
A high-throughput screening method for the exploration of optimal curing parameters and resistance to solvents of NANOMER[®] coating materials

Gerd Schäfer · Helmut K. Schmidt

Abstract A high-throughput screening method for the exploration of optimal curing parameters and resistance to solvents of NANOMER[®] coating materials based on the temperature-dependent swellability was developed. The screening method was first tested using a model sol made of pre-hydrolyzed (3-glycidoxypropyl)triethoxysilane (GPTES), tetraethoxysilane (TEOS), (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (FTS) and zirconium complex (prepared of zirconium-*tert*-butoxide complexed with acetylacetonate) charged with reactive diluent trimethylolpropan-triglycidether and defined amounts of fluorescein and cured at different temperatures. Afterwards, fluorescein was extracted with sodium hydroxide solution and the optical density of the supernatant of all samples was measured at 490 nm which is sensitive to the dye concentration. The optical density (OD) correlates with the degree of curing. According to this screening a temperature $\geq 140^\circ\text{C}$ is necessary for proper curing. The time dependence of extraction reveals information on resistance against sodium hydroxide solution, i. e. alkali resistance. The time dependent extraction of fluorescein at 60°C of coatings cured at 100 and 140°C , respectively, shows a better resistance against 0.1 M sodium hydroxide solution for the one cured at 140°C , especially in the time range $10\text{--}60\text{ min}$. The whole process — sol preparation, mixing of sols with dye, extraction, and optical spectroscopy—can be performed automatically. Further testes were made to proof the usability of this process. 96 hybrid materials were screened in regard to their alkali

resistance and finally, a total number of 14 clear organic-inorganic hybrid coating systems with improved stability against sodium hydroxide solution were derived from this study.

Keywords High-throughput screening · Curing temperature · Alkaline resistance

Introduction

The usability of high-throughput methods for the exploration and optimization of new materials was demonstrated in several fields of material science [1, 2]. After the pioneering work on phosphors and oxo-cuprate high T_C superconductors [3, 4] the emphasis shifted to research and development of heterogeneous catalysts where a high state of development both in preparation and screening of catalytic properties was reached up to date [5, 6]. During the last years progress in development of coating materials and screening methods for some of their important properties was mainly stimulated by industry researchers. Potyrailo et al. demonstrated the usability of a “combinatorial factory” for the exploration of scratch resistant coating materials which includes preparation, fast screening of curing parameters and abrasion testing [7, 8].

A recently reported high-throughput screening method for optimization of curing parameters based on the temperature and time dependent swellability of organic clear coatings [9, 10] was adapted in this contribution for exploration of organic-inorganic hybrid coating materials with an easy-to-clean (ETC) effect [11] as a versatile tool for both optimization of curing conditions and improvement of alkaline resistance.

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Experimental section

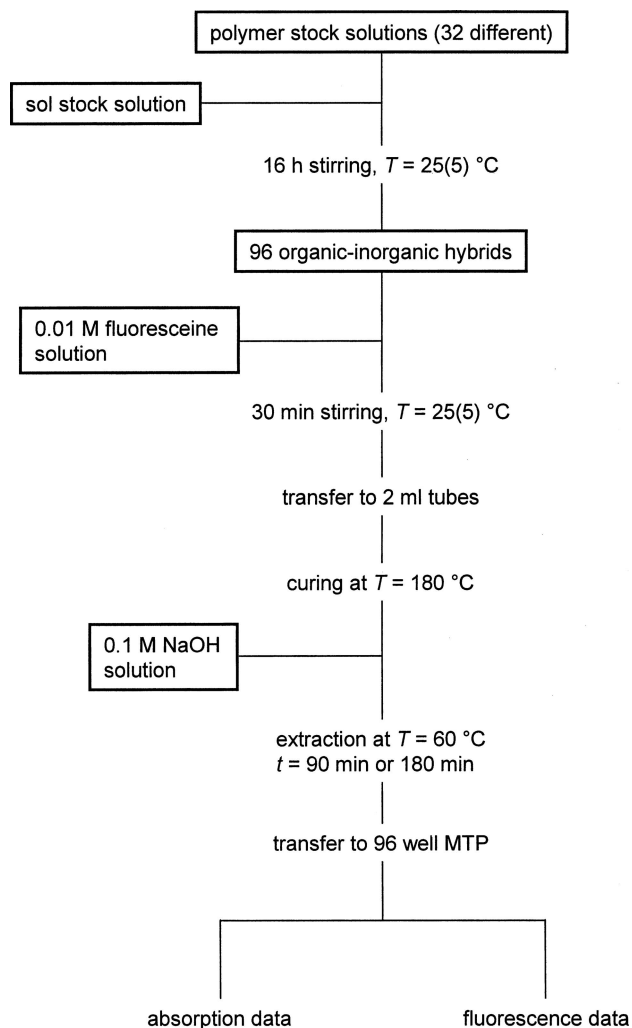
Evaluation of the screening method

A Zirconium complex was prepared by mixing 1-butanol, zirconium-tert-butoxid and acetylacetonate in the molar ratio (21:1.8:1). Afterwards, for model sol preparation TEOS, GPTES, hydrochloric acid, zirconium complex, FTS and trimethylolpropan-triglycidether (2,2'-(2-ethyl-2-((oxiran-2-ylmethoxy)methyl)propane-1,3-diyl)bis(oxy)bis(methylene) dioxirane, Polypox R20 were mixed in the weight ratio 4.2:1.9:1.5:6.7:1.0:4.6. In detail, TEOS and GPTES were mixed with hydrochloric acid (0.5 N, $R_{OR} = 0.9$) (4.2:1.9:1.5). After clearance 6.7 parts of the zirconium complex were added. Finally, 1.0 part FTS and 4.6 parts of the reactive diluent Polypox R20 (UPPC, Germany) were mixed into the sol and stirred for 16 hours. The investigation of optimal curing parameters for the model sol was carried out with the following procedure: 500 μl of a 0.01 M fluorescein in ethanol solution were added to 2 ml sol, the sol-dye mixtures stirred for 10 min, and 30 μl delivered into 2 ml glass tubes and cured for one hour at a desired temperature in the range 40–180°C. 350 μl 0.1 M aqueous sodium hydroxide solution (pH = 12.98(1)) were injected onto the dye doped coating on the bottom of the 2 ml vial and left for one hour at room temperature. Afterwards, 150 μl of the sodium hydroxide solution were transferred to a 96-well Multi-Titer Plate (MTP) and the amount of extracted fluorescein was determined by measuring the optical density OD at 490 nm with a microplate UV-Vis reader (Molecular Devices Spectramax 190). The time-dependent extraction behavior was tested in a similar way as described above. The major difference is an increased extraction temperature of 60°C and samples were taken for spectroscopic measurements in the time interval 10–180 min. The delivery of liquids was carried out with a Tecan Genesis RSP 150 automated liquid handling system.

Screening of the alkaline resistance properties of 96 organic-inorganic hybrid materials

A pre-hydrolyzed mixture of TEOS, GPTES, FTS and Zirconium complex (see above) was added with stirring to each polymer/reactive diluent solution in 10 ml glass test tubes placed in an H+P 48-reaction-chamber reaction block. The reaction block was embedded in an automated liquid handling system. Three different volume-ratio mixtures sol / polymer solution were screened for each polymer/reactive diluent solution (76, 91, and 97 vol.% polymer solution). This mixtures were stirred for 16 h at room temperature, mixed with 0.01 M fluorescein in ethanol solution at a fixed

ratio calculated on base of the solid content in the sol and in the fluorescein solution and then 40–98 μl were transferred to 2 ml glass vials. After curing (1 h at 180°C, heating/cooling rate: 1.25°C/min) 350 μl of 0.1 M aqueous sodium hydroxide solution was added to each vial and fluorescein was extracted for 90 and 180 min at 60°C. A comparative spectroscopic investigation using absorption (microplate reader, see above) and fluorescence measurements (Tecan Spectra Fluor microplate reader, $\lambda_{\text{ex}} = 485 \text{ nm}$, $\lambda_{\text{em}} = 535 \text{ nm}$, 30 flashes per well, top reading mode) was carried out. The whole automated process described here is summarized in Scheme 1.



Scheme 1 Flow chart of the high-throughput screening of alkali resistance of organic-inorganic hybrid sols with an ETC effect

The selection of organic moieties used for the screening was mainly guided by the presence of functional groups suitable to react with functional groups of the pre-hydrolyzed TEOS, GPTES, FTS and Zirconium complex mixture, i.e. leading to covalently linked inorganic-organic networks in the final coatings.

Results and discussion

The intrinsic properties of silica based nanocomposite coating materials can cause problems in applications where a high resistance against alkaline solvents is required. One well known strategy to overcome this problem leads to the incorporation of organic epoxy-functionalized moieties. The aim of the study presented here was the improvement of resistance to alkaline solvents of nanocomposite coating materials with an ETC-effect using a new, rational preparation and testing method.

The results are presented in two parts: first, a high-throughput method for preparation, curing, and testing of alkaline durability was applied to a model sol containing an organic epoxy-functionalized moiety, e.g. Polylox R20. Second, the high-throughput method was applied for preparation and screening of 96 different sols which lead to new materials with an improved stability against sodium hydroxide solution.

Evaluation of the high-throughput screening method for model sol (GPTES, TEOS, FTS, Zirconium complex, and Polylox R20)

The results of the curing conditions screening are presented in Fig. 1. The optimal temperature for a proper curing is $\geq 140^\circ\text{C}$ with a measured optical density (OD) of 0.13 at 140°C and a decrease to 0.06 at 180°C . Higher curing temperatures are not suitable, because of a degradation of Polylox R20. The time-dependent extraction experiment of coatings cured for one hour at 100 and 140°C , respectively, are presented in Fig. 2 and support the results from Fig. 1, i.e. a sufficient curing is not achieved at 100°C . OD values from coatings cured at 140°C are smaller in the whole time scale and significant below the OD values of coatings cured at 100°C in the time range 10–60 min. The maximum extractable amount of fluorescein in this experiment corresponds to the OD value of 2.55 which is almost reached for both samples after 180 min of extraction at 60°C .

Within the method evaluation stage and for reproducibility check same volumes of each sample were dispensed into three different, neighbored cavities of a 96-well MTP. After plate measurement the estimated standard deviations (esd's) confirm a sufficient accuracy of both precise sample delivery by the automated liquid handling system and spectroscopic measurement.

Preparation and screening of 96 organic-inorganic hybrid materials for their alkali resistance

A complete workflow including sample preparation, doping with fluorescein solution, curing, extraction and spectroscopy was established with the aim of maximal

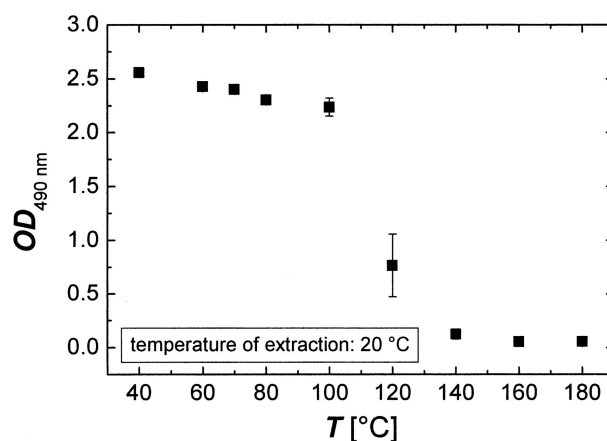


Fig. 1 Optical density OD at 490 nm vs. curing temperature of the screening method test run with a hybrid sol consisting of pre-hydrolyzed GPTES/TEOS/FTS/Zirconium complex and 30 wt.% reactive diluent Polylox R20

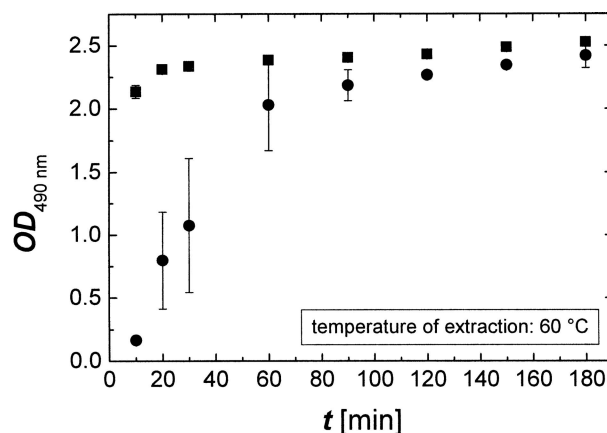


Fig. 2 optical density OD at 490 nm vs. extraction time of the screening method test run with a hybrid sol consisting of pre-hydrolyzed GPTES/TEOS/FTS/Zirconium complex and 30 wt.% reactive diluent Polylox R20 (■: curing temperature 100°C , ●: 140°C)

reproducibility and stage of automation (Scheme 1). In the first step 10 wt.% solutions of polymers (Tables 1 and 2), and a stock solution of the pre-hydrolyzed GPTES/TEOS/FTS/Zirconium complex sol were prepared using conventional lab techniques. From the next stage on—delivering and mixing of sol and polymer solutions—an automated liquid handling system equipped with a 48-reaction-chamber block was used. The blocks control features like stirring, heating and cooling are fully included in the liquid handling system software and provide a convenient use. The screening was performed in two steps each with 48 different mixtures and the same control program.

Clouding of each hybrid sol was qualitatively checked before doping with fluorescein and classified in clear, slightly cloudy and cloudy. Data of clouding are given in Fig. 3 together with assignment of reaction chambers with polymer stock solutions. The same assignment and numeration is also used later for presentation of spectroscopic data. Gelation of

Table 1 Reactive diluents, epoxy resins and epoxy functionalized (e.f.) polymers used for the screening as 10 wt.% solutions

Polymer	abbr	Solvent	abbr
polyox R20 ($M = 302$ g/mol)	PPR20	2-butanol	b
polyox R16 ($M = 360$ g/mol)	PPR16	2-butanol	b
polyox R11 ($M = 256$ g/mol)	PPR11	2-butanol	b
EHPE	EHPE	ethanol	e
linseed oil (e.f.)	LO	2-butanol	b
Araldit CY 179	ACY	2-butanol	b
Araldit DY-F BD F	ADY	2-butanol	b
Araldit GY 257	AGY	2-butanol	b
Araldit PY 309	APY	2-butanol	b
poly(bisphenol A)-epichlor-hydrin, glycidyl end-capped ($M_n \sim 1075$ g/mol)	BAE-G	2-butanol	b
poly(bisphenol A)- epichlorhydrin (Epoxide equivalent weight: 1700–2300 g/mol)	BAE	Ethylacetate	ea
bisphenol F epoxy resin ($M \leq 700$ g/mol)	BFE	2-butanol	b
poly(propylenglycol) di-glycidylether ($M_n \sim 640$ g/mol)	PPG	2-butanol	b
poly[(phenylglycidyl ether)- <i>co</i> -formaldehyde] ($M_w = 345$ g/mol)	PPEF	2-butanol	b
poly[(phenylglycidyl ether)- <i>co</i> -formaldehyde] ($M_w = 345$ g/mol)	PPEF	Ethylacetate	ea
polybutene monoepoxide ($M = 365$ g/mol)	PB	Toluene	t
Polybutadiene e. f. ($M_n = 1300$ g/mol, $M_w = 2300$ g/mol)	PBD	Toluene	t

Table 2 Other polymers used for the screening as 10 wt.% solutions

Polymer	abbr	Solvent	abbr
poly(ethylene-co-vinyl acetate) (Levapren 500 HV, LanXess)	EVA	Toluene	t
poly(ethylene-co-vinyl acetate) (Levapren 500 HV, LanXess)	EVA	Ethylacetate	ea
poly(vinyl acetate) ($M_w = 176000$ g/mol)	PVAc	Butylacetate	ba
polyvinylpyrrolidone $M \sim 360000$ g/mol	PVP-K90	2-propanol	p
polyvinylpyrrolidone $M_w \sim 2900000$ g/mol	PVP-K120	Butyl glycol	bg
poly(dimethylsiloxane) trimethylsiloxy terminated	DMSOME	2-propanol	p
poly(dimethylsiloxane) Silanol terminated	DMS	2-propanol	p
poly(ethyleneimine) average $M_w = 2000$	PEI	Water	w
poly(ethyleneimine) average $M_w = 800$	PEI-L	2-propanol	p
poly(ethyleneimine) average $M_w = 25000$	PEI-H	2-propanol	p
poly[N,N'-bis(2,2,6,6-teramethyl-4-piperinyl-1,6-hexandiamin-co-2,4-dichloro-6-morpholino-1,3,5-triazine)] ($M_w \sim 1600$ g/mol)	PNN	2-propanol	p
poly[N,N'-bis(2,2,6,6-teramethyl-4-piperinyl-1,6-hexandiamin-co-2,4-dichloro-6-morpholino-1,3,5-triazine)] ($M_w \sim 1600$ g/mol)	PNN	Toluene	t
poly(2-vinylpyridin- <i>co</i> -styrene) ($M_n = 130000$, $M_w = 220000$)	PVS	Toluene	t
poly(ethylene glycol) 600 ($M \sim 570$ bis 630 g/mol)	PEG600	Ethanol	e
poly(propylene glycol)- <i>block</i> -(ethylenglycol)- <i>block</i> -(propylene)-bis(2-aminopropylether) ($M_n \sim 2000$)	PPEP	Ethylacetate	ea

hybrid sols during reaction was observed for mixtures containing poly (vinyl pyrrolidone) (PVP-K90 and PVP-K120) and poly(2-vinyl pyridine-*co*-styrene) (PVS) (Table 2). Because of their high viscosity preventing an automated dilution by the liquid handling system, these mixtures were excluded from further screening. In most cases for both components pre-hydrolyzed sol and polymer solution compatible behavior was observed. Only Bisphenol F epoxy resin (≥ 50 vol.%) and poly [(phenylglycidyl ether)-*co*-formaldehyde] (PPEF) dissolved in 2-propanol did not, whereas PPEF dissolved in ethyl acetate led to clear hybrid sols.

The spectroscopic data from fluorescein containing sodium hydroxide solution after extraction of both screenings are summarized in Figs. 4 and 5. Absorption (OD) and fluorescence (RFU) data were measured for two samples of each mixture after 90 and 180 min extraction with 0.1 M sodium hydroxide solution at 60°C. Spectroscopic data evidence two general trends: (1) epoxy resin, epoxy functionalized reactive diluents, and epoxy functionalized polymer containing hybrid coatings show a higher alkali resistance compared with other types of polymers used in this study and (2) increasing content of polymer

Table 3 Composition of 14 clear hybrid sols from the total number of 96 screened mixtures which exhibit RFU values < 1500 after 180 min extraction with 0.1 M sodium hydroxide solution at 60°C (esd's are given in parentheses)

Polymer/reactive diluent	abbr	vol% polymer solution in hybrid sol	RFU value
Polyox R20	PPR20/b	91	671(29)
Polyox R20	PPR20/b	97	368(4)
Polyox R11	PPR11/b	91	438(11)
Poly(Bisphenol A)-epichlorhydrin/glycidyl end-capped	BAE-G/b	91	889(10)
Poly(Bisphenol A)-epichlorhydrin/glycidyl end-capped	BAE-G/b	97	693(18)
Poly[(phenylglycidyl ether)- <i>co</i> -formaldehyde]	PPEF/ea	76	1029(212)
Poly[(phenylglycidyl ether)- <i>co</i> -formaldehyde]	PPEF/ea	91	712(55)
Poly[(phenylglycidyl ether)- <i>co</i> -formaldehyde]	PPEF/ea	97	791(0)
Araldit CY 179	ACY/b	97	262(7)
Araldit GY 257	AGY/b	91	912(89)
Araldit GY 257	AGY/b	97	592(40)
Araldit PY 309	APY/b	97	792(19)
	EHPE/e	91	1227(37)
Araldit PY 309	EHPE/e	97	821(21)

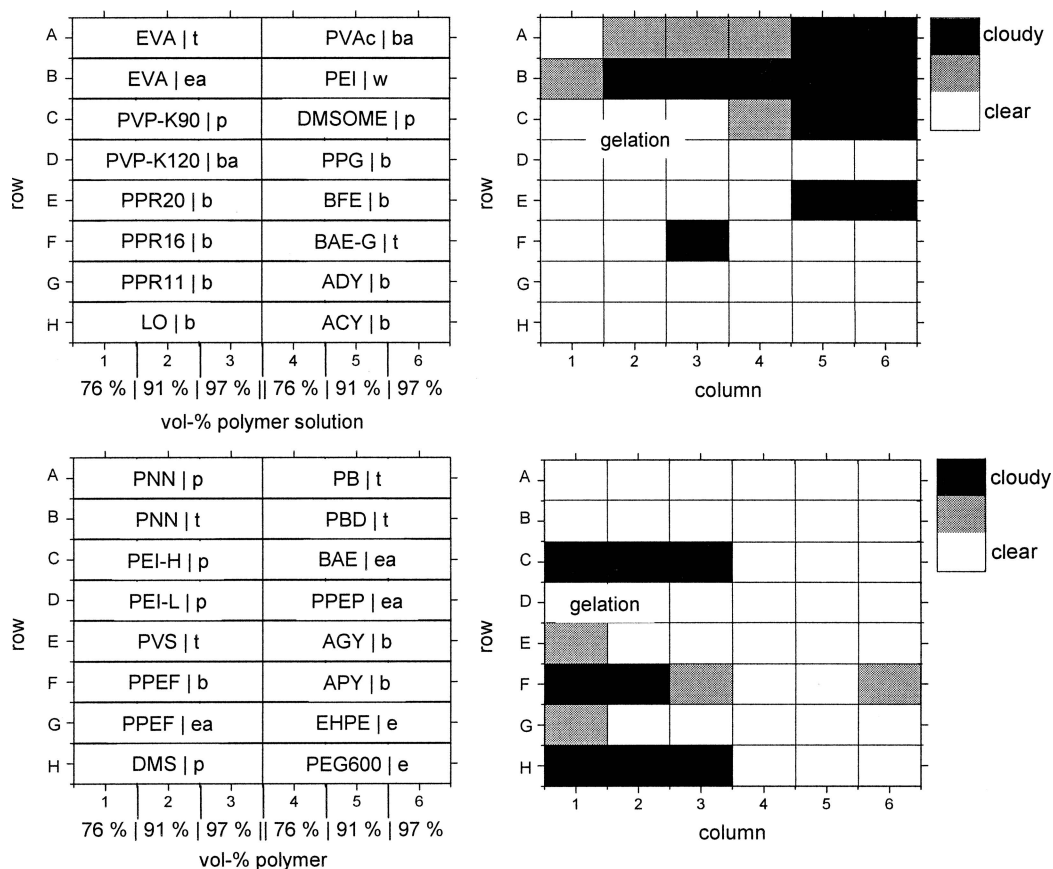


Fig. 3 Composition of the 96 organic-inorganic hybrid materials screened in this work, splitted in two 48 member blocks according to the experimental application flow (left side, details: see text). Right

side: corresponding results of the visual clouding test. The same addressing scheme (letter + number) is used also in the following figures

is associated with increasing alkali resistance. Deviations were found for epoxy functionalized polymers with a pure C–C or C=C backbone, e.g. poly(butene) monoepoxide (PB) and epoxy/hydroxy functionalized poly(butadiene)

(PBD) which exhibit a less observed alkali resistance than other tested epoxy functionalized polymers, e.g. BAE-G.

Spectroscopic data from fluorescence measurements will be used exclusively for the following detailed discussion

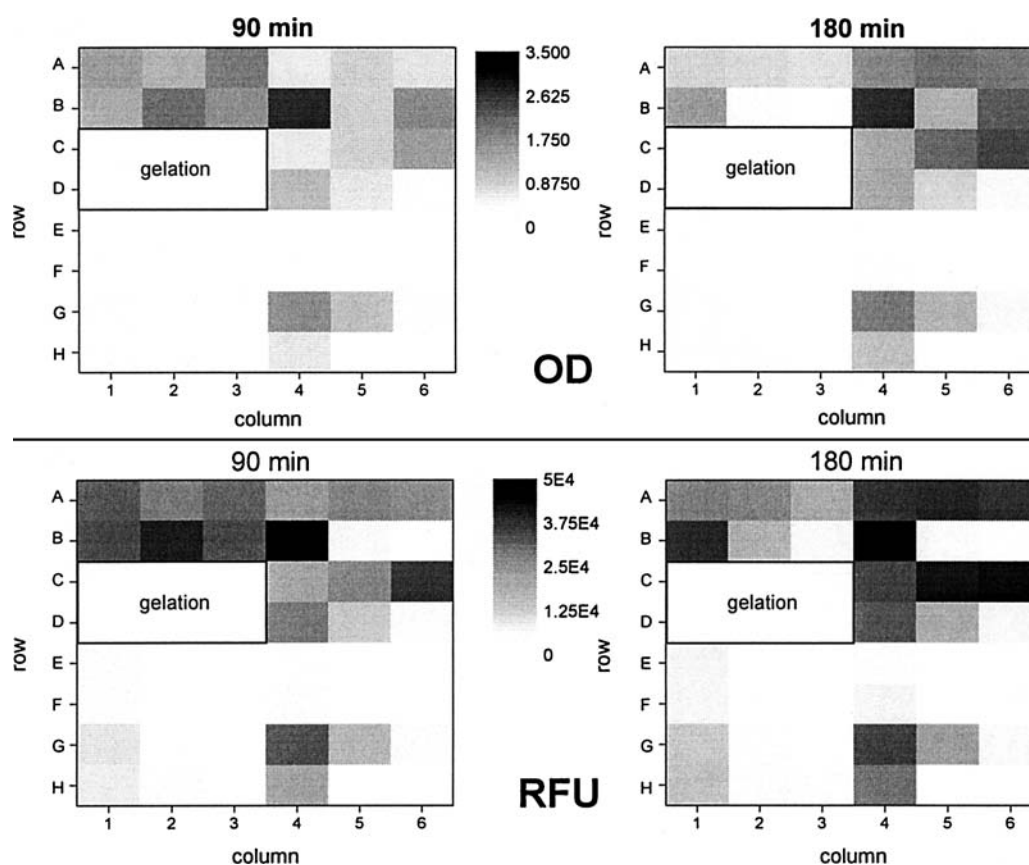


Fig. 4 Results from spectroscopy of the first 48 mixtures (their compositions are given in Fig. 1 top left). Top: OD values from absorbance measurement, bottom: RFU values from fluorescence measurements.

Plots on the left side are data after 90 min and right side after 180 min extraction

of alkali resistance. A general comparison of absorption and fluorescence data suggests a higher sensibility of fluorescence data. Furthermore, data of absorption measurements are more perturbed by sol clouding, whereas the top reading mode used for the fluorescence measurements is less sensitive to sol clouding.

A total number of 14 clear hybrid sols with RFU values below 1500 after 180 min extraction with sodium hydroxide solution remain from the whole screening of 96 hybrid sols. The composition of these sols together with their RFU values is given in Table 3.

A common system used for ETC coatings based on the same GPTES/TEOS/FTS/Zirconium complex sol used in this study and mixed with 30 wt.% Polypox R20 (sol : R20) exhibits a RFU value of 6401(133) and serves as a reference for a classification of the screening results given here. RFU values < 500 were reached for mixtures with 97 vol.% Polypox R20, Polypox R11, and Araldit CY 179 solutions. Lower polymer content is reasonable in the light of ETC properties of the cured hybrid coating system. Hence, the hybrid sol containing 76 vol.% poly ([phenylglycidyl ether)-co-formaldehyde] (PPFP) dissolved in ethyl acetate with a RFU value of 1029(212) after 180 min extraction with

sodium hydroxide solution seems to be the most promising candidate. On the other hand, increasing the polymer content in such hybrid coating systems affords a lowering of the costs for such materials by a partial replacement of expensive silane coupling agents [12].

Conclusions

The high-throughput screening method for optimization of the alkali resistance of organic-inorganic hybrid materials with an ETC effect led to 14 clear sols with noticeable increased stability against sodium hydroxide solution of the cured hybrid coating material compared with an established ETC coating systems. Applying this method it is possible to prepare, cure and screen for alkali resistance a total number of about 100–150 samples per week using our equipment. Because of the sufficient thermal stability of fluorescein (m.p.: 320°C), the described method is also applicable for mainly inorganic ETC systems. Therefore, this method allows also screenings using other strategies for improvement of alkali resistance described in literature, e.g. increase of ZrO₂ content [13], and application of different

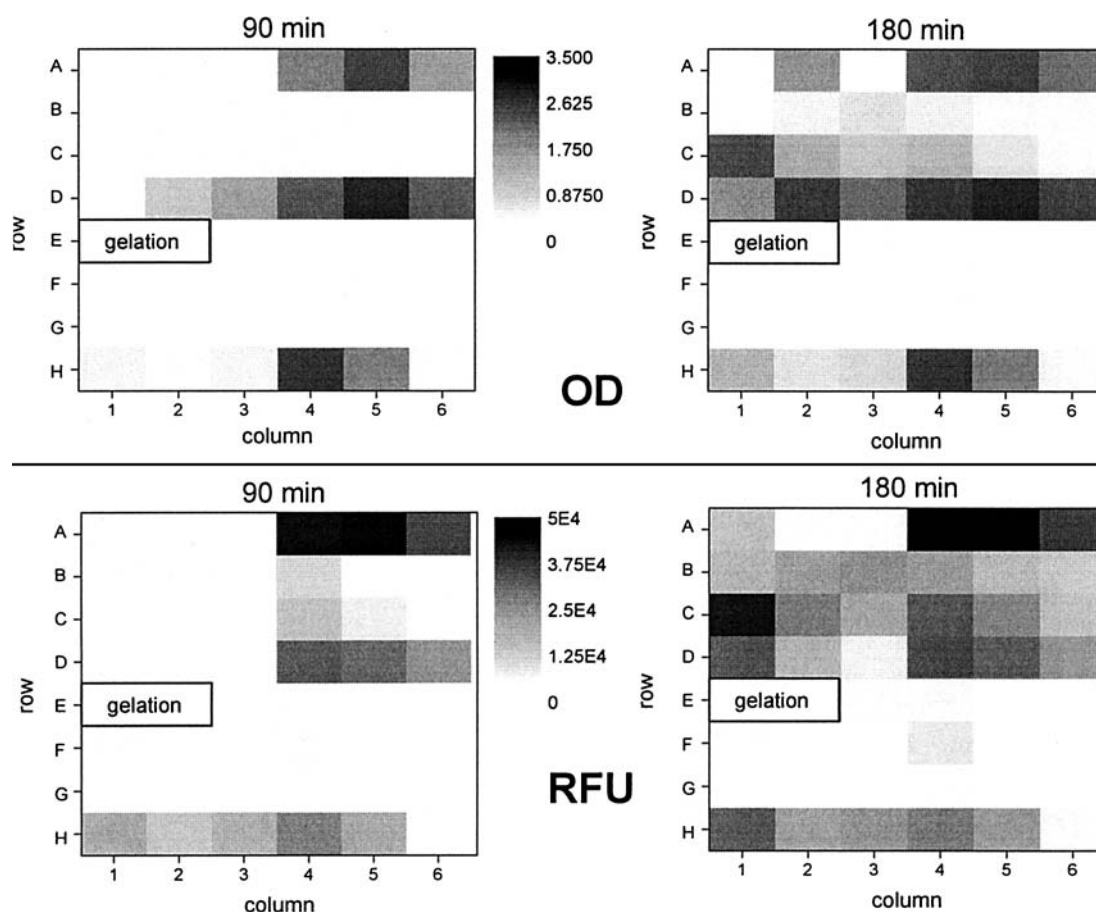


Fig. 5 Results from spectroscopy of the second 48 mixtures (their compositions are given in Fig. 1 bottom left). Top: OD values from absorbance measurement, bottom: RFU values from fluorescence mea-

surements. Plots on the left side are data after 90 min and right side after 180 min extraction

silane coupling agents like 1,4-bis (trimethoxysilylethyl) benzene [14].

A replacement of the aqueous sodium hydroxide solution by other solvents/liquids provides a more general usability of this method for sol-gel derived coating materials for advanced applications.

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