

## Nanoscaled Filled Sol-Gel Hybrid Materials for Powder Coatings

S. Sebeur, C. Danforth, J. Muhle, A. Poppe and H. Schmidt,  
Institut für Neue Materialien, Im Stadtwald, Geb. 43, D-66123 Saarbrücken, Germany

### Abstract

The sol-gel process has been applied for the synthesis of inorganic-organic powder materials. For this purpose, low reactivity and, for reasons of comparison, nanoscaled sol-gel precursors and nanoscaled silica filler were used to synthesize a low molecular weight inorganic-organic composite which was meltable between 85°C and 100°C and curable at temperatures of 150°C - 200°C. The powders were used for electrostatic coating of aluminum sheets. The resulting coatings of the unfilled system exhibited excellent mechanical properties, e. g. a high abrasion resistance (weight losses between 6 mg and 10 mg per 1000 cycles by taber abrader test (ASTM D1044)) and high values for hardness (universal hardness (DIN 55676): 150 N/mm<sup>2</sup>). The hardness of the materials was increased up to 210 N/mm<sup>2</sup> by the addition of silica, while the abrasion resistance remained unaffected.

### Introduction and State of The Art

Especially for applications where solvent emissions have to be avoided, powder coatings exhibit numerous advantages in comparison to solvent - born paints. Due to effective application processes and recycling of oversprayed powder, superior material efficiencies of nearly 100 % can be achieved for these systems. Generally, powder coating systems are divided into two different groups, thermoplastic powder coatings and thermosetting powder coatings. Because of technological constraints, the processing of the thermoplastic systems results in rather thick coatings (180µm - 200µm) [1]. Hence, this type of powder coating is used for applications where rather thick coatings are requested. Examples are coatings on consumer goods, such as wires, furniture or refrigerators. Typical thermoplastic powder coatings consist of polymeric materials, e. g. polyethylene, polypropylene and polyvinylchloride [1]. Thermosetting powder coatings are normally applied electrostatically resulting in coatings of a thickness around 50 µm. Typical fields of application are automotive coatings and architectural coatings. Common available thermosetting powder coatings are systems based on epoxy resins, polyester- and polyurethane systems [2]. Since only organic materials are used for thermosetting powder coatings, these materials exhibit mechanical properties not sufficient for many applications.

As it was shown elsewhere [3, 4], solvent - born inorganic-organic composites have been developed as scratch resistant coatings for polymers and metals. Very good results were obtained by incorporation of inorganic nanoparticles into the coating systems. Since, up to now, only organic powder coating systems have been available, the aim of this paper is to investigate routes for making remeltable sol-gel powders and the influence of nanoparticles on the mechanical properties of the coating materials. For this reason, precursors based on phenylsilanes are investigated, since they are able to form thermoplastic materials as described elsewhere [5,6].

## Experimental

The powder coatings under investigation were prepared by mixing 24.44 g (0.1 mole) Diphenyldimethoxysilane (DPDMS) and 24.63 g (0.1 mole) [ $\beta$ -(3,4-Epoxy)cyclohexyl]ethyl]trimethylsilane (ETMS) at room temperature. To this mixture, an aqueous solution of maleic acid (8.7 g (0.075 mole) maleic acid in 18 g deionized water) was added slowly at 0°C. In order to modify the properties of the powder coating, SiO<sub>2</sub>-nanoparticles (0 - 30.00 g (0 - 0.15 mole) Organosol<sup>®</sup>, a 30% solution of SiO<sub>2</sub> particles in 2-propanol) were optionally further added to the mixture of the silanes. After stirring the resulting solution at room temperature for at least 5h, the reaction was completed. The resulting polysiloxane was precipitated by adding the solution to an excess volume (400 ml) of water. The precipitate was isolated by filtration, washed several times with water and dried at 50°C under vacuum. The dried solid was ground in a lab scale mill and sieved employing an airstream sieve apparatus (separation of particles > 100 $\mu$ m), to yield the applicable powder. For coating, an electrostatically assisted spray gun system (Wagner-ESB, EPG 2020 CG) was used and transparent, dense coatings between 25  $\mu$ m and 40  $\mu$ m were obtained after melting at 85°C-100°C and curing at 150°C-200°C. As a substrate for the coatings, aluminum sheets (A199.5, AlMg3) were used. In order to investigate the liquid sol, <sup>13</sup>C-NMR and <sup>29</sup>Si-NMR spectroscopy (AC 200 spectrometer, Bruker) and FTIR spectroscopy (Bruker IFS 25) were employed. The viscous properties of the powders were examined by rheological measurements (Physica, cone-plate geometry).

## Results and Discussion

### Investigation of the unfilled system in the liquid phase by NMR-spectroscopy

The educts DPDMS, ETMS and maleic acid were chosen since it was expected to achieve a remeltable powder coating system. In comparison to other epoxy modified silanes, e. g. GPTMS, it was shown that ETMS can lead to applicable powder coating systems [7]. As a second condensable compound, DPDMS was used, because of its ability to form thermoplastic condensation products [5]. Thereby, it was assumed that the formation of three dimensional silicone networks is not promoted by DPDMS, in order to achieve remeltable materials. Maleic acid was used as a crosslinker for the curing process.

For the purpose of the investigation of the inorganic-organic materials by spectroscopic methods, the basic powder system comprised of ETMS, DPDMS and maleic acid without nanoscaled fillers was chosen. Thereby, the composition of the sol was the same as described above. This particular composition was used for the investigations, in order to avoid any influence of the filler on the spectroscopic data, the aim was to get an insight into the crosslinking process during the sol-gel process. All NMR investigations were performed in the liquid state, the sol was examined.

Since both, <sup>13</sup>C-NMR and <sup>29</sup>Si-NMR spectroscopy were applied, the organic compounds and the inorganic compounds were investigated separately. Here, the organic compounds serve as a starting point. The corresponding <sup>13</sup>C-NMR spectrum of the liquid sol is shown in Figure 1.

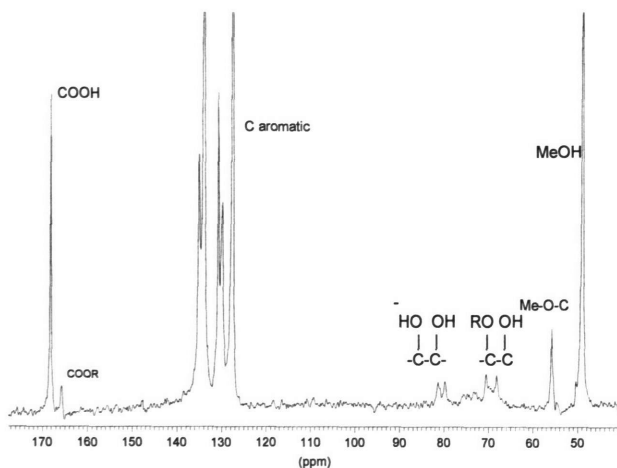


Figure 1:  $^{13}\text{C}$ -NMR spectrum of a sol synthesized from ETMS, DPDMS and an aqueous solution of maleic acid (0.1 mole ETMS, 0.1 mole DPDMS, 0.075 mole maleic acid in 1 mole deionized water).

Chemical shift	signal	assignment
50 ppm	singlet	MeOH
56 ppm	singlet	C-O-Me
68 - 72 ppm	doublet	-CH(OR)-
79 - 83 ppm	doublet	-CH(OH)-
125 - 137 ppm	multiplet	aromatic
166 ppm	singlet	-COOR
169 ppm	singlet	-COOH

Table 1: Results of the  $^{13}\text{C}$ -NMR investigation.

The spectrum exhibits no evidence for unreacted epoxy groups. Instead, signals from ring-opening products (methyl ethers, 56 ppm,  $\alpha$ -hydroxy ethers, 68-72 ppm, diols, 79 - 83 ppm) and those of the educts (maleic acid, 169 ppm) were detected. Besides the formation of diols and methoxy ethers, also the formation of ester groups (166 ppm) was found to take place to a small extent in the sol. From the signal intensities, it can be concluded that the major part of the maleic acid groups remained unreacted in the sol (as shown in figure 1).

Hence, it follows that in the sol, the organic compounds react only to a small extent, a precrosslinking takes place. The oxirane rings were opened rapidly in the acid medium (pH = 1) leading to addition products such as methoxy ethers and diols. In addition to this,  $^{29}\text{Si}$ -NMR spectroscopy was performed. Investigation of the results showed that the inorganic crosslinking process was not completed, but has been advanced to a great extent in the sol.

In conclusion, it was shown by  $^{13}\text{C}$ -NMR and  $^{29}\text{Si}$  NMR spectroscopy that the organic crosslinking process has only proceeded to a small extent while the inorganic crosslinking process was nearly complete.

### Investigation of the curing process by IR-spectroscopy

For crosslinking, the powder was heated for 30 minutes to  $200^\circ\text{C}$ . FT-IR-spectroscopy was used to investigate the uncured and the cured powder coating. The corresponding spectra of the basic system before and after curing are shown in Figure 2.

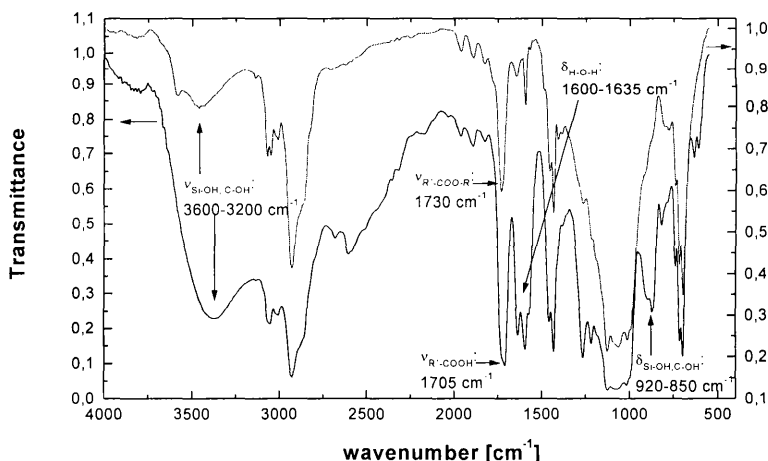


Figure 2: IR spectra of the basic powder coating (0.1 mole ETMS, 0.1 mole DPDMS condensed in an aqueous solution of 0.075 mole maleic acid in 1 mole deionized water) before curing (lower curve) and after curing (upper curve).

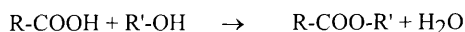
The spectrum indicates several different crosslinking processes. In order to interpret this, the most obvious differences of the spectra before crosslinking and after crosslinking are shown in table 2.

Wavenumber	assignment	intensity before curing	intensity after curing
850 - 920 cm-1	SiO-H, CO-H, deformation vibr., $\delta_{\text{SiO-H, CO-H}}$	strong	weak
1600-1635 cm-1	H-O-H deformation, $\delta_{\text{H-O-H}}$	strong	weak
1705 cm-1	C=O valence, vibr., $\nu_{\text{C=O}}$	strong, broad peak	weak
1730 cm-1	C=O valence vibr., $\nu_{\text{C=O}}$	middle, in the wing of the 1705 $\text{cm}^{-1}$ peak	strong, sharp peak
3200-3600 cm-1	SiO-H, CO-H, valence vibr., $\nu_{\text{SiO-H, CO-H}}$	strong	weak

Table 2: Results of the FTIR spectroscopy. The assignment of the peaks was performed following reference [8].

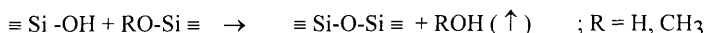
The most important crosslinking process is the conversion of free maleic acid into the corresponding esters as observed by the shift of the carbonyl vibration peak from

low wavenumbers ( $\nu_{C=O}$ , 1705  $\text{cm}^{-1}$ , corresponding to the free acid) to higher wavenumbers ( $\nu_{C=O}$ , 1730  $\text{cm}^{-1}$ , corresponding to an ester group) after the curing:



R:  $-\text{CH}=\text{CH}-\text{COOH}$  or other organic substituent R': methyl or ( $\alpha$ -hydroxy-cyclohexyl compound (diol)

Another process is the inorganic condensation of the hydroxysilyl groups which affects the most obvious difference between both spectra at high wavenumbers ( $\nu_{\text{SiO-H}}$  3200  $\text{cm}^{-1}$  - 3600  $\text{cm}^{-1}$ ). Also at lower wavenumbers ( $\delta_{\text{H-O-H}}$  1600  $\text{cm}^{-1}$ -1635  $\text{cm}^{-1}$   $\delta_{\text{SiO-H}}$  850  $\text{cm}^{-1}$  - 920  $\text{cm}^{-1}$ ), this process is observed:



It is evident from the results of NMR spectroscopy, that the same crosslinking processes have already taken place in the sol, but obviously they were not completed. From these results, it can be concluded that the use of DPDMS in combination with less reactive epoxy-functionalized silanes such as ETMS in sol-gel synthesis can lead to reactive and thus curable powder coating systems.

#### Thermal behavior of the powder coating

In rheological investigations the minimum melt viscosity of the unfilled powder system was determined to be 1-10 Pa  $\cdot$  s in the temperature range between 125°C and 135°C. The results of these investigations are shown in Figure 3.

The effect of nanoscaled silica fillers is twofold. First, the crosslinking temperature is shifted to lower values and second, the melting points are shifted to lower values. The origin of this influence is not clear yet. However, it is assumed that the large inner surface of the nanoparticles results in an adsorption of the acid groups on the fillers resulting in a decrease of the concentration of the hydrogen bridges in the network and a lower melting temperature. This model might give a reasonable melting temperature. Thus, the addition of nanoparticles reduces the organic precrosslinking and facilitates the melting process

After coating and curing the sol gel powder on aluminum sheets, the mechanical properties of the resulting coating were checked by various tests. Besides an excellent primerless adhesion, which was proven by tape test (ASTM D3359, grade 4B/5B) and cross cut: 0/1 (DIN EN ISO 2409), good values for the abrasion resistance were obtained: the taber abrader test (ASTM D1044) yielded weight losses between 6 mg and 10 mg per 1000 cycles. As shown elsewhere [9], the surface hardness of composite coatings can often be adjusted by the addition of  $\text{SiO}_2$  nanoparticles. For the system, an increase of the hardness was achieved by adding  $\text{SiO}_2$  nanoparticles. Best results were obtained at a content of 15 mole % of the additive, yielding values for the universal hardness (DIN 55676) of 210  $\text{N/mm}^2$  (in comparison to a commercial powder : 180  $\text{N/mm}^2$ ), while the abrasion resistance remained unaffected, which was witnessed by taber abrader tests (ASTM D1044) yielding weight losses between 6 mg and 10 mg per 100 cycles.

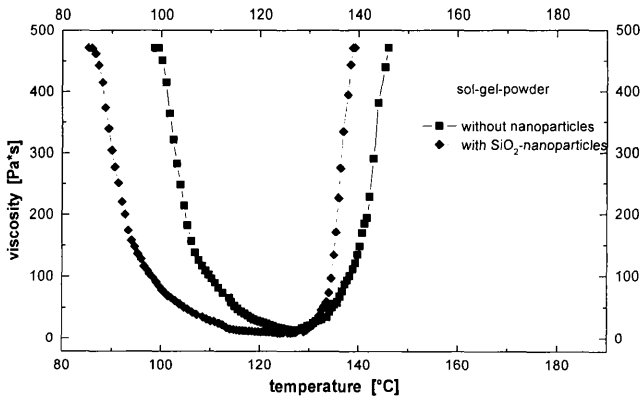


Figure 3: The viscosity of two different powder coating systems, without nanoparticles (0.1 mole ETMS, 0.1 mole DPDMS, 0.075 mole maleic acid in 1 mole deionized water) and with nanoparticles (0.1 mole ETMS, 0.1 mole DPDMS, 0.075 mole maleic acid in 1 mole deionized water and 30g Organosol<sup>®</sup>), plotted versus temperature.

## Conclusion and Outlook

In this work, it has been shown that inorganic-organic powder coatings can be obtained via the sol-gel process employing the educts ETMS and DPDMS in combination with the crosslinking additive maleic acid. By condensation and ester formation, these materials build a three dimensional inorganic-organic network at elevated temperatures (150°C-200°C). The systems can be filled by nanoscaled silica particles resulting in powders which exhibit after application excellent values for hardness. The results give strong evidence that the mechanical properties of the sol-gel powder coatings can be tailored by the addition of these particles. Further systematic investigations of the influence of silica and other nanoparticles on the mechanical properties of the coatings will be a topic of future research work.

## References

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