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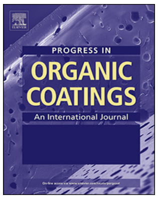

Monitoring of thickness and conversion of thick pigmented UV-cured coatings by NIR hyperspectral imaging

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ABSTRACT

Hyperspectral imaging using a near-infrared (NIR) camera was used for in-line monitoring of thickness and conversion of white pigmented UV-cured acrylate coatings. In particular, it was applied for the quantitative determination of both parameters as well as for the evaluation of the homogeneity of their spatial distribution. Quantitative data were obtained by means of chemometric approaches. Calibration models were built up on the basis of the partial least squares (PLS) regression algorithm using reference data of coatings with thicknesses in the range from about 20–200 µm and with a conversion between about 15 and 80%. Reference values for the conversion were determined by NIR reflection spectroscopy utilizing the acrylate band at 1620 nm. The resulting accuracies (in terms of the root mean square error of prediction, RMSEP) were found to be 8.7 µm for the prediction of the layer thickness and 2.5% for the acrylate conversion. The developed methods were also used for the visualization of the spatial distribution of both parameters across the surface of the UV-cured coating and the detection of inhomogeneities within the layers. The performance of this approach was demonstrated with coatings that formed a pronounced heterogeneous surface structure after UV curing resulting from shrinkage. All NIR measurements were carried under conditions that were similar to those in technical coating processes. Consequently, the results of this study prove that hyperspectral imaging has considerable potential for in-line process and quality control.

1. Introduction

Coatings are present everywhere in our daily life. Beside the application of coatings in automotive and furniture industries, they are used in a broad spectrum of applications ranging from architecture via food packaging to fiber optics. UV-curable coatings are advantageous with respect to saving of energy, environmental protection and waste reduction since UV curing consumes less energy than thermal drying or curing. Moreover, solvent-free varnishes are widely used in UV curing technology, which may reduce environmental pollution.

The requirements to the functional properties and the quality of UV-cured coatings may be quite high. Depending on the area of usage, coatings have to satisfy specific criteria. Beside various protection functions (against scratches, abrasion, corrosion/weathering, migration, and chemical impacts), UV coatings should also provide a formidable appearance (color, gloss, special effects such as pearlescent appearance). In particular, coatings intended for use in special outdoor applications such as yacht and sporting boat building, wooden garden furniture and outdoor flooring have to withstand exceeding environmental impacts like weathering, water (possibly saltwater), fouling etc. On the other hand, they are expected to show an exquisite high-value appearance. Therefore, such coatings are extremely demanding with respect to their properties. In order to fulfill these harsh requirements, such coatings are typically multi-layered with a final thickness in the order of about 100–300 µm [1].

Both the thickness and the conversion of the layer have crucial impact on the resulting quality of the coating. In particular, thick pigmented coatings represent a considerable challenge for sufficient through cure due to the fact that pigments – especially white pigments like titania – strongly limit the penetration of UV light into the coating. Incomplete through cure of the coatings may lead to inadequate application properties of the coating with respect to adhesion, resistance, appearance, migration of volatile components to the surrounding etc. Additionally, a broad range of chemical influences such as varnish formulation, technical factors (e.g. irradiation dose, conveyor speed) and environmental parameters (temperature, inertization etc.) during UV irradiation may influence the resulting conversion significantly. Thus, in order to be able to guarantee a constantly high level of the quality of the UV-cured coatings, in-line monitoring of film thickness and conversion is required for an efficient process control. Moreover,

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the wasting of materials and energy can be avoided in this way. Last but not least, this may have a significant positive effect on the final costs of the coatings.

Spectroscopic methods are widely used for process control due to their non-destructive and non-invasive nature, speed of analysis and robustness of the equipment. Especially, near-infrared (NIR) spectroscopy is frequently used for process control [2], since it is an exceedingly powerful tool for the analysis of many (mainly organic) materials [3], in particular if it is used in combination with chemometric data evaluation approaches. Due to its great benefits, NIR spectroscopy has found broad application in fields such as agriculture [4], food [5–7], petrochemistry [8–10] and pharmaceutics [11–14]. Due to the much lower extinction coefficients in the NIR range compared to the mid-infrared range of conventional infrared spectroscopy, it is particularly suited for the characterization of thick layers or even three-dimensional objects (e.g. fruits). It benefits from the resulting high penetration depth of the probe light, which might be in the order of millimeters or even more depending on the specific sample system. Moreover, the possibility to link the probe head to the NIR spectrometer via optical fibers definitely contributed to the success of NIR spectroscopy as a process control technique, since this allows the mounting of the probe head in poorly accessible areas inside process lines without significant modification of these manufacturing machines. However, only small spots with a size of a few millimeters can be typically monitored in this way. Consequently, only information about a small stripe of sample is available during operation of the machine. Even the use of traversing NIR probe heads, which are moving across the conveyor belt or the web, cannot cover the complete area of the sample in a continuous process.

Recent progress in the development of high-performance multichannel detectors and their commercial availability led to the development of novel imaging techniques, namely to NIR cameras. The basic principles of NIR hyperspectral imaging have been described elsewhere [15]. The use of a NIR camera allows determination and visualization of the requested parameters over the complete width of the conveyor belt or web and continuously during proceeding production processes. In combination with chemometric methods based on the PLS regression algorithm, quantitative data of the required parameters and their spatial distribution can be obtained from the recorded hyperspectral data cube, i.e. the recorded 3D data set consisting of two spatial and one spectral dimensions. In-line detection of inhomogeneities or accidental changes of critical parameters of the product provides an opportunity for prompt intervention into the production process in order to correct such deviations as soon as possible. Eventually, this may lead to a constant or at least more homogeneous quality of the product. In this way, hyperspectral imaging can support an economical use of available resources, the avoidance of production waste as well as the saving of energy. Although this analytical method is still quite new, it has already been shown that NIR imaging techniques can be successfully used in many areas such as in food industry [16–19], textile finishing [20,21], polymer processing [22–25], forensic science [26] and pharmaceutics [27–29].

In this study, it will be demonstrated that NIR chemical imaging can be also used for in-line monitoring of coating processes. In particular, thickness and chemical conversion of thick white pigmented UV-cured coatings were analyzed in order to characterize the spatial distribution of these parameters across the surface. This does not only allow the control of the compliance of these parameters with the specified or intended target values, but enables also the detection of unexpected inhomogeneities occurring during the coating and curing process. In summary, it is the intention of this work to produce reference that NIR hyperspectral imaging is a highly powerful tool for process and quality control in the manufacturing of coatings for demanding applications.

2. Experimental

2.1. Materials and sample preparation

The varnish used in this study was based on a difunctional urethane acrylate (LR8987; BASF, Ludwigshafen, Germany) and 1,6-hexanediol diacrylate (HDDA) in proportion of 70 to 30 wt%. As photoinitiator, 1 wt% ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L, IGM Resins B.V., Waalwijk, The Netherlands) was used. Moreover, 10 wt% of white pigment titania (TiO_2; Kronos 2300, Kronos Titan GmbH, Leverkusen, Germany) was added to the formulation. Air bubbles resulting from stirring were removed by treatment in an ultrasonic bath for about 15 min.

This varnish formulation was applied to glass fiber reinforced plastic (GRP) plates based on an epoxy resin (Carbonscout/CG TEC GmbH, Germany; size 200 × 105 × 1 mm). Coatings with different thicknesses required for calibration to the layer thickness were achieved using an automatic film applicator (Simex, Haan, Germany) or an adjustable doctor blade (Elcometer Instruments GmbH, Germany). The layer thicknesses were measured after curing by a digital thickness gauge with a resolution of 0.2 μm (Heidenhain ND 221B, Dr. Johannes Heidenhain GmbH, Traunreut, Germany). Curing was done in a pilot plant equipped with a medium pressure mercury lamp (100 $W\,cm^{-1}$, Meyer GmbH, Ortenberg, Germany). Irradiation was carried out in nitrogen atmosphere. For the preparation of thicker layers ($>$ 100 μm), the varnish was applied in several successive layers. After application of each layer the samples were cured. This procedure was chosen in order to achieve better through cure of the varnish layers. It is well known that white pigments such as TiO_2 strongly scatter UV light and prevent in this way its penetration to deeper layers of the coating.

Samples for calibration to the conversion were made by application of the same white pigmented varnish to GRP plates. All coatings were prepared with the same wet film thickness (150 μm) resulting in a thickness of ~90 μm in the cured state. Different degrees of conversion of the various samples were realized by changing the conveyer speed from 2.5 to 30 $m\,min^{-1}$ and/or by variation of the power of the UV lamp from 30 $W\,cm^{-1}$ to 100 $W\,cm^{-1}$. The resulting irradiation doses were lying in the range from 80 to 1750 $mJ\,cm^{-2}$. In most cases, hyperspectral images of the samples were recorded immediately after irradiation (see below).

2.2. Determination of the acrylate conversion

For chemometric calibration, reference values for the thickness of the coatings and the conversion after irradiation are required. FTIR spectroscopy using attenuated total reflection (ATR) cannot be used for the determination of the conversion in rather thick layers since infrared light in the mid-infrared (MIR) range penetrates only a few microns from the ATR crystal into the varnish layer. Even if the varnish layers are removed from the GRP plates and measured at several points on both sides of the film (at the top and the bottom), the resulting values are representative for the surface regions only.

The penetration depth of NIR radiation into the layer is much higher than in case of mid-IR spectroscopy. Therefore, NIR spectra represent an average of the conversion gradient within the layer, that is, they are more representative for the complete profile of the coating. NIR reflection spectra of the varnish layers on the GRP plates were recorded with the hyperspectral camera (see below). For the determination of the acrylate conversion, about 200 NIR spectra collected at different points of the sample were averaged. Subsequently, the band at 1620 nm (first overtone of the C–H stretching vibration of the C=C double bonds) was integrated. The NIR band at 1620 nm undergoes changes under UV irradiation as a consequence of the acrylate conversion. Therefore, the acrylate conversion (x) was calculated from the ratio of the integrated areas of the peak at 1620 nm of the cured and wet coatings according to $x = (1 - A_{1620}^{cured}/A_{1620}^{wet}) \times 100\%$.