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Water stability of a cheap sol-gel-based adhesive

Janne Puputti · Mika Lindén

Abstract The humidity and water tolerance of a sol-gel derived binder prepared using a cheap, multicomponent precursor has been studied. The sol was prepared by dissolving the precursor in water under acidic conditions using either formic acid or a mixture of formic acid and citric acid for pH adjustments. It is shown that a post-treatment temperature of 400 °C or higher is needed in order to achieve full binder stability under excess water conditions, as thermal decomposition of metal carboxylates leads to a pronounced decrease in water solubility of the gels. The mesoporous gel can be made hydrophobic by post-treatments with either a silane or an organophosphonate, showing that both silica and metal oxides are exposed on the surface of the binder. Surface functionalization is especially effective for gels heat-treated at higher temperatures where the metal carboxylates have decomposed to the corresponding oxides or carbonates. The results are expected to be of great importance for the use of this cheap binder in large scale industrial applications.

Keywords Silica precursor · Inorganic binder · Water adsorption · Green chemistry

1 Introduction

There is a strong current trend both in industry and in academia towards finding cheaper and greener ways for producing bulk-products with enhanced properties due to obvious reasons. This is also true for the production of insulation materials, such as fiber-based insulation elements like glass-wool- and rock-wool. Traditionally, organic resins have been used as binders for these fibers, but the thermal stability of such binders is poor at temperatures higher than about 300 °C.

Therefore, attempts to produce more thermally stable inorganic binders based on silicon-alkoxides have been reported (Schmidt et al. 2000). However, the high cost of metal-alkoxides does not make them very attractive as silica sources in bulk applications. We have recently shown that it is possible to overcome this problem by using an industrial waste-product, an amorphous aluminosilicate additionally containing calcium, magnesium, and iron oxide together with trace amounts of titania, as the precursor for a sol-gel-based binder for rock-wool fibers (Nilsen et al. 2003, 2005; Puputti et al. 2004). Here, a multicomponent metal oxide mineral is dissolved under acidic conditions, using organic acids for pH control. The use of organic acids is beneficial from a corrosion point of view, and these can easily be removed by heat-treatments, as remaining acid residues evaporate during the drying stage (Puputti et al. 2004, 2008; Nilsen et al. 2005), and different metal salts, such as formates and citrates, eventually decompose to corresponding oxides, dioxides or carbonates at temperatures specific for each compound (Puputti et al. 2008; Hon et al. 2001; Dollimore et al. 1979; Vassileva 2003; O'Connell and Dollimore 2000; Valor et al. 2002; Verma et al. 2005; Prasad et al. 1998; Maslowska 1984). Another advantage of this method, apart from being cheap, is that no solid waste is produced, as the sol used as the binder contains all the dissolved metal oxides present in the original mixed metal oxide precursor, and are thus part of the final product. The binder sol has shown good wetting properties,

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and the formed bonds are strong enough to allow shaping of the fiber mat.

In the initial reports, we used formic acid for pH adjustments during the dissolution of the mineral (Nilsen et al. 2003, 2005; Puputti et al. 2004). However, during drying and thermal treatment of the gels we observed pronounced crystallization of different metal formates, and also of $CaCO_3$ in the gels, which is not desirable from the point of view of the mechanical stability of the dried gels. This effect could be overcome by addition of small amounts of strongly complexing acids, like lactic acid, and especially citric acid, to the sol (Puputti et al. 2008). No crystalline products were observed in sols containing citric acid even after heat-treatments at temperatures up to 700 °C.

However, the humidity and water tolerance of the developed binder has not yet been reported. The water tolerance is naturally a key parameter for successful application of the binder. It is to be expected that the water stability of the binder is affected by the heat-treatment temperature, as metal carboxylates, which typically have a high solubility in water, decompose in several steps especially in the temperature range 200–400 °C. Furthermore, the stability of the silica network is dependent on the degree of silica condensation, which also is strongly influenced by the treatment temperature. We have therefore undertaken a study of the water stability as a function of thermal treatment temperature for gels derived from sols where the pH is adjusted using either formic acid or a mixture of formic acid and citric acid. Furthermore, we have investigated the influence of two different surface functionalization agents, hexamethyldisiloxane, HMDS, and a fluorocarbon-based organophosphonate, Zonyl® FSE, $((F(CF_2)_n\text{-}CH_2CH_2O)_2POO^-, n = 6.5)$ on the stability against water and humidity. Silanes are widely employed surface modifiers for silica (Wood and Sharma 1994; Angst 1991; Marinova et al. 2005; Silberzan et al. 1991; Wasserman et al. 1989). HMDS was applied through the gas phase according to the procedure recently described for the surface functionalization of mesoporous silica (Tang et al. 2006). Surface functionalization through the gas phase would be very interesting industrially. However, a silane-based surface modifier is expected to preferentially bind to the SiO_2 portion of the binder. Zonyl, on the other hand, could be expected to interact more strongly with metal oxides and less strongly with silica, and was recently used for selective surface functionalization of TiO_2 in $SiO_2{-}TiO_2$ composite films (Fisher et al. 2006). Organic phosphates and phosphonates have also been used in several other studies related to metal oxide surface modification (Trammel et al. 1999; Guerrero et al. 2001; Mutin et al. 2003; D'Andrea and Fadeev 2003). Surface modification of the binder using Zonyl FSE was carried out by surface grafting from ethanol. The gels were characterized both as coatings and as powders, by dissolution tests, nitrogen sorption, and water vapor sorption.

2 Experimental

2.1 Sol and gel preparation

An amorphous silicate mineral (Paroc Oy Ab) was used as a silicate source in preparation of sols. The main constituents of the mineral were silicon, aluminum, calcium, and magnesium oxides, and the corresponding molar ratio between these elements was 2.2–2.4:1–1.2:0.9–1.1:1.0–1.2. The mineral also contained trace amounts of transition metal oxides. The mineral content of the sols was adjusted to 8 wt%. As earlier described (Puputti et al. 2008), the mineral was dissolved either in 3 M formic acid (98–100% Riedel-Haen) solution or in a corresponding solution additionally containing 0.16 M of citric acid.

2.2 Preparation of gel coatings

Coatings on thoroughly cleaned microscopy glass slides were prepared by placing 0.200 ml of sol on the glass sheet, which spread to form a thin layer of sol. The coatings were first pre-dried at RT overnight, before being heated at the desired temperature. HMDS functionalization was performed by placing coated glass sheets or crushed gel samples in saturated HMDS atmosphere for 1 hour, followed by drying at 60 °C for 1 hour. Zonyl surface modification was performed by surface grafting from ethanol (1 wt% of Zonyl FSE for 24 hours). Afterwards, the samples were carefully rinsed with a small amount of water and dried at RT.

2.3 Coating dissolution

The water stability of the gels were simply tested by immersing coated glass slides into water (experiments carried out in triplicate) followed by gravimetric determination of the mass loss. Elemental analysis was also performed on selected samples by energy dispersive x-ray analysis. Each coating was soaked in 50 ml of distilled water overnight followed by drying at 110 °C.

2.4 Contact angle measurements

Static water contact angles were determined for untreated and surface functionalized coatings using a CAM 200 contact angle goniometer (KSV Instruments Ltd., Helsinki, Finland)

2.5 Water adsorption measurements

Water adsorption measurements were performed at 25 °C using a Quantachrome Hydrosorb™ 1000 setup. The samples were degassed for 2 hours at 200 °C before measurements.

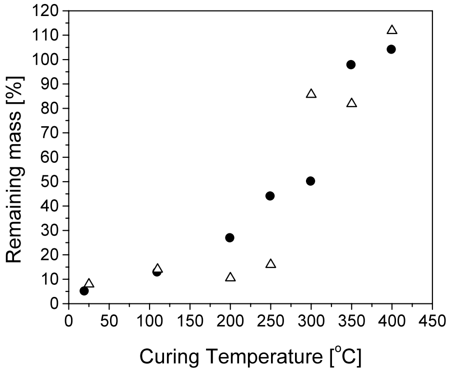

Fig. 1 Mass loss as a function of curing temperature.of coatings deposited on glass substrates immersed in water ($T = 25\,^\circ\mathrm{C}$) for 16 h. The coatings were prepared from sols containing (●) 3 M formic acid and (△) 3 M formic acid + 5 mol% citric acid. The dry-contents of the sols were 8 wt% in both cases

2.6 N_2-sorption analysis

The N_2-isotherms were determined at −196 °C using a Micromeritics ASAP 2010 sorptometer. The samples were outgassed at 250 °C for 12 hours before measurements. The Brunauer-Emmett-Teller (Brunauer et al. 1938) (BET) equation was used to calculate the surface area S_{BET}, and pore size determinations were performed using the Barret-Joyner-Halenda (Barret et al. 1951) (BJH) method using both the adsorption and the desorption isotherm.

3 Results

As a first test of the influence of water on the adhesion of the binder and towards binder dissolution, films of the binder on glass slides were prepared. The glass slides served as a model for glass and rock wool fibers. The films were dried at different temperatures in the interval 25 °C to 500 °C, before being immersed in a large excess of water for 16 h at 25 °C. The films were subsequently dried at 110 °C, and the mass losses of the films were determined by gravimetry. The results are presented in Fig. 1. This simple test clearly shows that only films treated at temperatures of 350 °C and higher are stable, while pronounced mass losses were observed for films heat-treated at lower temperatures. Note that the introduction of water as hydration water in the samples treated at higher temperatures leads to final masses exceeding the initial mass of the coatings. Some differences in the film stabilities were observed as a function of citric acid content of the sol for films treated at temperatures lower than 350 °C, and generally the stability of the films decreased with increasing citric acid content for these films. Elemental analysis of the films treated at 250 °C and 300 °C show that the non-siliceous parts of the films preferentially dissolve, as the corresponding metal/Si atomic ratios are lower for these films as compared to the reference film treated at 550 °C (see Table 1). However, the non-siliceous portion is higher for films treated at 300 °C as compared to films treated at 250 °C, and the elemental analysis show that especially the Al and Fe contents, and to a lesser extent Ca and Mg, are enhanced in the film treated at 300 °C. These results are in good agreement with what can be expected, as the water solubility of metal-formates and -citrates are higher than that of the corresponding oxides, and increasing portions of the metal carboxylates do decompose to the corresponding oxides, with Ca-carboxylates as the exceptions, which decompose to $CaCO_3$. Furthermore, Al- and Fe-carboxylates start to decompose at lower temperatures than the Mg- and Ca-carboxylates. The slightly higher non-silicous metal/Si ratio in the films derived from the citric acid containing sols can be related to the fact that less phase-separation is supposed to occur in these films, as pronounced crystallization of metal formates was observed for the purely formic acid based sols. Some of the metal citrates/formates may be embedded inside the silica network, thus leading to a slower dissolution rate. However, the metal/Si ratios are lower than in the stable reference film in all cases, showing the preferential dissolution of metal carboxylates from films treated at temperatures lower than 350 °C. Treatment of the films with HDMS or zonyl after heat-treatments did not have any influence on the mass-loss upon immersion in water, and also for these films a heat-treatment at 350 °C or higher was needed in order to obtain stable films.

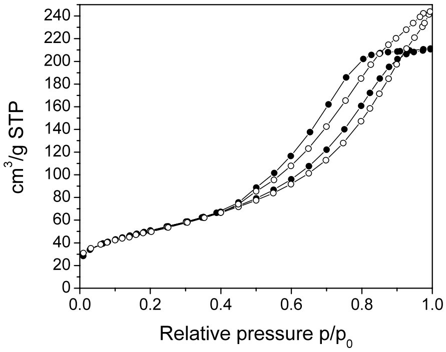

Fig. 2 N_2-sorption isotherms measured for gels derived from sols containing 8 wt% of mineral dissolved in 3 M formic acid. The gels were heat-treated at (○) 250 °C and (●) 550 °C

Nitrogen sorption isotherms measured for powder samples obtained by grinding dried gels followed by heat-treatments are shown in Fig. 2, and some key parameters are summarized in Table 2. Two heat-treatment temperatures were studied, 250 °C and 550 °C, where the former corresponds to the temperature normally used to cure organic binders in rock-wool processing, and the latter corresponds to a temperature where all metal carboxylates are decomposed to the corresponding metal oxide or carbonate. The isotherms obtained were characteristic for mesoporous

Table 1 Relative elemental composition of the coatings after immersion in water. FA refers to formic acid and CA to citric acid

Drying *T* (°C)		Mg	Al	Si	Ca	Fe	C	O
250	3M FA	0.00	0.18	1.00	0.00	0.01	0.36	3.64
	3M FA + 5% CA	0.04	0.09	1.00	0.03	0.03	0.14	2.93
300	3M FA	0.28	0.42	1.00	0.15	0.25	0.70	4.50
	3M FA 5% CA	0.43	0.50	1.00	0.39	0.43	0.68	5.42
550	3M FA	1.25	1.07	1.00	1.33	0.54	0.89	9.91

Table 2 Characteristic values extracted from the N_2 sorption isotherms for different heat-treated gels derived from sols containing 8 wt% of dissolved mineral. FA refers to formic acid and CA refers to citric acid

	3 M FA		3 M FA + 0.16 M CA	
	250 °C	550 °C	250 °C	550 °C
BET Surface area ($m^2 g^{-1}$)	185	181	146	198
BJH Pore diameter (Adsorption) (Å)	90	90	91	91
BJH Pore diameter (Desorption) (Å)	62	73	36	46
Pore volume ($cm^3 g^{-1}$)	0.33	0.39	0.21	0.29

materials in all cases, regardless of the acid catalyst compositions and the applied heat-treatment temperatures. The BET surface areas of the gels derived from sols containing formic acid as the only acid were almost identical for both treatment temperatures, around 180 m^2/g. However, while two pronounced uptakes was observed in the relative pressure range corresponding to capillary condensation in mesopores for the gel treated at 250 °C, one centered around 0.8 p/p_0 and one above 0.9 p/p_0, only one region of pronounced uptake centered around 0.8 p/p_0 was observed for the gel treated at 550 °C. Furthermore, the isotherm reaches a plateau at higher pressures for the gel treated at 550 °C, while no plateau is reached for the gel treated at 250 °C. Thus, one can conclude that the mesopore size distribution is bimodal in the first case, but rather monomodal in the second. The hysteresis is fairly narrow in both cases, suggesting limited restriction for desorption. Secondly, the total pore volume can only reliably be determined for the gel treated at higher temperatures. However, taking only the primary mesopores into account, the total pore volume is on the same level for both samples, around 0.33 cm^3/g. The BJH pore size distribution plots are shown in the supporting information. A maximum in the pore size distribution plot is observed at about 8 nm (desorption) and at about 9 nm (adsorption) for the gel treated at 250 °C, while the corresponding values for the gel treated at 550 °C is 7 nm (desorption) and 9 nm (adsorption).

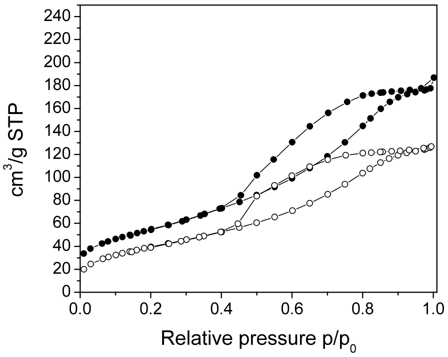

Fig. 3 N_2-sorption isotherms measured for gels derived from sols containing 8 wt% of mineral dissolved in 3 M formic acid and 0.16 M citric acid. The gels were heat-treated at (○) 250 °C and (●) 550 °C

The corresponding isotherms measured for the citric acid containing gels are shown in Fig. 3. The surface area of the gels heat-treated at 250 °C is clearly lower than that of the corresponding gels treated at 550 °C (see Table 2). Furthermore, both isotherms reach a plateau at high relative pressures. The mesopore dimensions are similar in both cases, about 9 nm (adsorption) and 5 nm (desorption) (see ESI). The pronounced difference in pore dimensions depending on if the adsorption or the desorption branch is used for the analysis shows that there are restrictions in the porosity for desorption, often referred to as ink-bottle shaped or cage-like pores (Rouquerol et al. 1999). However, the overall shapes of the two isotherms are very similar, suggesting that the microstructure of the gels are similar. This is in good agreement with our previous findings which showed

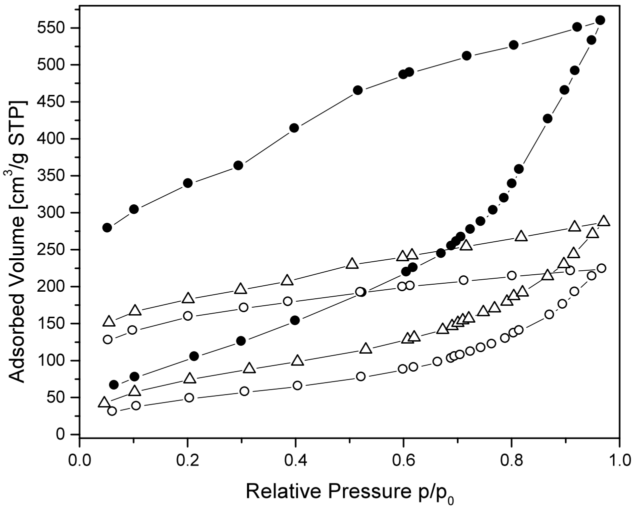

Fig. 4 Water sorption isotherms measured for native (●) HMDS (○) and zonyl treated (△) gels prepared from sols containing 8 wt% of mineral dissolved in 3 M formic acid. The gels were heat-treated at 250 °C

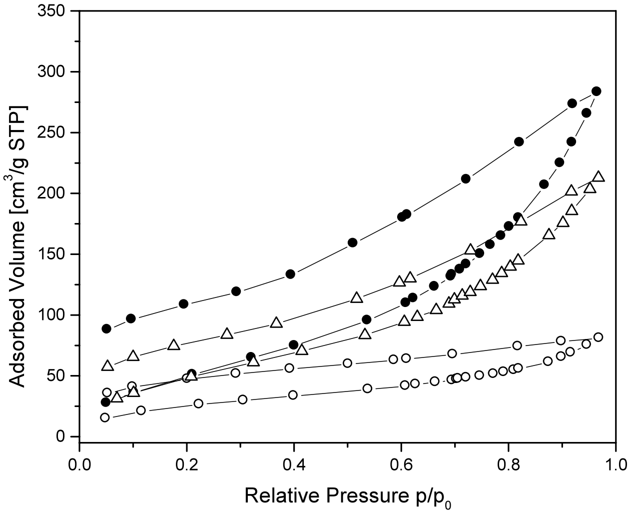

Fig. 5 Water sorption isotherms measured for native (●) HMDS (○) and zonyl treated (△) gels prepared from sols containing 8 wt% of mineral dissolved in 3 M formic acid. The gels were heat-treated at 550 °C

that no crystallization occurs in these films at these temperatures (Puputti et al. 2008).

Water sorption isotherms were measured at 25 °C for gels treated at 250 °C and 550 °C, respectively. The water sorption isotherm for the native gel derived from formic acid sols and pre-heat treated at 250 °C is presented in Fig. 4, and the key parameters are presented in Table 3. An almost linear increase in the amount of adsorbed water with increasing humidity was observed for the native gel up to a relative pressure of about 0.7 p/p_0, after which a pronounced uptake with two steps was observed. The two steps at higher relative pressures were similar to those observed in the nitrogen sorption isotherms, which suggests that the water adsorption at higher relative pressures corresponds to capillary condensation of water in mesopores. However, the hysteresis was very pronounced, suggesting that a fair amount of water was incorporated as hydration water in metal carboxylates. This makes it virtually impossible to derive reliable surface area and pore diameter values from the water sorption isotherms, but we note that the pore volumes filled with water and nitrogen respectively are similar for the films treated at 250 °C, if the amount of water not desorbing during desorption is subtracted. Thus, we can conclude that the mesopores are virtually fully filled with water at high humidities for these films. For films treated at 550 °C, however, the pore volumes filled with water at high humidities are clearly lower if compared to the pore volumes derived from nitrogen sorption measurements. The general shapes of the isotherms were similar for the HMDS and the zonyl treated gels, as also shown in Fig. 4. The amount of adsorbed water was about 60% lower for the surface functionalized gels than for the native gel, and the amount of remaining water at low pressures was also lower by about the same percentage. This difference cannot be explained by the mass increase (density) of the materials, as both the silane and zonyl contents were lower than 1 wt% in all studied cases, so the differences observed reflects the differences in water uptake, both by physisorption and chemisorption. The HMDS treated samples adsorbed slightly less water, but within a similar relative pressure range, as did the zonyl treated samples. The corresponding isotherms for gels pre-heat treated at 550 °C are shown in Fig. 5. The general shapes of the adsorption isotherm is similar as for the sample pre-heat treated at 250 °C, but the total water uptake is lower in all cases for the samples treated at higher temperatures. Furthermore, the water desorbed much more readily from these gels, as compared to the gels treated at lower temperatures. The hysteresis, especially at higher relative pressures, is much lower for the gels treated at 550 °C than for gels treated at 250 °C, suggesting that a lower amount of water is incorporated as hydration water into metal oxides and carbonates as compared to the corresponding carboxylates. This is also clearly seen in the smaller hysteresis in the low relative pressure-region. The HMDS treated gels appeared much more hydrophobic than the zonyl treated gels, and the total water adsorption of the HMDS treated gels was only one fourth of that of the zonyl treated gels.

The water sorption isotherms measured for gels derived from citric acid/formic-based sols pre-treated at 250 °C are shown in Fig. 6, and the corresponding isotherms measured for gels pretreated at 550 °C are shown in Fig. 7. The general shape of the water adsorption isotherms were similar for these gels as for the formic acid-based gels, but as seen in Figs. 6 and 7, zonyl treatment leads to a pronounced

Table 3 Characteristic values extracted from the water sorption isotherms for different heat-treated gels derived from sols containing 8 wt% of dissolved mineral. FA refers to formic acid and CA refers to citric acid

Sample	Drying T (C°)	Maximum adsorption (mg/g)	Desorbed water (mg/g)	Remaining water (mg/g)
3 M FA	550	208	144	64.7
	250	412	207	205
HMDS treated	550	60	34	26
3M FA	250	164	71	93
Zonyl treated	550	156	114	42
3M FA	250	213	101	112
3M FA +	550	194	118	77
5% CA	250	253	77	177
HMDS treated	550	62	23	40
3M FA + 5% CA	250	207	65	141
zonyl treated	550	75	69	5.9
3M FA + 5% CA	250	160	112	48
zonyl + HMDS	550	69	37	32
3M FA + 5% CA	250	194	74	120

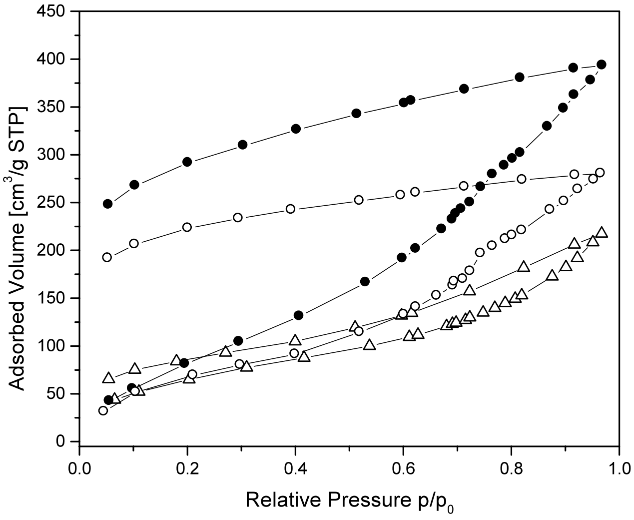

Fig. 6 Water sorption isotherms measured for native (●) HMDS (○) and zonyl treated (△) gels prepared from sols containing 8 wt% of mineral dissolved in 3 M formic acid and 0.16 M citric acid. The gels were heat-treated at 250 °C

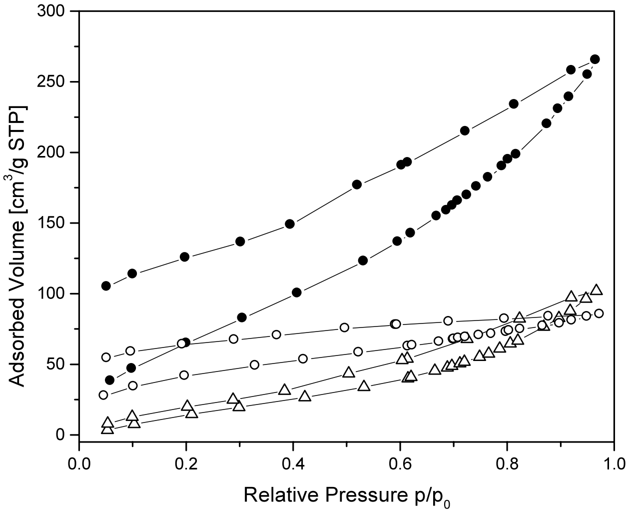

Fig. 7 Water sorption isotherms measured for native (●) HMDS (○) and zonyl treated (△) gels prepared from sols containing 8 wt% of mineral dissolved in 3 M formic acid and 0.16 M citric acid. The gels were heat-treated at 550 °C

decrease in the water adsorption, and also to a very small hysteresis. The HDMS treated gels on the other hand, still showed a pronounced hysteresis although the total water adsorption was clearly lower than that of the native gels. Thus, it appears that zonyl treatment is slightly more effective than HMDS treatment in reducing the water uptake for gels derived from citric acid containing sols, while HMDS was clearly more effective than zonyl for gels derived from formic acid-based sols. This observation seems to suggest that a larger fraction of the surface consists of silica in the latter case, while metal oxides play an important part in defining the surface characteristics for gels derived from citric acid/formic acid-based sols. This is again in good agreement with the previously observed higher metal oxide dispersion in gels derived from citric acid-containing sols (Puputti et al. 2008).

Finally, the much stronger influence of zonyl as compared to HMDS on the hydrophobicity of gels derived from citric acid/formic acid-based sols is also seen in contact an-

Table 4 Water contact angles measured for native and surface functionalized coatings made from sols containing 8 wt% of mineral dissolved in 3 M HCOOH and 0.16 M citric acid solutions

Contact angle (°)			
Heat-treatment temperature (°C)	HMDS	Zonyl® FSE	No surface functionalization
300	30	100	<5
350	35	110	<5
400	40	125	<5

gle measurements performed on films with a corresponding composition as the powder samples. The water contact angles measured for films heat-treated within the critical temperature range 300–400 °C, with or without further surface functionalization are shown in Table 4. Contact angles were also measured for films heat treated at temperatures lower than 300 °C, but the values were not stable due to dissolution of portion of the film being covered by the water droplet. The native films were all strongly hydrophilic, with contact angles below 5°. The contact angles increased upon HDMS treatment and with increasing treatment temperature to a maximum of 40° for the film treated at 400 °C, but the films must still be regarded as fairly hydrophilic. Zonyl treatment, on the other hand, made the films hydrophobic with contact angle values well above 100°. Also in this case higher contact angles were obtained with increasing film pre-treatment temperature. These findings suggest that decomposition of metal carboxylates indeed is a prerequisite for an efficient covalent binding of zonyl to the surface.

4 Conclusions

The humidity and water tolerance of a sol-gel derived binder prepared using a cheap, multicomponent precursor has been studied. A post-treatment temperature of 400 °C or higher is needed in order to achieve full binder stability under excess water conditions, as thermal decomposition of metal carboxylates is leading to a pronounced decrease in water solubility of the gels. Silanization, in the present case carried out using HMDS, or organophosphates can be used to hydrophobize the gel surface. HMDS is especially effective for the hydrophobization of gels derived from formic acid-based sols, and is an attractive surface functionalization agent as it can be processed through the gas phase. For gels derived from citric acid-containing sols, surface functionalization using an organophosphate or phosphonate appears to be slightly more effective than HMDS, most probably due to a higher fraction of the gel surface consisting of metal oxides and carbonates as in the case of the formic acid-based gels.

References

Angst, D.L.: Langmuir **7**, 2236 (1991)

Barret, E.P., Joyner, L.G., Halenda, P.P.: J. Am. Chem. Soc. **73**, 373 (1951)

Brunauer, S., Emmett, P.H., Teller, E.J.: J. Am. Chem. Soc. **60**, 309 (1938)

D'Andrea, S.C., Fadeev, A.Y.: Langmuir **19**, 7904 (2003)

Dollimore, D., Gupta, J.P., Novell, D.V.: Thermochim. Acta **30**, 339 (1979)

Fisher, A., Kuemmel, M., Järn, M., Lindén, M., Boissière, C., Nicole, L., Sanchez, C., Grosso, D.: Small **2**, 569 (2006)

Guerrero, G., Mutin, P.H., Vioux, A.: Chem. Mater. **13**, 4667 (2001)

Hon, Y.M., Fing, K.Z., Hon, M.H.: J. Eur. Cer. Soc. **21**, 515 (2001)

Marinova, K.G., Christova, D., Tcholakova, S., Efremov, E., Denkov, N.D.: Langmuir **21**, 11729 (2005)

Maslowska, J.: J. Thermal Anal. **29**, 895 (1984)

Mutin, P.H., Guerrero, G., Vioux, A.: C.R. Chim. **6**, 1153 (2003)

Nilsen, E., Einarsrud, M.-A., Puputti, J., Linden, M., Le Bell, J., Perander, M.: J. Sol-Gel Sci. Tech. **35**, 143 (2005)

Nilsen, E., Puputti, J., Linden, M., Le Bell, J., Perander, M., Einarsrud, M.-A.: J. Sol-Gel Sci. Tech. **26**, 1239 (2003)

O'Connell, C.A., Dollimore, D.: Thermochim. Acta **357–358**, 79 (2000)

Prasad, S., Vijayalakshmi, A., Gajbhiye, N.S.: J. Thermal Anal. **52**, 595 (1998)

Puputti, J., Nilsen, E., Einarsrud, M.-A., Le Bell, J., Perander, M., Linden, M.: J. Non-Cryst. Solids **342**, 59 (2004)

Puputti, J., Xu, Q., Lindén, M.: J. Sol-Gel Sci. Tech. **47**, 347–353 (2008). doi:10.1007/s10971-008-1785-1

Rouquerol, F., Rouquerol, J., Sing, K.: Adsorption by Powders and Porous Solids. Academic Press, San Diego (1999)

Schmidt, H., Jonschker, G., Goedicke, S., Mening, M.: J. Sol-Gel Sci. Tech. **19**, 39 (2000)

Silberzan, P., Leger, J.L., Ausserr, D., Benattar, J.J.: Langmuir **7**, 1647 (1991)

Tang, Q., Xu, Y., Wu, D., Sun, Y., Wang, J., Xu, J., Deng, F.: J. Control. Release **114**, 41 (2006)

Trammel, S.A., Moss, J.A., Yang, J.C., Nakhle, B.M., Slate, C.A., Odoble, F., Sykora, M., Erickson, B.W., Meyer, T.J.: Inorg. Chem. **38**, 3665 (1999)

Valor, A., Reguera, E., Torres-García, E., Mendoza, S., Sanchez-Sinencio, F.: Thermochim. Acta **389**, 133 (2002)

Vassileva, V.Z.: Thermochim. Acta **399**, 57 (2003)

Verma, R.K., Chandra, M., Bushan, A.: J. Thermal Anal. Calorim. **80**, 351 (2005)

Wasserman, S.R., Whitesides, G.M., Tidswel, I.M., Ocko, B.M., Pershan, P.S., Axel, J.D.: J. Am. Chem. Soc. **111**, 5852 (1989)

Wood, J., Sharma, R.: Langmuir **10**, 2307 (1994)