

# The Effect of Nanoscaled Metal Oxide Sols on the Structure and Properties of Glycidoxypropyltrimethoxysilane Derived Sols and Gels

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**Abstract.** Glycidoxypropyltrimethoxysilane (GPTS) is frequently used as precursor for the preparation of sol-gel derived nanoscaled hybrid polymers. The influence of nanoscaled metal oxide sols of silica, boehmite, zirconia and ceria on reactions of GPTS in ethanolic hydrolysates and in corresponding gels (epoxide ring-opening, condensation degree) was examined by liquid- and solid-state  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR with regard to a better correlation between structure and material properties. Generally, a higher condensation degree of  $\text{RSi}(\text{O}_{0.5})_3$  units of GPTS is found after addition of metal oxide sols compared to GPTS without additives. The metal oxide sols (10 mole% series) cause an epoxide ring-opening up to 20% in GPTS hydrolysates after 24 h. A nearly complete ring opening was found in the boehmite and silica containing hybrid gels whereas gels containing ceria and other types of silica only show a low degree of ring-opening. The results show an accelerated ring-opening with increasing content of  $\text{AlO/OH}$ -species in silica sols.  $^{13}\text{C}$  NMR studies reveal that the epoxide ring-opening does not completely lead to polyether structures but to considerable amounts (up to 40%) of ethylether groups which can influence the material properties (hardness).

**Keywords:** epoxide, ring-opening, condensation, NMR, hardness, nanoparticles

## 1. Introduction

Glycidoxypropyltrimethoxysilane (GPTS) hydrolysates and nanoscaled metal oxide sols are frequently used for the preparation of sol-gel derived hybrid polymers. The metal oxide sols are incorporated into hybrid materials to improve their scratch resistance, to adjust the refractive index, or as carriers of special functions [1, 2]. It is known from previous works [3] that nano-sized boehmite sols show a strong catalytic effect on the condensation rates of GPTS in sols and on the epoxide ring-opening. So far, a lack of knowledge exists concerning the effect of differently composed and structured nanoscaled particles on the epoxide ring-opening and condensation degree of  $\text{RSi}(\text{O}_{0.5})_3$  units of GPTS in hybrid sols and gels. The objectives of this work are to find out the influence of nanoscaled  $\text{SiO}_2$ ,  $\text{AlO/OH}$ ,  $\text{ZrO}_2$  and  $\text{CeO}_2$  particles on these reactions in hybrid

sols and gels by means of  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR and to correlate the structural data of the materials with their mechanical properties.

## 2. Experimental

*Chemicals.* The zirconia sol was prepared by a controlled hydrolysis/condensation of  $\text{Zr}(\text{OPr}^t)_4$  (ABCR) in isopropoxyethanol and the boehmite ( $\text{AlO}(\text{OH})$ ) sol by dispersion of boehmite powder Disperal P3 (Condea Chemie) in 0.1 M HCl. The acidic stabilized  $\text{SiO}_2$  sol (200S/30), the alkaline stabilized  $\text{SiO}_2$  sol (300/30) and the  $\text{SiO}_2$  sol (iPr) in isopropanol were obtained from Bayer company. The alkaline  $\text{SiO}_2$  sol was acidified with 3 M HCl to pH 2 before use ( $\text{SiO}_2$  300/30s). The ceria sol was purchased from Rhone-Poulenc company. The characteristic properties of the metal oxide sols are summarized in Table 1.

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Table 1. Characterization of the metal oxide sols.

Sol type	SiO <sub>2</sub> (200S/30)	SiO <sub>2</sub> (300/30s)	SiO <sub>2</sub> (iPr)	AlO/OH boehmite	ZrO <sub>2</sub>	CeO <sub>2</sub>
Solvent	Water	Water	i-Propanol	Water	i-Propoxyethanol	Water
Concentr. (M)	5.20	5.65	4.95	0.64	0.9	1.42
Atomic ratio Si : Al	9 : 1	235 : 1	57 : 1			Ce : Fe = 61 : 1
Water cont. (%)	69	68	1	94	<0.1	77
pH (electrom.)	3.8	2.0	(1.4)	3.8		3.4
Particle size (nm)	15–20	10	16	10–15	2–10	2–4 (irregular)

**Procedure.** 1 mol GPTS diluted with ethanol to 2.87 M solution was hydrolyzed with 1.5 mole water (0.1 M HCl) and stored for 0.5 h at 25°C. The metal oxide sols were added to the hydrolysate at molar ratios GPTS : metal oxide [(MO)<sub>x</sub>] = 1 : 1 (50 mole% additive) and 0.9 : 0.1 (10 mole%) except the ZrO<sub>2</sub> system (41; 7 mole%). Additional ethanol was added for the adjustment of a defined GPTS concentration in the sols (GPTS concentration of the 50 mole% series: 0.71 M (ZrO<sub>2</sub>), 0.88 M (AlO/OH), 0.93 M (CeO<sub>2</sub>), 1.26 M (SiO<sub>2</sub> sols); 10 mol% series: 1.26 M (exception ZrO<sub>2</sub> : 1.0 M). The gels were prepared from the hybrid sols after their storage at 25°C for 24 h followed by heating at 130°C for 7 h. Likewise, the layers were obtained from the 24 h hybrid sols by dip coating on a glass support and the same heating procedure. The hardness of layers (thickness 2.2–2.6 μm) was determined by indentation hardness measurements.

**Measurements.** The <sup>29</sup>Si and <sup>13</sup>C NMR spectra were obtained using a Bruker AC 200 spectrometer (liquid-state) and a Bruker MSL 200 (solid-state) operating at fields of 4.7 T. <sup>29</sup>Si NMR: inverse gated sequence, external reference: tetramethylsilane (TMS), internal standard for quantitative evaluation: phenyltrimethylsilane, repetition time (r.t.): 40 s, pulse angle (p.a.): 63°, number of scans (n.s.): 1260. <sup>13</sup>C NMR: inverse gated sequence, r.t.: 10 s, p.a.: 60°, n.s.: 180. Generally, the <sup>13</sup>C and <sup>29</sup>Si NMR measurements of sols were started 15 min after their preparation. Solid-state <sup>29</sup>Si NMR: <sup>29</sup>Si{<sup>1</sup>H} sequence, external standard Q<sub>8</sub>M<sub>8</sub> (M signal = 11.58 ppm related to TMS), MAS 3 kHz, p.a.: 63°, r.t.: 60 s, n.s.: 600–720. Solid-state <sup>13</sup>C NMR: single pulse <sup>13</sup>C{<sup>1</sup>H} high power decoupling, external standard adamantane, p.a.: 50° r.t.: 4 s, n.s.: 7000–9000.

### 3. Results and Discussion

#### 3.1. Condensation Degree of RSi(O<sub>0.5</sub>)<sub>3</sub> Units

The condensation degree (c.d.) of the RSi(O<sub>0.5</sub>)<sub>3</sub> unit of the GPTS component in hybrid sols and gels in presence of the different nanoscaled sols were examined by liquid- and solid-state <sup>29</sup>Si NMR. The calculation of the c.d. was carried out according to the formula c.d. (%) = 100 – (T<sup>0</sup> + 0.67 T<sup>1</sup> + 0.33 T<sup>2</sup>) on the basis of the signal intensities of the different condensed structural units which are indicated with the conventional T notation. The results of <sup>29</sup>Si NMR are summarized in Fig. 1. The addition of 10 mole% SiO<sub>2</sub>(iPr) sol does not significantly influence the c.d. (8%) in comparison to the c.d. of the GPTS hydrolysate without additives (4%). A higher activity shows the boehmite sol (22%) and especially the other types of silica sols, ZrO<sub>2</sub> and CeO<sub>2</sub> sols (33–40%). Generally, the c.d. increases

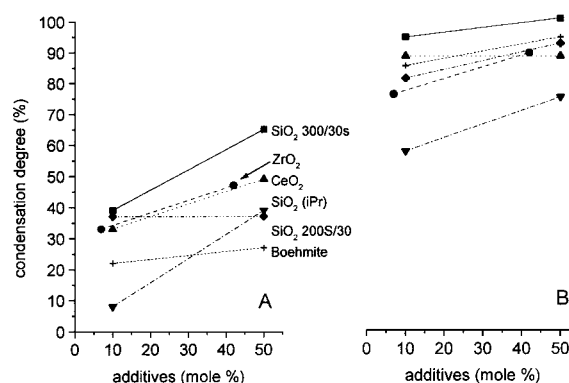


Figure 1. Condensation degree of hybrid sols (A) and gels (B) of GPTS-1.5 H<sub>2</sub>O hydrolysates in dependence on the amount of additives.

with increasing content of additives. The addition of 50 mole%  $\text{SiO}_2(300/30\text{s})$  lead to the highest c.d. (65%) in hybrid sols. As expected, a further increase of the c.d. to 80–98% occurs during transformation of the hybrid sols into gels except for  $\text{SiO}_2(\text{iPr})$  as an additive. The use of the alcohol containing  $\text{SiO}_2(\text{iPr})$  sol leads to a relatively low c.d. in hybrid gels due to the insufficient amount of water for extended hydrolysis and condensation reactions. A reliable explanation for the significantly different c.d. in dependence on the sol additives is difficult because it is not possible to make all parameters of the GPTS hybrid sols comparable to each other. Apart from the nearly comparable GPTS concentrations and molar GPTS/metal oxide ratios differences exist in the ratio water/GPTS, in the content of alcohols and in the concentration of condensation accelerating components (e.g.  $\text{AlO}/\text{OH}$  species, Table 1).

### 3.2. Epoxide Ring-Opening

Figure 2 shows  $^{13}\text{C}$  NMR spectra of hybrid sols of the system 1 GPTS-1.5  $\text{H}_2\text{O}$ -1  $\text{SiO}_2(\text{iPr})$  after 0.5 h and 24 h reaction time and of the corresponding gel. The assignment of relevant signals is based on the measurement of standard samples and on the values of chemical shifts taken from the literature [4, 5]. For evaluation of the ring-opening reaction in sols the signal intensity of the terminal C-atom (6) of the epoxide ring at  $\delta = 44.2$  ppm was compared to that of the internal standard ( $\delta = -1.25$  ppm). For estimation of the amount of epoxide rings in the gel the intensity of the signal (6) was related to those of the signal (2) at 23.4 ppm whose intensity is not affected by the GPTS reactions. The intensity of signal (6) decreases with increasing reaction time at constant intensity of the standard signal. No signal of epoxide C-atoms can be detected in the gel spectrum. The results of the effect of nanoscaled additives on epoxide ring-opening in hybrid sols and gels are summarised in Fig. 3.

The comparison of the black bars shows that the epoxide rings in hybrid sols were opened only to a small extent (0–10%) 0.5 h after the addition of the metal oxide sols. A stronger opening occurs after 24 h up to 70% in dependence on the type of additives and their concentration in the hybrid sols. A nearly complete opening was found in 10 mole% (Fig. 3(A)) as well as 50 mol% (B) hybrid gels deriving from  $\text{SiO}_2(200\text{S}/30)$  and boehmite. The  $\text{ZrO}_2$  sol shows a similarly strong activity in hybrid gels which can be seen in connec-

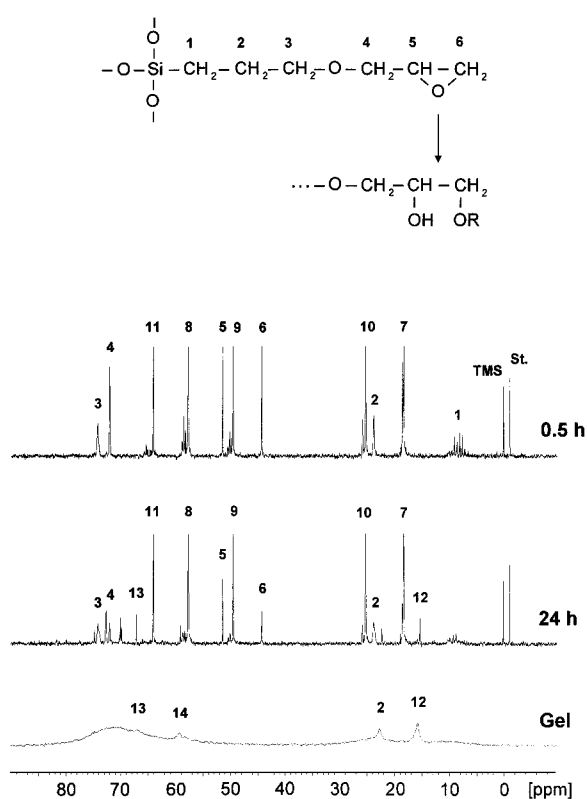
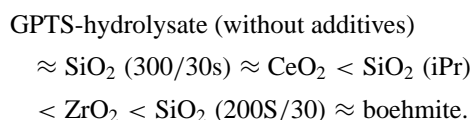


Figure 2.  $^{13}\text{C}$  NMR spectra of hybrid sols (0.5 h, 24 h reaction time) and of the gel of the system 1 GPTS-1.5  $\text{H}_2\text{O}$ -1  $\text{SiO}_2(\text{iPr})$ . Signals (7, 8):  $\text{CH}_3\text{CH}_2\text{OH}$ ; (9):  $\text{CH}_3\text{OH}$ ; (10):  $(\text{CH}_3)_2\text{CHOH}$ ; (11):  $(\text{CH}_3)_2\text{CHOH}$ ,  $\text{CH}_2\text{OR}(\text{R}=\text{H})$ ; (12, 13):  $\text{R} = \text{CH}_3\text{CH}_2$ ; (14):  $\text{CH}_3\text{CH}_2\text{OSi}\equiv$ ;  $\text{R} = \text{CH}_3$ .

tion with the known high activity of Zr-alkoxides for epoxide ring-opening [6].  $\text{CeO}_2$  sols (10 mole%) show only a low activity of ring-opening in gels which increases strongly with increasing  $\text{CeO}_2$  amounts. The following order in the activity of additives (10 mole%) concerning epoxide ring-opening in hybrid gels was found:



The silica components should only have a low influence in electrophilic ring opening like tetraalkoxysilanes [6] due to their low Lewis acidity and the higher electronegativity of the Si atom in comparison to the Al atom. Probably, the ring-opening activity of the silica sols was caused by catalytic active components in

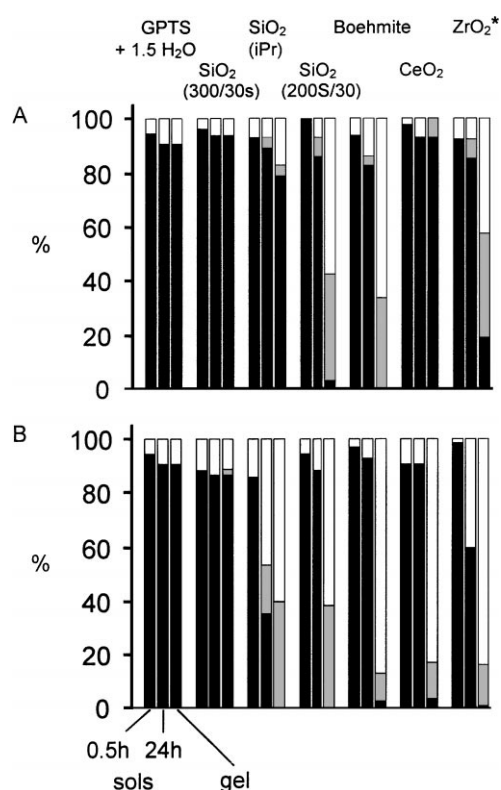


Figure 3. Amount of unopened epoxide rings (black bars) and ethylether groups (grey bars) in GPTS derived hybrid sols and gels with 10 (\*7) mole% (A) and 50 (\*41) mole% (B) metal oxide sol.

the used commercial  $\text{SiO}_2$  sols. The analysis of foreign oxides in the  $\text{SiO}_2$  sols shows significant differences in the Al-content which varies from ratios at  $\text{Si}:\text{Al} = 9:1$  to  $235:1$  (Table 1). The different content of Al containing components like aluminium-oxo-hydroxo species (AlO/OH) in silica sols can be accounted for by their preparation procedure. The alkali or amine stabilized silica sol  $\text{SiO}_2$  300/30 contains the lowest amount of AlO/OH which derives only from the natural content of the water glass solutions used as source for the sol preparation [7, 8]. The  $\text{SiO}_2$  200S/30 and  $\text{SiO}_2$  (iPr) are stabilized by aluminium salt solutions [7] which produce a cover from positively charged Al-oxo-hydroxo species which stabilize the  $\text{SiO}_2$  particles by electrostatic repulsion. Comparing the AlO/OH content of the silica sols [ $\text{SiO}_2$  (200S/30) >  $\text{SiO}_2$  (iPr) >  $\text{SiO}_2$  (300/30s)] with their activity in epoxide ring-opening the silica sols show an increased activity with increasing amount of AlO/OH. Despite their significantly different Al-contents the

similar activity of  $\text{SiO}_2$  300S/30 and boehmite sols is caused by a similar covering density of the particle surface with active AlO/OH units. From this it follows that not the absolute Al-amount of the additives is responsible for the activity but only the amount of easily accessible AlO/OH groups on the surface of the particles.

The  $^{13}\text{C}$  NMR allows a reliable determination of the content of unreacted epoxide rings in sols and gels. However, difficulties arise with the identification of the manifold reaction products of epoxide ring-opening due to signal overlappings. Regardless of the formation of polyethers the epoxide ring can react in presence of alcohols, water and additives to the structural group  $-\text{CH}_2-\text{CH}(\text{OR}^1)-\text{CH}_2\text{OR}^2$  with  $\text{R}^1, \text{R}^2 = \text{H}$ , alkyl,  $-\text{Al}/-\text{Zr}(\text{O})_x$ ,  $-\text{SiR}^*(\text{O}_{0.5})_2$  or  $-\text{Si}(\text{O}_{0.5})_3$  units [5, 9]. The signals of the  $\alpha$ -C-atom in diol groups at  $\delta = 64.1$  ppm and of the C-atoms in ethylether group ( $\text{R} = \text{CH}_3\text{CH}_2-$ ) at  $\delta = 15.3$  and  $67.1$  ppm (Fig. 2, signal 12, 13) give the best chance for their identification in the  $^{13}\text{C}$  NMR spectrum. The grey bars in Fig. 3 show the results of a rough estimation of the amount of ethylether groups in hybrid sols (up to 15%) and gels (up to 40%). The presence of significant amounts of ethylether groups means that a considerable part of the epoxide did not polymerize to polyether chains. This result could effect the properties of the resulting materials, e.g. their hardness.

Figure 4 shows an attempt to correlate the obtained data of the c.d., of the amount of epoxide and ethylether groups with the hardness of selected hybrid layers. The relatively high condensation degree (82–98%) of the  $\text{RSi}(\text{O}_{0.5})_3$  units in all layers does not significantly influence their hardness. A high hardness was found in four hybrid layers with complete epoxide ring-opening. The layer (50% boehmite) with complete ring opening and with a low content (11%) of ethylether groups shows the highest hardness. From this it could be concluded that a low number of ethylether groups is connected with a high number of polyether bonds which effect the hardness. However, the following three hybrid layers show a complete ring-opening and a comparable amount of ethylether groups (30–37%) but significant differences in the hardness. From this it follows that the three determined structural elements are not sufficient to describe the correlation between structure and mechanical property. This means that additional factors e.g. content of diol groups and other possible ether groups and also the formation of oxygen-bridged heterometal bonds between

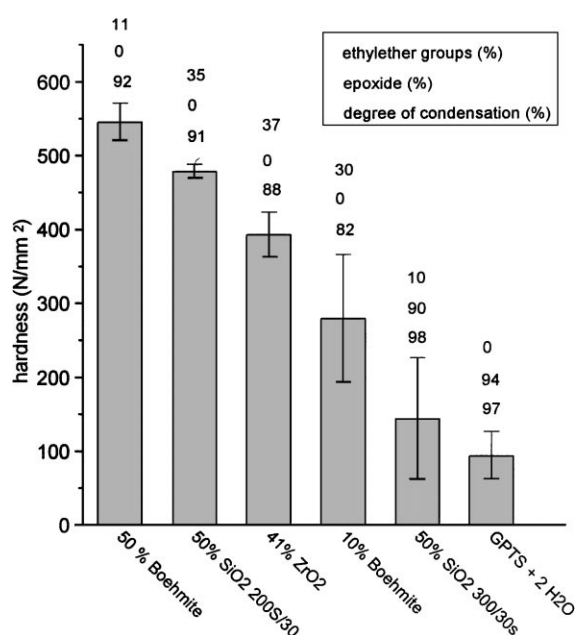


Figure 4. Hardness of GPTS derived hybrid layers (2.2–2.6  $\mu\text{m}$ ) on glass in dependence on the type of metal oxide additives and structural parameters.

nanoparticles and the matrix have to be considered in future works.

#### 4. Conclusions

- The addition of nanoparticulate sols leads to an increased condensation degree of  $\text{RSi}(\text{O}_{0.5})_3$  units in GPTS derived hybrid sols.
- A high condensation degree of  $\text{RSi}(\text{O}_{0.5})_3$  units (>80%) in GPTS derived hybrid gels does not

significantly influence the hardness of hybrid layers.

- An increasing content of  $\text{AlO/OH}$  units in silica sols leads to an increased epoxide ring-opening reaction.
- Significant amounts of ethylether groups can be formed during the epoxide ring-opening reaction in alcoholic media which lower the amount of polyether groups. However, the knowledge of the amount of ethylether groups and a complete epoxide ring-opening in hybrid gels are not sufficient parameters for a satisfactory explanation of the hardness of hybrid layers.

#### Acknowledgment

The authors gratefully acknowledge the Fonds der Chemischen Industrie for financial support and thank Ms S. Carstensen and Dr. A. Tholey for preparative work.

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