MONITORING OF THE DEGREE OF CONDENSATION IN THIN ALKOXYSILOXANE LAYERS BY NIR REFLECTION SPECTROSCOPY

Tom Scherzer,* Gabriele Mirschel, Ulrike Helmstedt, Lutz Prager, Ulrich Decker

Leibniz Institute of Surface Modification, Chemical Department, Permoserstr. 15, D-04318 Leipzig, Germany

*Corresponding author: <u>tom.scherzer@iom-leipzig.de</u>

ABSTRACT

The degree of condensation in thin alkoxysilane layers was monitored by NIR reflection spectroscopy in combination with chemometric approaches. In particular, the state of the formation of the inorganic Si-O-Si network in layers from partially condensed 3-methacryloxypropyltrimethoxysilane (MEMO) batches was analyzed. Reference data were obtained by inverse gated ^{29}Si NMR spectroscopy. The relative amounts of the different T^i species (i.e. structures with different numbers of Si-O-Si units per Si atom) were used for the calibration of the PLS2 models. The alkoxy- silane batches were applied to a polyethylene naphthalate film with a thickness of about 2 g m^{-2} in a printing process. The relative amounts of the T^i species in the layers were predicted from their NIR spectra with a RMSEP being less than 3 %. Considering the error of the reference data (4 %), the overall error was 5 %. Moreover, the coating weight of the siloxane layers was determined with a similar method using a PLS1 calibration model and gravimetry as reference method (prediction error ~0.3 g m^{-2}). Both methods are potentially suitable for in-line process control during the deposition of such layers to polymer films.

KEYWORDS: Alkoxysilanes, Silica Coatings, Degree of Condensation, ^{29}Si NMR Spectroscopy, Coating Weight Introduction

INTRODUCTION

Inorganic-organic hybrid polymers are widely applied for high grade coatings, adhesives and planarization layers in various areas of applications. Common precursors are functionalized alkoxysilanes. Generally, the preparation of such networks proceeds via a combined hydrolysis/condensation reaction in a sol-gel process and consecutive curing, which adjusts the inorganic Si-O-Si network for optimal material properties. In this study, an alkoxysilane functionalized with methacrylate groups was used as precursor, which polymerizes in a UV-induced reaction leading to an organic subnetwork.

After application of the partially condensed alkoxysilanes, further condensation of the remaining silanol groups to Si- O-Si bonds occurs. Each Si atom in the MEMO precursor can form 0, 1, 2 or 3 Si-O-Si units (species termed as T^0, T^1, T^2 and T^3, see Scheme 1). The statistical distribution of T^i species is a measure for the current state of the condensation reaction and consequently an essential parameter required for control of the curing process. In this paper, we introduce a novel analytical method for monitoring the state of the formation of the inorganic network, which has the potential for in-line monitoring of technical deposition processes. ^{29}Si NMR spectroscopy is the only technique that is able to directly determine the concentration of the different T^i structures. However, it is obvious that this method is inapplicable for direct process control. Rather, there is a need for a cost-efficient and fast alternative. In this study, it was tested if NIR spectroscopy was suitable to predict the ratio of T^i species in thin siloxane layers.

Although NIR spectroscopy is primarily suited for the characterization of organic materials containing C-H, O-H, or N-H bonds, it was demonstrated in a preceding paper[1] that the thickness of silica layers can be measured with this method as well. The layers with a thickness in the submicrometer range had been prepared by photoinduced oxidative conversion of silazane precursors[2]. During deposition of such layers in a pilot-scale roll-to-roll process at web speeds up to 10 m min^{-1}, the thickness in the range of ~100 nm was monitored in-line with an error of about 20 %[3].

MATERIALS AND METHODS

The precursor 3-methacryloxypropyltrimethoxysilane (Dynasylan MEMO) was purchased from Evonik Industries (Hanau, Germany) and used as received. 22 siloxane batches with different degrees of condensation were prepared in a procedure described elsewhere[4]. They were analyzed by high-resolution ^{1}H NMR and ^{29}Si NMR spectroscopy using a Bruker Avance-600 II+ spectrometer. The percentages of the various T^i species that were required as reference values for the calibration of the NIR spectra were determined by signal integration[4].
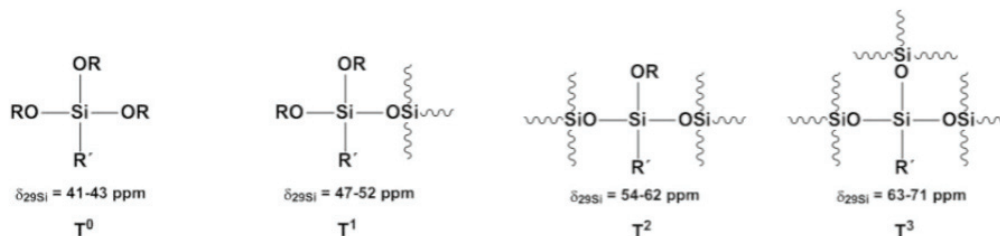
Scheme 1. T^i species with different numbers of Si−O−Si bonds per Si atom and the corresponding ^{29}Si chemical shift regions

Calibration samples were made by printing the different siloxane batches on a 100 µm polyethylene naphthalate (PEN) film using a laboratory-scale printing machine (Printability Tester; IGT Reprotest, Amsterdam, The Netherlands). Each batch was printed in quadruplicate. For UV curing, 3 wt% Irgacure 1173 (BASF, Ludwigshafen, Germany) was added as a photoinitiator. Layers intended for calibration of the NIR spectra to the degree of condensation were applied with a coating weight of (2.20 ± 0.05) g m^{-2}, whereas samples for calibration to the coating weight were prepared with a range from 2.5 to 5.5 g m^{-2}. All samples were irradiated under nitrogen in a UV curing unit equipped with a medium-pressure mercury lamp (100 W cm^{-1}, uv-technik meyer, Ortenberg, Germany). The coating weight was determined by gravimetry.

NIR spectra were recorded in reflection mode with a process analyzer system (uniSPEC2.2S; LLA Instruments, Berlin, Germany) consisting of a spectrometer unit and a separate probe head. The spectrometer is based on a holographic grating and a thermoelectrically cooled InGaAs photodiode array detector with 512 pixels covering a range from 1100 to 2220 nm. NIR spectra were taken in transflection mode using a ceramic reflector. A diffuser plate in front of the probe head suppressed interferences, which occur in optically high-grade films.

NIR spectra for calibration were recorded immediately after UV curing by taking a total of 1500 accumulations whilst the printed strip was moved through the probe beam in order to average the spectrum across the complete surface of the sample. For each sample, ten average spectra per sample were recorded. All calibrations were based on the PLS algorithm using the test set method for internal validation. Whereas the calibration models for the degree of condensation were based on the PLS2 algorithm, common PLS1 approaches were used for the prediction of the coating weight.

RESULTS AND DISCUSSION

Siloxane batches with quite different T^i ratios were prepared, which represent a broad range of intermediate states of the condensation reaction. Experimental details of each batch as well as the corresponding ratios of T^i derived from the NMR data are outlined elsewhere[4]. After printing and UV curing, NIR spectra of the layers were recorded.

For calibration, the spectra were split in equal parts into a calibration and a validation set. Both sets contained the spectra of two samples of each siloxane batch and therefore from the whole conversion range. The calculated PLS models were optimized by optional limitation of the spectral range as well as by application of various pre-processing methods such as normalization, baseline correction, linear tilt, derivatives, etc., which were used either individually or in combination. Internal validation of the models was carried out by the test set method. For each parameter T^i, the root mean square error of prediction (RMSEP), the standard error of prediction (SEP), the bias, and R^2 as a measure of the explained variance in the spectra were calculated separately. The model with the lowest RMSEP and the highest R^2 value was chosen for further analysis. The optimum model developed in this study was based on normalization of the spectra and application of the first derivative, and the spectral range was set to 1135 to 2217 nm. The calibration curves of this model are given in Fig. 1.

It is obvious that the data points are quite unevenly distributed over the range of relative T^i concentrations covered by the calibration model. In particular, the regions with moderate concentrations (i.e. between 10 and 35 to 45 %) are underrepresented for T^1 and T^3. However, this is due to the chemical complexity of the system and strong interdependencies between the various reactions, which proceed with different rate constants.

The developed PLS2 model was used to determine the degree of condensation in thin layers of independent samples. These samples were prepared separately and analyzed in a similar manner like the calibration samples. The contents of all T^i species were predicted simultaneously from the NIR spectra of the printed layers. The results are summarized in Fig. 2.
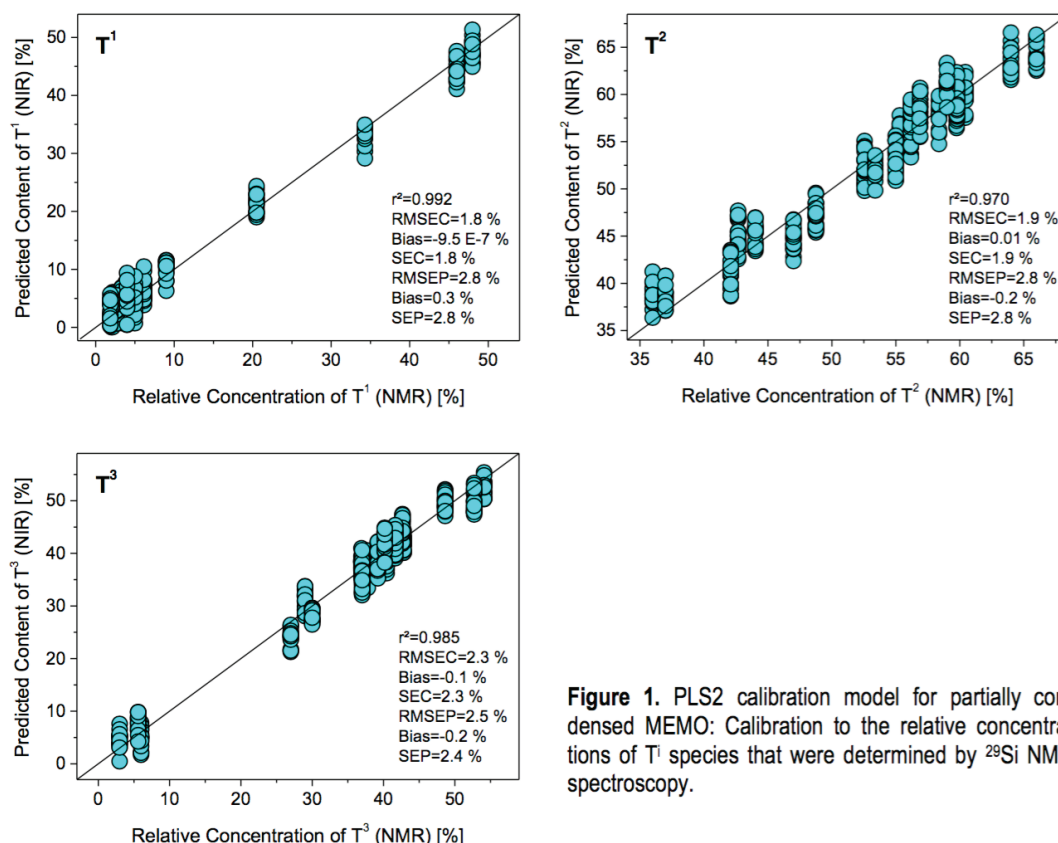

Figure 1. PLS2 calibration model for partially condensed MEMO: Calibration to the relative concentrations of T^i species that were determined by ^{29}Si NMR spectroscopy.

For each degree of condensation (i.e. for all T^i species), a close correlation between the values predicted from the NIR spectra and the reference data derived from ^{29}Si NMR measurements was found. The RMSEP errors resulting from the NIR data were determined to be 2.9 % for T^1 and T^2 and 2.5 % for T^3 (these errors refer to the percentages of the T^i species, i.e. they are not relative errors). However, for the determination of the total error of the measurements, the error of the reference data has to be considered. The measurement error of the values derived from ^{29}Si NMR spectra is 4 %, which results in an overall error of 5 %. These results clearly demonstrate that quantitative data on the progress of the condensation reaction in thin layers of siloxanes can be determined by NIR reflection spectroscopy after previous calibration of the method with NMR data.

In addition to the prediction of the state of the formation of the Si-O-Si network, the coating weight of the layers on PEN film was determined. NIR spectra of siloxane layers with different coating weights in the range from 2.5 to 5.5 g m^{-2} were recorded directly after UV curing. Reference data were determined by gravimetry. The spectral data were divided in a calibration and a validation set each of them containing the spectra of 16 samples. Several calibration models based on the PLS algorithm were built up by application of various spectral pre-treatments. Finally, application of the first derivative to the spectra was found to result in the model with the lowest RMSEP and SEP (both 0.23 g m^{-2}) and the highest R^2 (0.98).

The prediction capability of this model was tested with a series of independent samples. Their coating weight was predicted from the NIR spectra. RMSEP was found to be only about 0.3 g m^{-2} [4]. This error clearly reveals the high precision of the data that can be determined from NIR spectra in spite of the very low thickness and the largely inorganic character of the layers. Consequently, this spectroscopic approach cannot only be used for quantitative

determination of the degree of condensation, but it is also suited for the prediction of the coating weight of thin siloxane layers on polymer film.
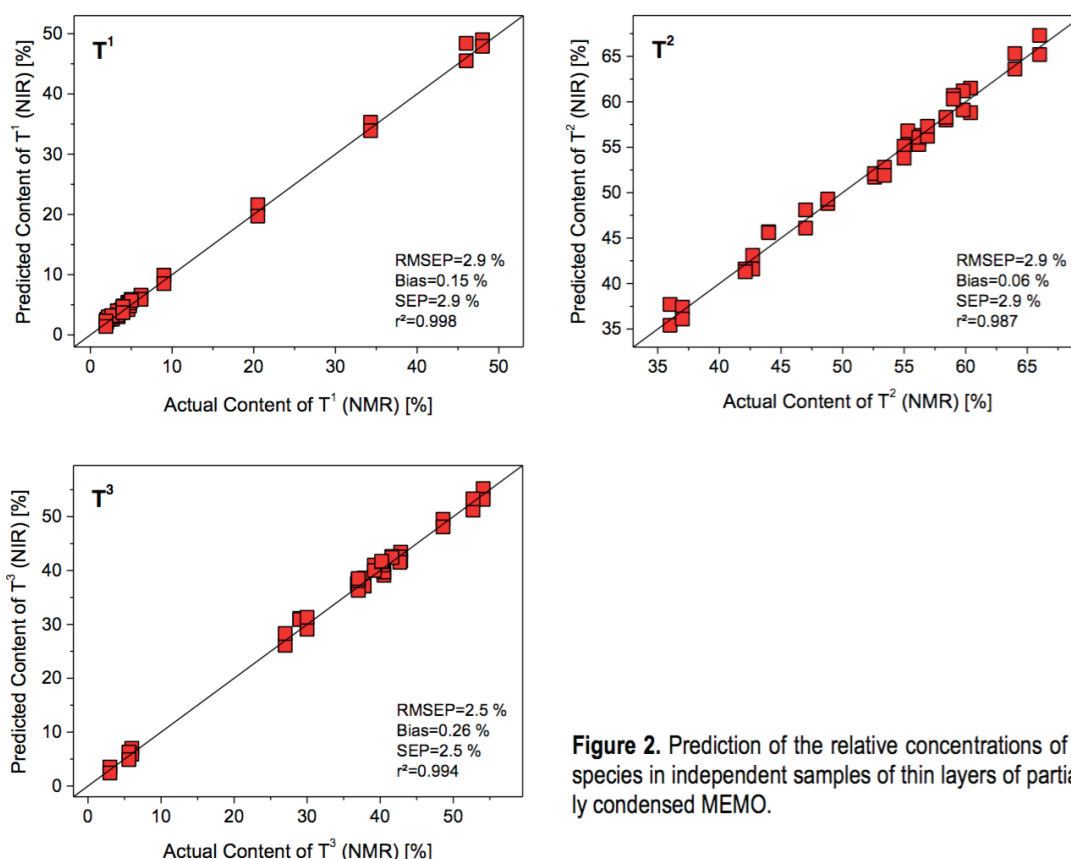

Figure 2. Prediction of the relative concentrations of T^i species in independent samples of thin layers of partially condensed MEMO.

CONCLUSION

NIR reflection spectroscopy was demonstrated to be suited for monitoring of material properties and other parameters of thin siloxane layers. The degree of condensation state of the developing Si-O-Si network (expressed in terms of the relative concentrations of the T^i species) in UV-cured alkoxysilane-based layers with a thickness of only about 2 g m^{-2} was predicted after calibration of the method with data obtained from inverse gated ^{29}Si NMR spectroscopy. The overall error comprising the measurements by both NIR and NMR spectroscopy was found to be 5 %. Moreover, the coating weight of siloxane layers was determined by a similar approach in the range from 2.5 to 5.5 g m^{-2} with a prediction error 0.3 g m^{-2}. Both methods are potentially applicable for in-line process control during the deposition and cure of such layers on polymer films.

Acknowledgments

References

1. Scherzer, T.; Mirschel, G.; Heymann, K.; Prager, L.; Buchmeiser, M. R. Appl. Spectrosc. 2009, 63, 239-245.
2. Prager, L.; Dierdorf, A.; Liebe, H.; Naumov, S.; Stojanović, S.; Heller, R.; Wennrich, L.; Buchmeiser, M. R. Chem. Eur. J. 2007, 13, 8522-8529.
3. Scherzer, T.; Mirschel, G.; Heymann, K.; Prager, L., in: Near Infrared Spectroscopy, ed. Saranwong, S., Kasem- sumran, S., Thanapase, W., Williams, P. IM Publications: Chichester, 2010, pp. 803-807.
4. Mirschel, G.; Helmstedt, U.; Scherzer, T.; Decker, U.; Prager, L. Ind. Eng. Chem. Res. 2014, 53, 16813-16819.