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In-line determination of the conversion in acrylate coatings after UV curing using near-infrared reflection spectroscopy

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Abstract

Near-infrared (NIR) reflection spectroscopy was used to determine the conversion of acrylic double bonds after UV photopolymerization. Quantitative analysis of the spectra was performed with chemometric methods using FTIR spectroscopy for calibration. Moreover, it was shown that the calibration of the PLS algorithm can also be performed directly to specific properties of the coatings such as their hardness which responds extremely sensitively even to small changes of the conversion. In-line monitoring of the conversion by NIR spectroscopy was carried out for acrylate coatings with a thickness of some micrometers applied to polymer foils and panels and for thick layers of UV-curable adhesives on the basis of acrylic hot-melts. The effect of changes of the irradiation dose, the emission spectrum of the UV source and other parameters on the conversion was studied.

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1. Introduction

UV curing has become an established technology which has found a broad range of commercial applications in coating technology, printing, adhesive processing etc. [1]. The functional and handling properties of UV-cured layers strongly depend on the conversion of the (meth)acrylic double bonds which is achieved during irradiation. On the other hand, the conversion is influenced by a large number of factors which only in part can be controlled. In order to avoid a deleterious effect of poor conversion on the properties of a coating, a

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continuous control of its extent would be necessary. In the past, various analytical methods such as ion mobility spectroscopy [2] and fluorescence emission [3,4] have been tested for this purpose but none of them was found to be suitable for in-line measurements under the conditions of technical production environments.

Near-infrared (NIR) spectroscopy is widely used for process control in the chemical industry and in other commercial applications [5–8]. In this paper it will be shown that NIR reflection spectroscopy also meets the specific needs of the monitoring of the conversion in thin (meth)acrylate coatings after photopolymerization reactions. It is based on the analysis of the first overtone of the CH stretching vibration of acrylic double bonds at 1620 nm [9]. This method provides the high time resolution and the sensitivity which are necessary for in-line measurements on layers with a thickness in the range of some micro-meters.

2. Experimental

2.1. NIR reflection spectroscopy

The NIR spectrometer (Kusta 4004 P; from LLA) is based on a holographic concave grating and an InGaAs photodiode array detector with extended wavelength range consisting of 256 elements. It is linked to a dedicated home-made probe head by an optical fiber. The probe head is equipped with an UV filter in order to prevent postpolymerization of the acrylate coatings by the short-wavelength part of the emission of the tungsten halogen lamp. A diffusor plate serves to suppress interferences which occur when thin transparent foils of optically high-grade polymers are used as substrate [10]. Reflection spectra are measured against a ceramic plate as reflectance standard. The spectrometer system is described in more detail elsewhere [11].

2.2. FTIR spectroscopy

FTIR transmission spectra were recorded on a Digilab FTS 6000 spectrometer. The acrylate conversion was determined from the band of the CH_2 scissor deformation at 1405 cm^{-1} [12].

2.3. Microhardness

The microhardness was determined with a Fischerscope H100C hardness tester according to the technical standard ISO 14577. A force of 5 mN was applied to the Vickers indentor.

3. Results and discussion

3.1. Multivariate calibration

Quantitative analysis in NIR spectroscopy is usually performed by using sophisticated chemometric evaluation methods such as PLS (partial least squares) regression [13]. At first, the use of chemometrics requires the setup of a calibration model in order to relate the spectral variation in the NIR spectra to the actual conversion in the coatings. Calibration was performed with layers of a clear acrylate formulation based on various multifunctional monomers which were drawn on a thin polyethylene (LDPE) foil and subsequently irradiated under nitrogen. In order to cover a wide range of conversions, the concentration of the photoinitiator (Lucirin TPO-L; BASF), the power of the UV lamp and the speed of the conveyor belt were varied. The conversion in the coatings was determined with FTIR spectroscopy as independent reference method. Moreover, NIR spectra were recorded in transreflectance.

On the basis of the resulting 51 data sets a calibration model was build up using the PLS algorithm. In Fig. 1 the conversion predicted with this calibration model from the NIR spectra of the calibration samples is plotted against the conversion from FTIR spectroscopy. Moreover, the data points of some test samples which did not belong to the calibration set are shown. The conversion in these coatings was also determined using the PLS model in order to validate its predictive capabilities. The results show a close correlation between NIR and FTIR data and prove the potential of the created model for in-line monitoring of the acrylate conversion.

Specific calibration is needed for each acrylate formulation. However, UV-cured coatings with a predetermined conversion are generally hardly to