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Monitoring of the Sol-Gel Synthesis of Organic-inorganic Hybrids by FTIR Transmission, FTIR/ATR, NIR and Raman Spectroscopy

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Summary: The sol-gel synthesis of organic-inorganic hybrids based on triethoxysilane-terminated poly(ethylene oxide) and tetraethylorthosilicate was monitored in-situ using three spectroscopic methods (FTIR/ATR, Raman, NIR). These spectroscopic methods allow in-situ monitoring of the evolution of hybrid materials starting from the modification of the polymer and the early steps of hydrolysis up to the network formation. By application of ^{29}Si solid-state NMR spectroscopy the assignment and quantification of the Raman bands to different end groups and different cross-linking states was made. The sol-gel reaction was also followed by in-line NIR spectroscopy. A multivariate data analysis was accomplished to obtain a conversion-time curve. Furthermore, we investigated spin-coated films on wafers using FTIR transmission spectroscopy.

Keywords: in-line spectroscopy; In-situ monitoring; organic-inorganic hybrids; poly(ethylene oxide); sol-gel

Introduction

Organic-inorganic hybrids based on polymers and silicon alkoxides represent an important class of materials because they allow the chemical and mechanical resistance of silica to combine with the properties of the polymer (e.g., flexibility of polyethers,[1] biocompatibility and hydrophilicity of poly(ethylene oxide),[2] abrasion resistance of silicones[3] and transparency of poly(methylmethacrylates)[4]). Thus, sol-gel chemistry with polymers has been developed as an important tool used to create new materials, in particular, coatings with improved scratch, chemical, UV and flame resistance, and the inclusion of special functions such as antibacterial behaviour, high transparency and barrier properties.[5] Advantages of sol-gel reactions in polymers technology are the low cost of the chemical educts, their versatility, preparation under mild conditions, and cheap and well-known technologies for application.[6]

Factors affecting the resulting silica network and, hence, the resulting properties of the materials are the type of metal alkoxide used, pH, temperature, time of reaction, reagent concentrations, catalyst nature and concentration, water/ethoxysilane-group molar ratio, aging temperature and aging time. The number of influencing parameters is rather high and the reaction, thus, not easy to control. Therefore, the main aim of our investigation was to monitor sol-gel reactions between tetraethylorthosilicate (TEOS) and telechelic poly(ethylene glycol) (PEO) by simultaneously applying FTIR/ATR, NIR, and Raman spectroscopy, in-situ in the reaction flask to find a procedure to control the sol-gel reaction for reproducible results of the resulting material properties.

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FTIR and Raman spectroscopy are often used to describe sol-gel reactions and to characterize thin films of the hybrid materials on wafers. Some research groups investigated the relevant wavenumber range between 400 and 1300 cm^{-1}, where the Si–O–Si and Si–O–R/Si–OH bands are located. Detailed information about vibration modes, assignments, interpretation of the bands and band deconvolution for FTIR- and Raman spectra are available in ref. [7–17]. Vibrational spectroscopic in-line monitoring has been shown as a powerful tool to understand reactions.[18–20] This method has already been applied to hybrid material sol-gel preparations using a setup different from that of the present study, with the Raman probe outside the reaction flask.[21,22] Furthermore, ^{29}Si solid-state NMR spectroscopy was used to characterize our final hybrids and for the correlation of NMR and Raman spectra. Assignments and interpretation of the NMR signals were taken from ref. [23–26].

Experimental Part

Materials

Tetraethylorthosilicate (TEOS, Sigma Aldrich), (3-isocyanatopropyl)-triethoxysilane (ICPTES, Fluka), absolute ethanol (Fluka) and conc. HCl (VWR) were used as received. Poly(oxyethylene), (poly(ethylene glycol), PEG, from Sigma Aldrich) with a molar mass of 1000 g/mol was dried in vacuum at 50 °C for 8 hours prior to use.

Synthesis

The PEO/silica hybrids were synthesized in a two-step synthesis as reported by Leonelli et al.[27] and Messori et al.[28]

In the first step, the reaction of the two OH-end groups of PEG 1000 (30 g; 0.03 mol) with

ICPTES (14.8 g; 0.06 mol) to triethoxysilane-terminated PEO (PEO-Si) (see **1**) was carried out at 120 °C in a three-necked flask equipped with ATR/FTIR silicon probe, condenser with CaCl2 trap, thermometer and magnetic stirrer under nitrogen and monitored by in-situ ATR-IR spectroscopy. An ATR/IR spectrum was taken every two minutes to observe the end of the reaction.

$$2\ O{=}C{=}N\text{-}(CH_2)_3\text{-}Si(OC_2H_5)_3 \ + \ HO\text{-}(CH_2CH_2O)_n\text{-}H$$

$$\longrightarrow (C_2H_5O)_3\text{-}Si\text{-}(CH_2)_3NH\text{-}CO\text{-}O\text{-}(CH_2CH_2O)_n\text{-}CO\text{-}NH(CH_2)_3\text{-}Si(OC_2H_5)_3$$

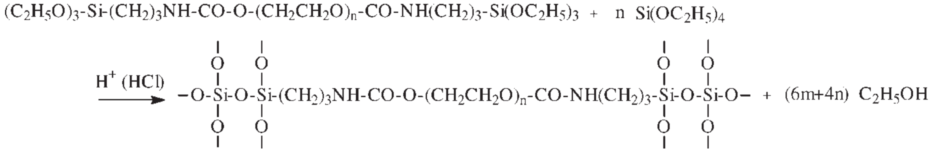
In the second step, the sol-gel synthesis of the triethoxysilane-modified PEO-Si obtained in step **1** with TEOS to a polymeric organic-inorganic hybrid (monomer ratio focused on a final polymer/SiO_2 ratio of 70/30 wt/wt) (see **2**) was performed and monitored. The reaction of PEO-Si (10.4 g; 0.006 mol) with TEOS (13.4 g; 0.064 mol) was carried out in ethanol with different solvent concentrations, the

Table 1.
Experimental conditions of the sol-gel reactions performed.

No.	$m_{(PEO\text{-}Si + TEOS)}/m_{EtOH}$	T	t_{gel} 1)	SiO_2 content of dried hybrid
	(g/g)	(°C)	(min)	(wt%)
1 (TEOS only)	1.0	70	100	93.9
2 (PEO-Si only)	1.0	70	–	10.2
3	1.0	70	106	
4-1	no ethanol	20	15	36.6
4-2	3.0	20	13	17.9
4-3	1.0	20	960	38.4
5-1	1.0	30	300	
5-2	0.7	30	480	
5-3	0.34	30	–	
6	1.0	40	120	36.4

1) time after which a gel formation was visibly observed.

stoichiometrically necessary amount of water (1 mol water/mol ethoxy) and HCl as catalyst (water/HCl molar ratio of 1/0.1 mol/mol) in a four-necked flask equipped with NIR, Raman and FTIR/ATR diamond probe, condenser with CaCl2 trap, thermometer and magnetic stirrer at different temperature (between 20 and 70 °C). FTIR/ATR and NIR spectra were taken every two minutes and Raman spectra were taken every four minutes. The performed experiments are summarized in Table 1.



$$(C_2H_5O)_3\text{-Si-}(CH_2)_3NH\text{-CO-O-}(CH_2CH_2O)_n\text{-CO-NH}(CH_2)_3\text{-Si}(OC_2H_5)_3 + n\ Si(OC_2H_5)_4$$

$$\xrightarrow{H^+ (HCl)} -O\text{-}\overset{|}{\underset{|}{\overset{O}{\underset{O}{\text{Si}}}}}\text{-O-}\overset{|}{\underset{|}{\overset{O}{\underset{O}{\text{Si}}}}}\text{-}(CH_2)_3NH\text{-CO-O-}(CH_2CH_2O)_n\text{-CO-NH}(CH_2)_3\text{-}\overset{|}{\underset{|}{\overset{O}{\underset{O}{\text{Si}}}}}\text{-O-}\overset{|}{\underset{|}{\overset{O}{\underset{O}{\text{Si}}}}}\text{-O}- + (6m+4n)\ C_2H_5OH$$

Ethanol was removed after the sol-gel reaction by distillation. The SiO_2 content of sample 4-2 is low because more ethanol was used than in the other samples and so Si as $Si(OH)_4$ was lost through evaporation during distillation. The resulting products were further dried for four days at 80 °C in a vacuum oven. The inorganic contents of the dried hybrids were determined gravimetrically by microwave treatment at 550 °C for 40 min.

Spectroscopic Techniques

The FTIR/ATR spectrometer ReactIR 4000 (Mettler Toledo), wavelength range between 4000 and 650 cm^{-1} (resolution 4 cm^{-1}, 100 scans per spectrum), equipped with silicon or diamond ATR probes, gold coated moveable tubes as lightpipe and MCT detector was used. The ATR crystal material was silicon in step 1 and diamond in step 2.

The Raman measurements were done with the Raman spectrometer HoloProbe785 (Kaiser Optical) which works in the range between 3500 and 150 cm^{-1} (resolution 4 cm^{-1}, 80 scans per spectrum). The Raman spectrometer is equipped with a 400 mW diode laser with an excitation frequency at 785 nm, a holographic notch filter and a CCD detector array and connected by optical fibers to a high temperature Raman probe.

NIR monitoring was performed by a diode array process spectrometer SentroProc (Sentronic) which works in the range from 10000 to 6000 cm^{-1} (resolution 4 nm, 1000 scans per spectrum) and a NIR transflectance probe (Solvias) connected by optical fibers to the spectrometer. Chemometric calculations were performed with the program GRAMS/AI/PLSplus/IQ (ThermoGalactic). Fitting of the conversion-time curve was done by polynominal 4-parameter fit using the software Origin 8.1.

All three optical probes dipped directly into the solution in the reaction flask.

FTIR transmission spectra were recorded with the spectrometer IFS66v (Bruker) under vacuum, equipped with a MCT detector, in the wavelength region from 600 to 4000 cm^{-1} (resolution 4 cm^{-1}, 200 scans per spectrum).

^{29}Si solid-state NMR of the dried organic-inorganic hybrids were acquired on a Bruker Avance 500 NMR spectrometer operating at a Larmor frequency of 99 MHz for ^{29}Si using a Bruker BL4 MAS probehead accepting 4 mm o.d. rotors with a sample spinning frequency of 10 kHz. Single pulse spectra have been acquired under continous-wave proton decoupling with an excitation pulse duration of 5 μs and a recycle delay of 20 s.

Thin Films

The sol obtained in experiment 5-3 was spin-coated after 3 and 7 hours reaction time on pre-cleaned silicon wafers using a Headway spin-coater (USA) at 2000 rpm for 90 seconds, resulting in film thicknesses of 300 nm and 780 nm, respectively, measured by ellipsometry. We used a

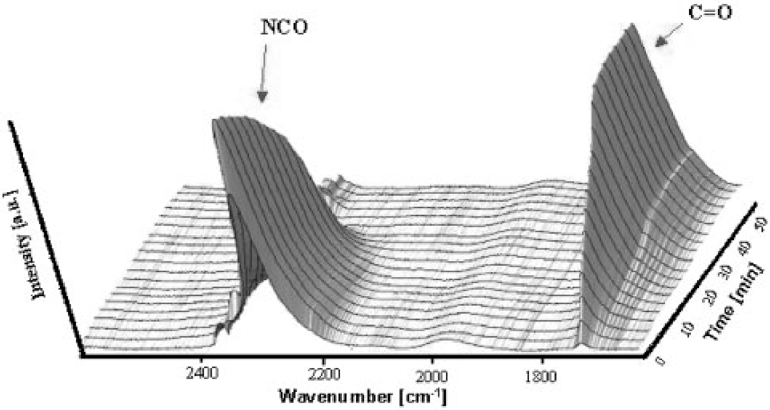


Figure 1.
In-line FTIR/ATR spectra (N=C=O/C=O region) of the reaction of PEO with (3-isocyanatopropyl)-triethoxysilane.

rotating analyzer type variable angle multi-wavelength ellipsometer M-44, for details see ref.[29]

Results and Discussion

The synthetic route to obtain the hybrid materials was carried out in two steps as already outlined. In the first step the polymer-analogous reaction of PEG with (3-isocyanatopropyl)-triethoxysilane leads to the functionalization of the polymer chains with two triethoxysilane groups. Thus, the polymer can participate in the following sol-gel process and will be incorporated into the inorganic network, finally forming the organic-inorganic hybrid. The reaction carried out in melt at 120 °C was followed by FTIR/ATR spectroscopy. Figure 1 shows the intensity changes of the isocyanate and the carbonyl bands.

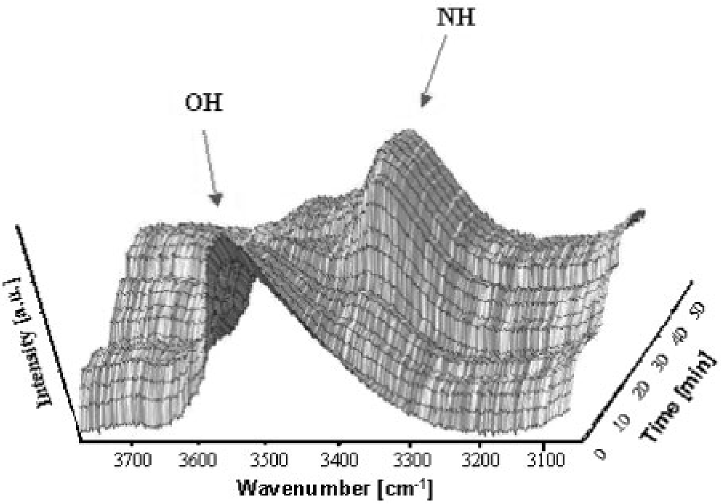


Figure 2.
In-line FTIR/ATR spectra (N–H/O–H region).of the reaction of PEO with (3-isocyanatopropyl)-triethoxysilane.

The intensity of the isocyanate band at 2270 cm^{-1} gradually reduces during the reaction, while the intensity of the urethane linkage formed at 1700 cm^{-1} increases. At the end of the reaction, the isocyanate band has completely vanished while the intensity of the modified polymer band has remained constant. The reaction was completed after 60 minutes at 120 °C. We could quantify the reaction and determine the conversion rate (not given here).

Figure 2 shows the shift of the maximum of the broad signal between 3200 and 3600 cm^{-1}. The intensity of the OH band of PEO is reduced with time while the NH band of the urethane group of the modified polymer are formed. Raman and NIR spectroscopy were not so suitable for the reaction of step1 like the ATR technique.

The triethoxysilane-terminated PEO (PEO-Si) obtained above (as shown in Figure 1 and 2) was used in the acid-catalyzed sol-gel reaction with TEOS in ethanol as solvent in second step. This reaction was carried out at different temperatures and ethanol concentrations at constant polymer/TEOS ratio, as outlined in Table 1. A molar ratio of ethoxysilane groups (TEOS + PEO-Si)/H2O of 1:1 was maintained. In all experiments, except 2 and 5-3, the gelation of the sol was observed (visible gelation point). After addition of TEOS, HCl and H_2O to the ethanol solution of PEO-Si the complete hydrolysis of TEOS and PEO-Si could be determined after 10 to 20 minutes. Figure 3 contains the Raman spectra of PEO-Si in ethanol, the reaction mixture after the addition of TEOS, water and HCl (hydrolysis), the spectrum after visible gelation in ethanol and the dried hybrid material. The spectrum after the addition of TEOS, water and HCl shows the disappearance of the TEOS bands at 930 cm^{-1} and 1291 cm^{-1} indicating the hydrolysis of TEOS. The visible gel in ethanol does not show the Si–O–Si cross-linking bands. Therefore, only a physically cross-linked state of the gel in ethanol at this reaction time can be assumed.

After removal of the solvent through distillation and annealing, these cross-linking bands can be observed by formation of the –Si–O–Si– bands at 840 and 1140 cm^{-1} and the internal Si–OH at 960 cm^{-1}. There is some controversy concerning the assignments of these bands in the literature. However, for our investigations, it is only important that we be able to differentiate the bands relevant for cross-linking or no cross-linking. It has to be stated that in the in-line measurements in

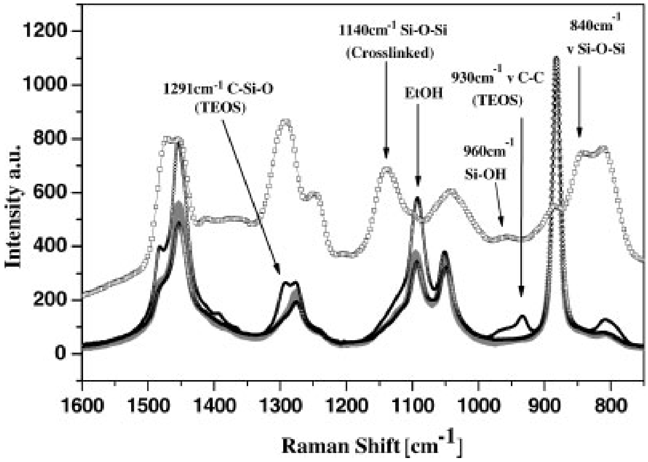
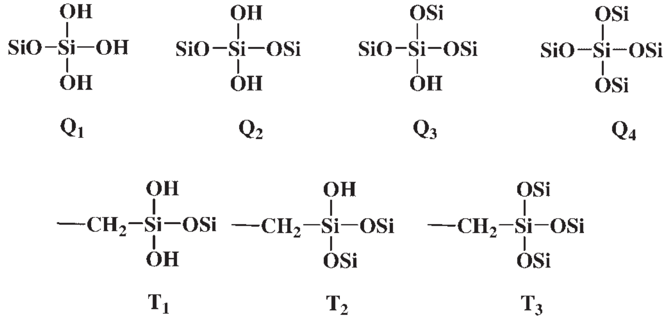


Figure 3.

Raman spectra in the range from 800 to 1600 cm^{-1} of the reaction mixture of experiment **4-3** (–: PEO-Si + EtOH; ,: PEO-Si + EtOH + TEOS; 8: ethanol-containing gel (after 960 min reaction time); #: dried hybrid 4-3.



Scheme 1.
Types of Si atoms possibly contained in a PEO/SiO_2 network according to ref. [26].

ethanol solution under the conditions used in our study only the hydrolysis of TEOS can be observed spectroscopically.

The different times of visible gelation (physical network formation) are given in Table 1. They increase with decreasing concentration and reaction temperature, as expected.

We monitored the sol-gel reaction of PEO-Si with TEOS simultaneously with FTIR/ATR, NIR and Raman spectroscopy. The ATR-IR spectra, not given here, also show these cross-linking bands, so both applied spectroscopic methods demonstrate network formation by emerging of Si–O–Si bands.

Raman spectroscopy can also distinguish between different network formations and different end group modes in the range from 300 to 700 cm^{-1}. Here we can correlate Raman spectra with ^{29}Si solid-state NMR spectra of the dried samples. The types of Si atoms which can be expected according to reference[30,31] are given in Scheme 1. Q groups represent Si–O–Si linkages while T groups reflect covalent –C–Si–O– bonds. Figure 4 illustrates the ^{29}Si solid-state NMR spectrum of the dried PEO/SiO_2 hybrid sample 4-3.

The ^{29}Si-NMR spectrum of the final hybrid is dominated by Q_3 and Q_4 groups at −101 ppm and −110 ppm, respectively. The

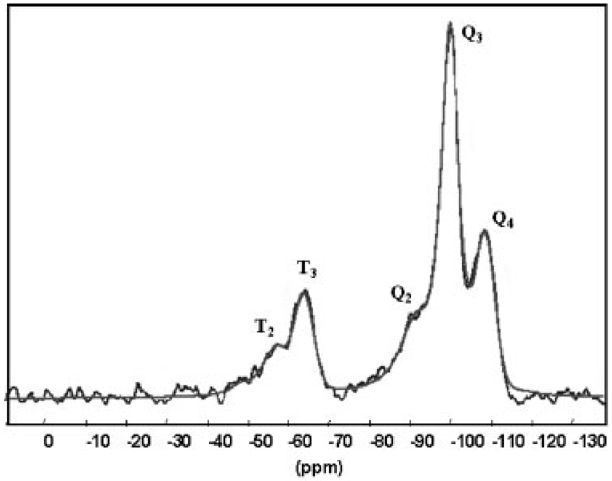


Figure 4.
^{29}Si solid-state NMR spectrum (direct polarization) of dried sample 4-3.

Table 2.

Quantitative analysis of T- and Q-groups in the organic-inorganicPEO/SiO_2 hybrids (after drying) as obtained from the ^{29}Si direct polarization spectra area. Intergration results were estimated from peaks derived via deconvolution using a Gaussian-Lorenzian model using DMFit.[32]

Sample	T_1	T_2	T_3	Q_2	Q_3	Q_4
	mol%	mol%	mol%	mol%	mol%	mol%
1 (TEOS only)	–	–	–	0	76	24
2 (PEO-Si only)	3	41	56	–	–	–
3	4	9	14	11	52	10
4-1	1	2	10	10	57	20
4-2	1	10	14	5	61	9
4-3	–	10	10	8	53	19
5-1	–	7	12	3	45	33
5-2	–	7	12	7	53	21
6	–	9	16	5	44	26

signal around -60 ppm originates from T_2 groups and that at -70 ppm from T_3 groups, respectively. Table 2 contains the calculated amounts of the groups after quantitative analysis.

The NMR spectra show the expected result that PEO-Si alone (**2**) cannot form Q-groups, while TEOS alone forms exclusively Q_3 and Q_4 groups. Mixtures of PEO-Si and TEOS give different ratios of T- and Q-groups, depending on the reaction conditions.

Figure 5 shows the Raman spectra of the dried hybrid (sample 4-3).

We could identify the following T and Q groups in the Raman spectra: Q_4 at 417 cm^{-1}, Q_3 at 488 cm^{-1},T_3 at 503 cm^{-1} T_2 at 532 cm^{-1}. The intensity ratio between Q and T bands in the Raman spectra is nearly the same as the ratios found by solid state NMR in Table 2.

The sol-gel process was also monitored in-situ using NIR spectroscopy. The NIR spectra of the reaction are illustrated in Figure 6.

The NIR spectra over reaction time show only small differences, mainly in intensities and in a shift of the baseline.

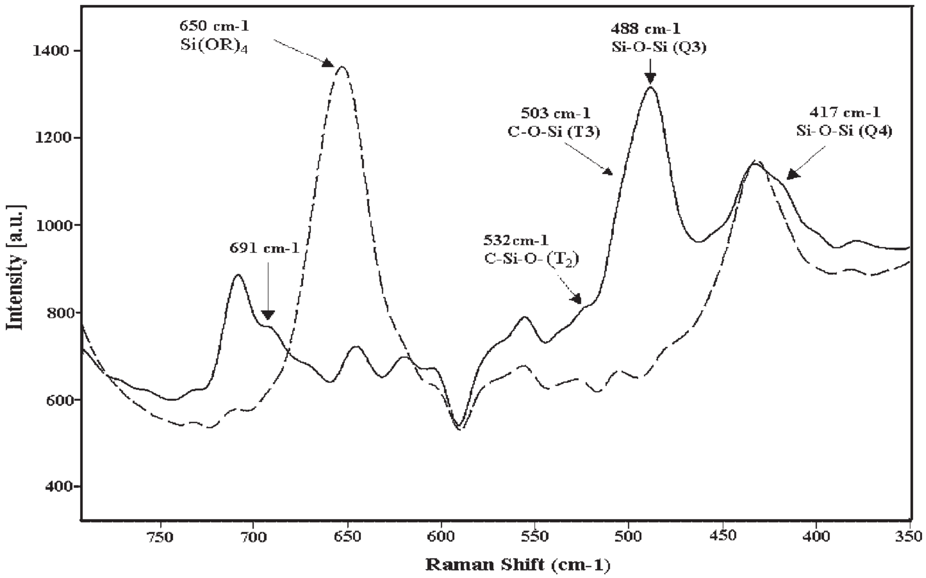


Figure 5.

Types of T and Q groups found in the Raman spectrum of the dried PEO/SiO2 hybrid (sample 4-3).

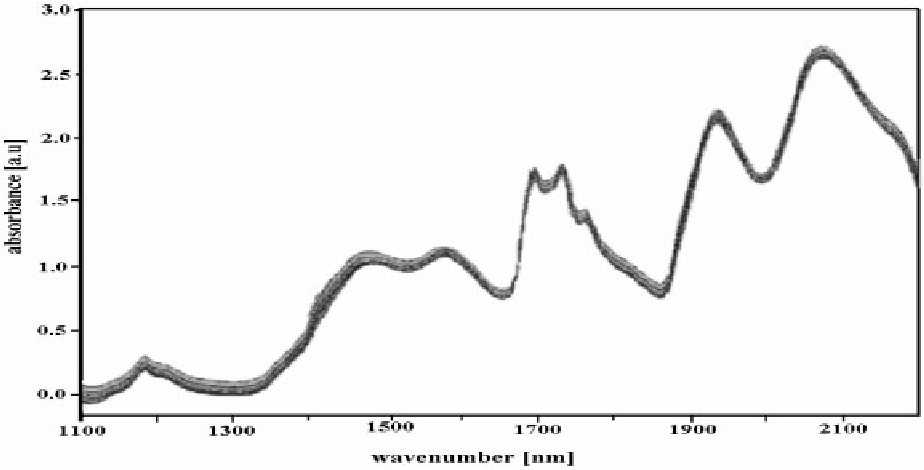


Figure 6.
In-line NIR spectra of the sol-gel reaction of PEO-Si/TEOS (sample 4-3).

A multivariate data analysis (chemometrics) is thus needed to extract the chemical information.

The partial least square regression method (PLS) was applied. The prediction model from the PLS method using two principle components allowed to track the conversion-time curve of the reaction by correlation of the complete spectra with the monitored time (t = 0 min; conversion = 0%, to t = 390 min; conversion = 100%) as regression parameter. We calculated the conversion curve until the visible gelation point, defining that the conversion at the end of the measurement is 100%. This value contains the changes in the spectra during the monitored time, and does not represent 100% cross-linking. Figure 7 displays the calculated and fitted conversion (time) curves expressing the reaction time in percent. The figure shows a typical conversion-time curve for a polycondensation reaction[33] which was expected from the chemistry of the system.

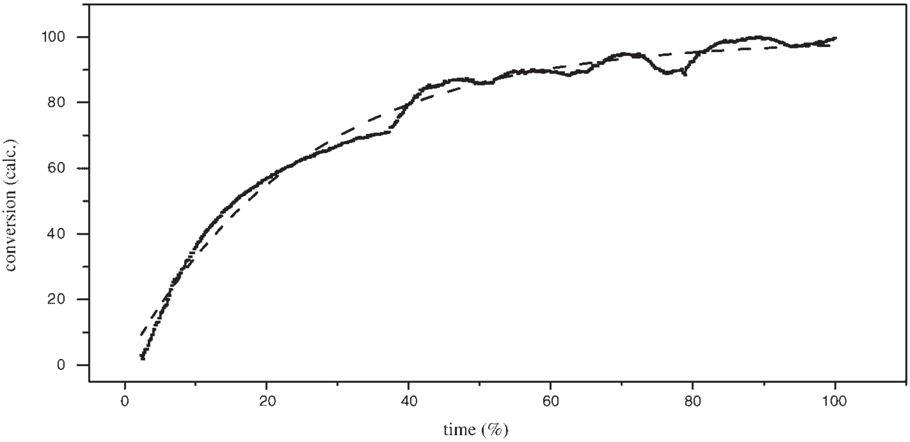


Figure 7.
Predicted and fitted conversion curve of the sol-gel reaction of PEO-Si/TEOS (sample 4-3) by PLS using NIR spectra (- calculated, --- fitted).

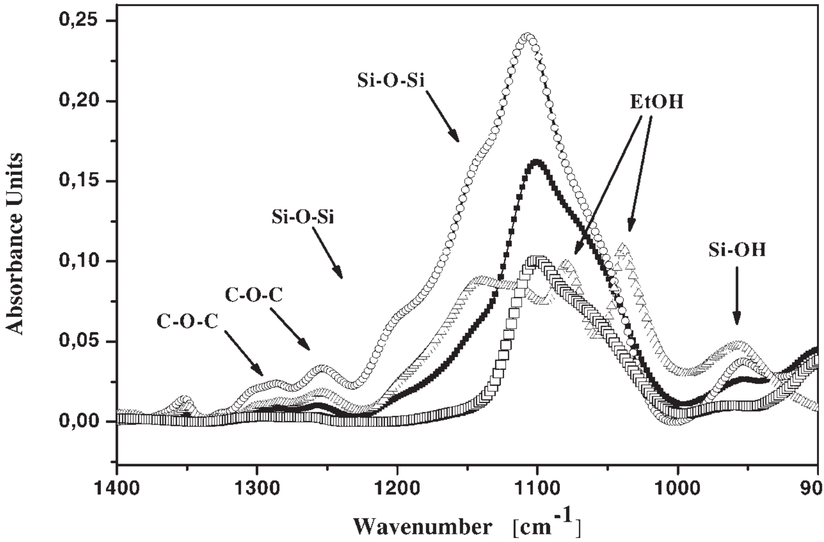


Figure 8.

FTIR-Transmission spectra of sample 5-3 (—300 nm film of the cross-linked hybrid on silicon wafer; 780 nm film of the cross-linked hybrid on silicon wafer; 8 ethanol-containing gel (partially cross-linked) 8: Reference wafer).

Besides in-line monitoring within the reaction vessel, the hybrid material as thin films were investigated. Thin films were prepared using the sol of sample 5-3 for spin-coating on Si-wafers after 3 and 7 hours reaction time (film thickness 300 and 780 nm, respectively). The samples were measured by FTIR in transmission technique. The spectra displayed in Figure 8 show the reference wafer, a partially cross-linked hybrid with solvent and two cross-linked hybrid films. One can clearly identify the –Si–O–Si–O– networking modes at 1140 and 1200 cm^{-1}, which are described in the references.[7–17] The detection of cross-linking bands in the thin films provides the opportunity to follow the cross-linking process in coatings.

Conclusions

Spectroscopic methods (ATR/IR, NIR, Raman) were used for the monitoring of the two-step sol-gel synthesis of organic-inorganic hybrid materials based on triethoxysilane-terminated poly(ethylene oxide) and tetraethylorthosilicate in ethanol catalyzed by HCl.

These spectroscopic methods allowed in-situ monitoring of the evolution of hybrid materials starting from the modification of the polymer (FTIR/ATR) and from the early steps of hydrolysis up to the physical network formation (NIR, Raman). A comparison with ^{29}Si solid-state NMR spectroscopic data allows an assignment and a quantification of the Raman bands to different end groups and to different cross-linking states. Additionally, we could also monitor the sol-gel reaction by in-line NIR spectroscopy until the visible gelation point. A conversion-time curve by multivariate analysis (PLS) was calculated. Thus, in-line NIR spectra can be a powerful and easy-to-handle method of following the reaction up to the visible gelation point. However, both Raman and NIR spectroscopy, need continued research to find the opportunities and limits for routine application as monitoring methods.

Furthermore, we could show with the investigation of spin-coated films on wafers by FTIR transmission spectroscopy that the cross-linking process in coatings can be investigated.

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