μm)	Dye	OTR [cm ³ /(m ² d bar)]	
		Sample 1	Sample 2
20	No	<0.05	<0.05
20	Yes	<0.05	<0.05
10	No	<0.05	<0.05
10	Yes	<0.05	<0.05

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