

Aqueous wet coatings for transparent plastic glazing

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Abstract

Electrostatically stabilized particulate sols, e.g. aqueous silica or alumina sols, have been surface-modified to reduce the particle/particle interaction and to obtain electrosterically stabilized sols. Epoxy functionalized alkoxy silanes were used as surface modifiers for alumina, silica or zirconia particles to achieve water dispersible nanoparticulate coating materials. After evaporating the organic solvent (produced by hydrolysis and condensation) aqueous sol-gel coatings have been prepared with organic solvent contents below 5%. The storage stability of these materials has been investigated by ²⁹Si-NMR. An amino functionalized alkoxy silane was used as condensation catalyst and the nanocomposite material was thermally cured at 130°C after flow or spray coating on pretreated polycarbonate substrates. The coatings show excellent adhesion which was shown by cross cut and tape test. After 1000 cycles Taber abrasion test (CS-10F, 500 g, DIN 52347) losses of transmittance due to scattering of 2–6% were achieved with a coating thickness of about 5 μm.

Keywords: Coatings; Silane; Silicon oxide; Water; Wetting

1. Introduction

Nanocomposite coating materials prepared by the sol-gel process are usually solvent based systems due to the typical sol-gel reaction conditions and have been successfully used in large scale coating technologies for transparent plastics [1–9]. Typical solvents in the coating systems are methanol and ethanol, which are not desired for ecological, health and safety reasons. To improve the environmental soundness of the process a new basis technology based on a sol-gel processing route has been developed by incorporating electrosterically stabilized particles in a nearly solvent free sol-gel-based matrix system as described in [10].

In order to bring these results into an application, the storage stability of the water based material was investigated, performing ²⁹Si-NMR and viscosity measurements. It was also of interest to examine if other particles than SiO₂, such as boehmite with an average diameter of about 10–15 nm, could be incorporated as well.

2. Experimental

The preparation scheme of the material is given in Fig. 1.

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Commercially available nanoscaled particulate sols (for example Bayer Levasil[®] 200S, Condea Disperal[®] Sol P3 in 0,1 mol/l HCl, Nissan IP-AST) were treated with GPTES (glycidyoxypropyl-triethoxysilane) by stirring at ambient temperature for 5 h.

Besides the surface modification of the nanoscaled particles, the hydrolysis and condensation of GPTES was achieved by adding 0.01 to 0.1 mol/l HCl in a molar ratio of 1.5 mol HCl/mol GPTES at room temperature for 24 h. After mixing the two components, the solvent (ethanol) produced by the hydrolysis and condensation of the silane was evaporated at a pressure of 60 mbar and a temperature of 30–40°C, until the content of residual ethanol was about 5 wt.%.

Approximately 5 mol.% of DIAMO (2-aminoethyl-3-aminopropyltrimethoxysilane) referring to GPTES were added before coating the substrates in order to catalyze the inorganic and organic polymerization. Finally, wetting agents were added to improve the wetting behavior of the sol and the optical quality of the coating.

Polycarbonate substrates (Makrolon[®] 2808) were plasma-treated (O₂-Plasma, 200 mbar) and then coated by spin coating at 200–1200 rev./min.

²⁹Si liquid NMR measurements were recorded with a multicore NMR spectrometer (BRUKER). The ζ-potential measurements were carried out with a MALVERN zetasizer 4 by titration with NaOH.

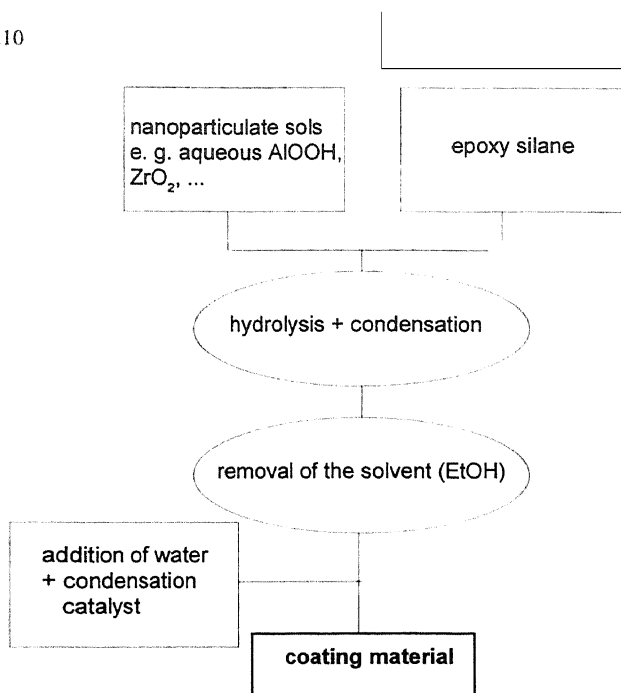


Fig. 1. Preparation scheme of the synthesis of the coating material.

3. Results

Silica containing coating material was prepared using Bayer Levasil 200S as nanoscaled particles. To investigate the storage stability of this coating material at room temperature, ^{29}Si -NMR measurements were carried out from 10–700 h after the preparation. Fig. 2 shows the ^{29}Si -NMR spectra after 10, 200 and 700 h storage time. The degree of condensation (percentage of built Si—O—Si bonds compared to the theoretical maximum) was calculated out of these spectra. Fig. 3 shows that the degree of condensation first increases starting at 45%, reaches 80% after about 500 h and then stays constant. The evaluation of the distribution of the T -groups with time, is plotted in Fig.

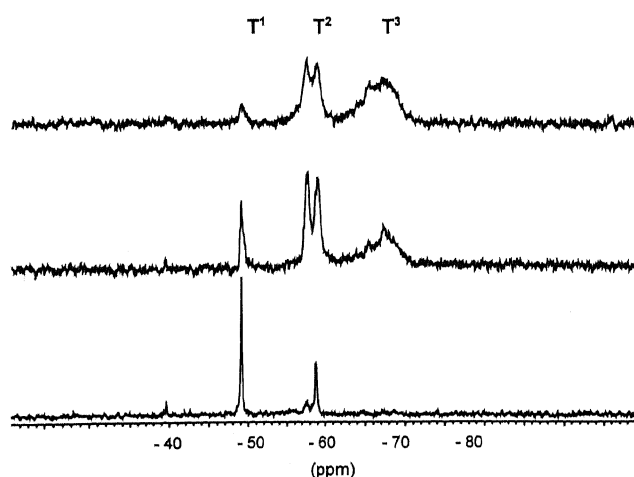


Fig. 2. ^{29}Si -NMR of the solvent free coating material after 10 h (below), 200 h (middle) and 700 h (above) of storage time at room temperature.

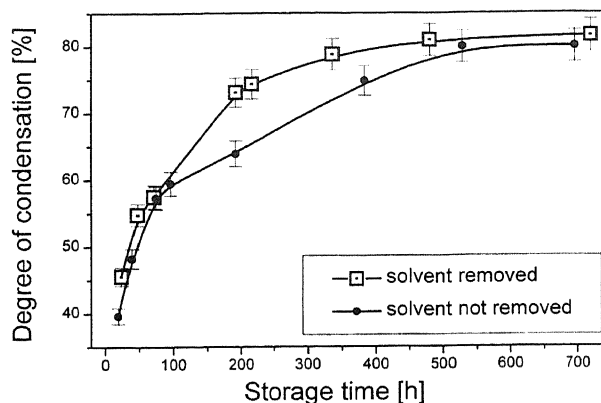


Fig. 3. Degree of condensation of the solvent free coating material in comparison to the solvent containing material versus storage time at room temperature. The lines are drawn as a guide for the eye.

4. In the first 70 h the amount of T^2 increases strongly, while the amount of T^1 decreases. Due to the condensation process ethanol and water are released, which explains that the viscosity decreases in that time (Fig. 5). After about 70 h the amount of T^3 begins to increase, which means that a three-dimensional crosslinking of the GPTES occurs. Therefore the viscosity of the coating material begins to raise too. After a storage time of 700 h, the viscosity of the nearly solvent free material has increased from 36 to 57 mPas, which was still in a range suitable for application. No gelation occurred until at least three months storage time at room temperature.

The surface modification of nanoscaled silica particles has already been described in [10]. In the same way it was tried to modify boehmite nanoparticles (Disperal Sol P3 in 0,1 mol/l HCl, average diameter about 10 nm). In order to proof the surface modification of the boehmite nanoparticles, ζ -potential measurements were performed in a range of about pH2 to pH11. It is shown that the isoelectric point (ip) of the boehmite sol (electrostatic acid stabilization) shifts from about 10.1 to 8.8 (Fig. 6). This is due to the

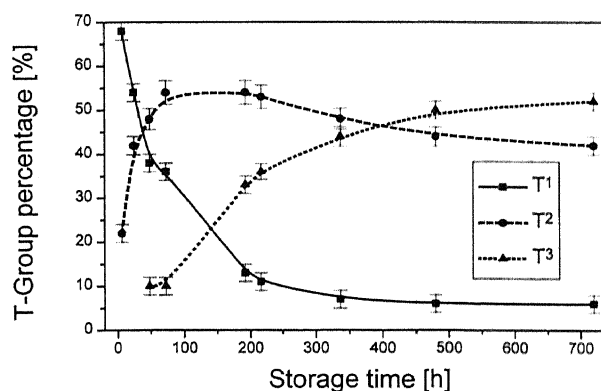


Fig. 4. Evaluation of the T -group share on the degree of condensation of the solvent free coating material versus storage time at room temperature. The lines are drawn as a guide for the eye.

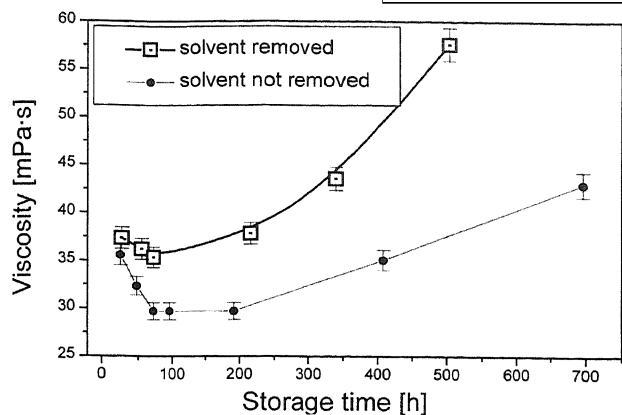


Fig. 5. Viscosity of the solvent free coating material in comparison to the solvent containing material versus storage time at room temperature. The lines are drawn as a guide for the eye.

adsorption of GPTES molecules on the surface of the boehmite nanoparticles. By this surface modification the electrostatic stabilization is replaced by an electrosteric stabilization, which leads to a better compatibility of the particles with the sol-gel matrix system.

The clear transparent coatings prepared with the silica containing materials were cured at 130°C for 2 h and showed excellent optical properties and abrasion resistance. The adhesion according to cross cut and haze test was excellent (cc/tt 0/0 DIN EN ISO 2409). After 1000 cycles of Taber abrasion test (500 g load, CS10F wheels, DIN 52347) the increase in haze was only 2–6% for a coating thickness of about 5 μm . The refractive index of the coating was determined by spectral ellipsometry. The value depends on the content and kind of nanoparticles and is 1.50 for a silica content of 20 wt.%.

4. Conclusion

The surface treatment of nanoscaled SiO_2 or boehmite with silanes like epoxyfunctionalized silanes provides a way to alter the stabilization mechanism of the particles from electrostatic to electrosteric stabilization and therefore

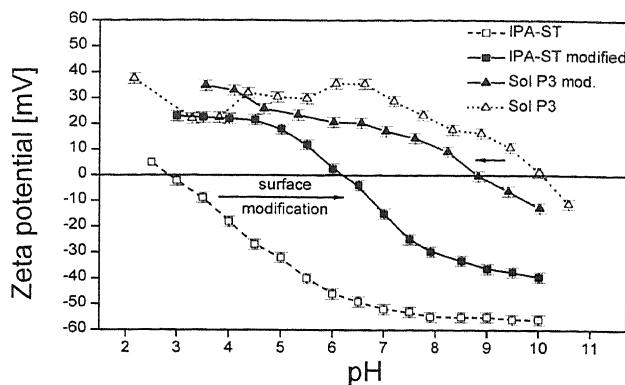


Fig. 6. Zetapotential measurements of IP-AST and Disperal Sol P3 in 0,1 mol/l HCl with and without epoxy silane particle surface modification. The lines are drawn as a guide for the eye.

opens the opportunity to achieve water based organic-inorganic nanocomposite coating materials with solvent contents lower than 5 wt.%. The storage stability of the materials is at least 1 month, in which time the viscosity of the coating materials is in a suitable range for application. The transparent hard coatings show an abrasion resistance comparable to solvent based systems. This technique could set up new fields for sol gel materials, especially in large area applications.

References

- [1] B. Wang, G.L. Wilkes, US 5,316,855: 31.5.94.
- [2] J. Zarzycki, J. Sol-Gel, Sci. 8 (1997) 17.
- [3] J.S. Humphrey Jr., US 4,188,451: 12.2.80
- [4] J. Wen, K. Jordens, G.L. Wilkes, Mater. Res. Soc. Symp. Proc. 435 (1996) 20713.
- [5] K. -H. Haas, S. Amberg-Schwab, K. Rose, E. Schottner, GAK 2 (1997) 102.
- [6] G. Philipp, H. Schmidt, DE 3,407,087: 27.3.86.
- [7] E. Takeuchi, JP 05,306,339.
- [8] B.A. Ashby, US 4,390,660: 28.6.83.
- [9] R. Kasemann, H. Schmidt, E. Arpac, V. Gerhard, DE 4,338,361 A1: 11.05.95.
- [10] H.K. Schmidt, E. Arpac, H. Schirra, S. Sepeur, G. Jonschker, Mater. Res. Soc. Symp. Proc. 519 (1998) 297.