Preparation of polymer-derived ceramic coatings by dip-coating

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Abstract. Polysilazane-based coatings were prepared on dense and porous substrates by dip-coating. Both the pure, liquid polymer and polymer solutions in cyclohexane were investigated. Relevant properties of the coating solutions, including rheological properties and surface tension, were determined and used to predict the resulting layer thickness as a function of dip-coating parameters on dense borosilicate glass substrates. A good correlation between existing model (Landau and Levich) and experiment was found for the pure polymer. In the presence of a solvent, evaporation phenomena led to a predicted coating thickness that is much less than the experimental value for all dip coating withdrawal spends. The introduction of a correction factor was found to adequately describe the deviation. In case of porous substrates, the coating thickness could not be predicted using the model due to infiltration of the base structure, resulting in an interpenetrating ceramic composite layer after pyrolytic conversion of the preceramic polymer compound. When preparing polymer-derived ceramic films on porous base materials, e.g. for membrane applications, this phenomenon has to be taken into account.

Introduction

Ceramic coatings present a way to tailor the surface of a material to a specific application by providing additional mechanical, chemical, or functional properties. Recently, an increased interest in ceramic coatings has emerged in energy- and sustainability-related fields, with proposed applications ranging from thermal barrier coatings and environmental barrier coatings to membranes [1-3].

Generally, ceramic coatings are generated either via the gas phase using chemical vapor deposition (CVD) or physical vapor deposition (PVD), or by plasma-assisted spraying techniques. However, these methods require significant instrumental and financial expenditure. As an alternative, the use of preceramic polymers as precursors to ceramic coatings has been investigated in recent years [4]. In this approach, Si-containing polymers are generally used as precursors to obtain oxide or non-oxide ceramics through a controlled thermal decomposition step (pyrolysis). Some examples of starting precursors include polysiloxanes, polysilazanes or polycarbosilanes, used as precursors for Si-O-C-, Si-C-N, or Si-C-based ceramics, respectively [5]. Since the majority of precursors are either well soluble in a wide range of solvents or even liquid at ambient temperature, inexpensive coating techniques such as spray-coating or dip-coating can be used with relative ease.

Most reports dealing with polymer-derived ceramic coatings focus on their deposition on dense substrates, primarily used as thermal or environmental barrier coatings [6-11]. However, some applications, specifically in the field of membrane science, require the deposition of continuous polymer-derived ceramic layers on porous substrates [12,13].

This paper focuses on the systematic approach for the generation of thin layers of controlled and predictable thickness of polysilazane precursor on dense and porous substrates via a dip-coating approach. The objective of this work is the evaluation of rheological characteristics of the polymer or polymer solutions, a correlation between dip-coating parameters and subsequent layer morphology and thickness, and finally the evaluation of the deposition of preceramic polymer layers on porous substrates with subsequent pyrolytic conversion.

Materials and Methods

The preceramic polymer used in this work was a poly(vinylsilazane) (*PVS*; KiON HTT 1800, AZ Electronic Materials, USA), which is a colorless, low-viscosity liquid with a nominal structural composition as shown in Fig. 1. After thermal cross-linking, generally conducted at temperatures up to 300 °C, PVS can be converted into an amorphous Si-C-N-(O) ceramic upon controlled thermal conversion in inert atmosphere at 800 °C [5]. Due to its sensitivity towards moisture, handling of the polymer was conducted in inert atmosphere using either a glove box or a dry nitrogen flow. PVS was used either in pure form or as a solution in cyclohexane (50 Vol.%). In both cases, dicumyl peroxide was added as cross-linking promotor (1 wt.% with respect to PVS).
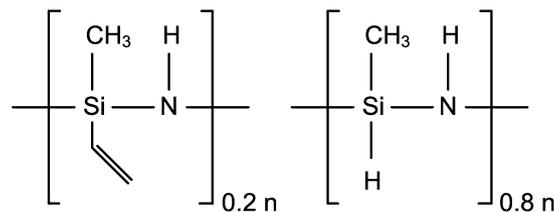

Fig. 1: Nominal structure of poly(vinylsilazane) used in this study.

Rheological investigations were carried out at 25 °C using a cone-plate rheometer setup (HADV-III Ultra C/P, Brookfield, USA). The surface tension of the liquids was determined using a dynamic contact angle analyzer (DCA 322, Cahn Instruments, USA) employing the Wilhelmy method [14]. The standard probe consisted of a platinum wire with a 220 µm cross-sectional diameter which had been cleaned in acetone and in an oxidizing flame. The surface tension of the liquid, σ, was calculated from the Wilhelmy equation:

$$F = \sigma P \cos \theta. \tag{1}$$

In this equation, F is the wetting force, P the probe perimeter, and θ the contact angle on the platinum wire which was assumed to be $\theta = 0°$ [15] because of the high surface energy of platinum resulting in complete wetting.

Borosilicate glass slides were used as dense model substrates for dip-coating. The substrates were ultrasonicated in acetone for 5 min, rinsed with acetone and isopropanol, and dried before dip-coating. Dip-coating was generally conducted by immersing the substrates into the respective coating solution at a speed of 200 mm min^{-1}, holding them in the solution for 1 s, and withdrawing them at various speeds ranging from 10 mm min^{-1} to 200 mm min^{-1}.

After coating, the glass slides were horizontally placed into a furnace, and the PVS films were thermally cross-linked in flowing nitrogen (105 °C, 16 h). The coating thickness of cross-linked films was determined by surface profilometry (Alpha-Step IQ, KLA-Tencor, USA), an average calculated from 5 profile runs per specimen.

As porous substrates, commercially available ceramic filters made of ZrO_2/TiO_2 with a nominal top layer pore size of 200 nm were used (Sterlitech, USA). Dip-coating was conducted in the same manner as the coating on glass slides. The coated substrates were placed into a tube furnace (Lindberg Blue M HTF5534C, Thermo Scientific, USA) and heat treated in high-purity flowing nitrogen at a temperature of 800 °C for a duration of 4 h, with a maximum heating rate of 1 K min^{-1} and an isothermal hold at 130 °C for 2 h for cross-linking.

The morphology of the obtained coatings was evaluated by scanning electron microscopy (*SEM*, S4800, Hitachi, Japan).

Results and Discussion

Rheological characteristics. In order to evaluate and predict the dip-coating performance, the rheological characteristics of the coating liquids have to be known. Results of rheometry studies showed a linear relationship between shear rate and shear stress for both PVS and PVS dissolved in cyclohexane (Fig. 2). This is an indication for Newtonian behavior of the liquids in the shear rate range investigated, which includes typical shear rates encountered in dip-coating applications (10 s^{-1} to 100 s^{-1}, [16]). From the results of the shear stress as a function of shear rate, viscosity can be calculated as a function of the shear rate (Fig. 2). The results of rheometric investigations as well as the determination of the surface tension are listed in Table 1.
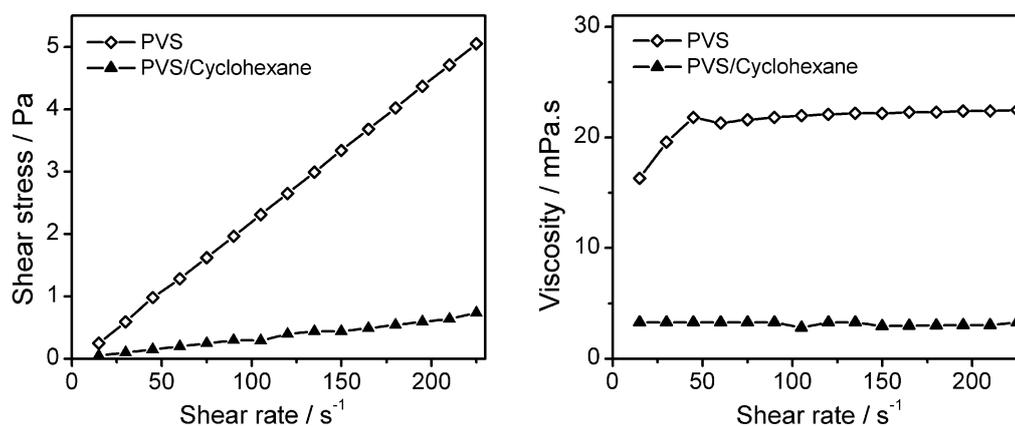

Fig. 2: Shear stress and viscosity of PVS and PVS/cyclohexane (50 Vol.%) as a function of shear rate.

Table 1: Average viscosity, surface tension, and density of coating solutions

	PVS	PVS/Cyclohexane (50 Vol.%)
Viscosity μ, 25 °C [mPa s]	21.5	3.2
Surface tension σ [mN m^{-1}]	25.4	24.9
Density ρ [g cm^{-3}]	1.05	0.92

Dip-coating on dense substrates. Dip-coating experiments on borosilicate glass slides were carried out to evaluate the influence of the withdrawal speed on the resulting thickness of cross-linked PVS layers. The layer thickness was determined using profilometry (Fig. 3). As expected, an increase in PVS layer thickness was observed with increasing withdrawal speeds. The height profiles show that a stationary coating regime is reached after an initial transition region, spanning 2-3 mm from the top boundary of the coating. After this, layers with constant thickness were formed. An exception was found when dip-coating with solvent-free PVS at the maximum withdrawal speed (200 mm min^{-1}), where a steadily increasing layer thickness was observed. This was most likely caused by the high amount of liquid present on the substrate in this case, and subsequent flow processes during withdrawal and/or cross-linking as a result of imperfect horizontal orientation.
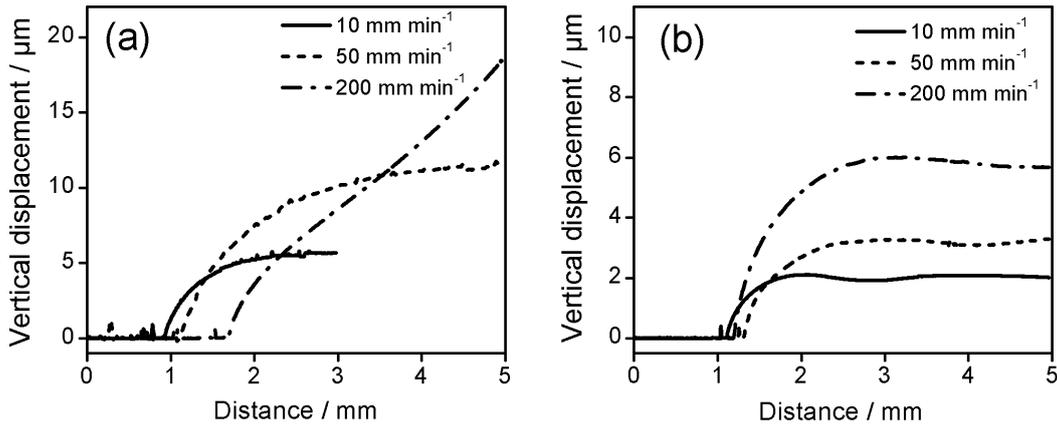

Fig. 3: Typical height profiles of cross-linked PVS layers on glass substrates as a function of withdrawal speed during dip-coating; (a) PVS, (b) PVS dissolved in cyclohexane (50 Vol.%). A vertical displacement of 0 corresponds to the uncoated surface of the glass slide.

The prediction of the coating behavior for a particular system is of interest to achieve a predictable control of the resulting coating thickness. A widely used model to predict the thickness of layers after dip-coating with Newtonian fluids was proposed by Landau and Levich [17], (eq. 2):

$$h_0 = 0.944 \left(\frac{\mu U}{\sigma} \right)^{\frac{1}{6}} \left(\frac{\mu U}{\sigma g} \right)^{\frac{1}{2}}.$$

(2)

In this relationship, the film thickness h_0 is a function of the viscosity μ, the withdrawal speed U, the surface tension of the liquid σ, the acceleration of gravity g, as well as the density of the dip-coating liquid ρ. The model was applied to calculate the layer thickness as a function of withdrawal speed for PVS and PVS/cyclohexane solutions, using the determined parameters listed in Table 1. For PVS/cyclohexane, the obtained model values were further corrected for the volume fraction of the solvent (50 %), assuming a complete evaporation of the solvent and an equivalent reduction in

layer thickness by 50 % (Fig. 4). Furthermore, the layer thickness was assumed to be unaffected by the cross-linking step.
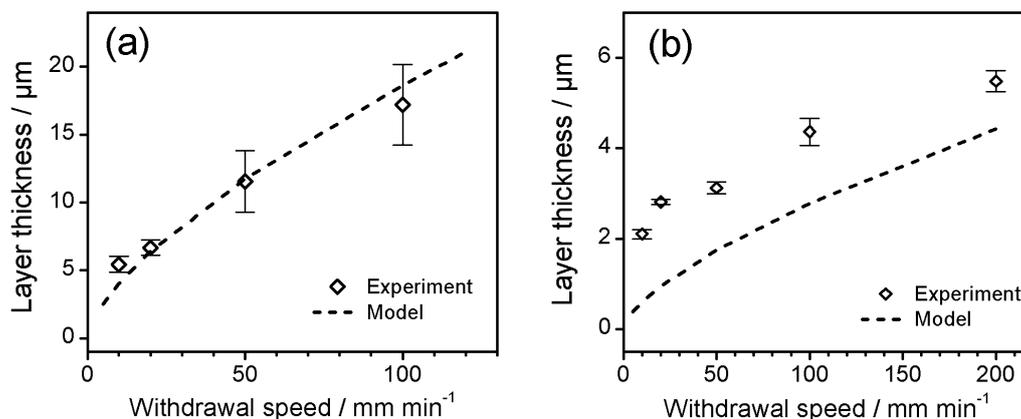

Fig. 4: Thickness of cross-linked PVS layers on glass slides as a function of withdrawal speed during dip-coating for (a) PVS or (b) PVS/cyclohexane as coating fluids. The dashed lines represent theoretical layer thicknesses as predicted by the Landau-Levich model (eq. 2).

For solvent-free PVS, a good fit between experiment and model was achieved up to withdrawal speeds of 100 mm min^{-1}. No evaluation was possible for 200 mm min^{-1} as a result of the heterogeneous coating thickness (see Fig. 3a).

In contrast, for PVS/cyclohexane solutions, the resulting layer thicknesses are significantly higher than the thickness predicted by the classical Landau-Levich approximation. This phenomenon can be explained by evaporation of the solvent, which had been reported to be of crucial importance when investigating dip-coating processes [18]. However, modelling of this phenomenon is mathematically demanding. Yimsiri and Mackley [19] proposed the introduction of an arbitrary viscosity μ_{arb} of the coating solution, increasing with evaporation of the solvent. μ_{arb} is not equivalent to the actual viscosity in the coating solution, but is used as a tool to account for evaporation-dependent changes in the formed layer, such as increases in viscosity and concentration. The introduction of μ_{arb} when evaluating the PVS/cyclohexane system yielded a better-suited model for the prediction of the layer thickness (Fig. 5). In this case, equation 2 is modified by replacing μ with μ_{arb}. It was found that in the parameter range observed, the arbitrary viscosity term can be adequately approximated by the relationship $\mu_{arb} = a\,U^b$, a and b being fitting parameters. In our case, the fitting parameters $a = 71.34$ and $b = -0.526$ were found suitable (still assuming a reduction of the film thickness by 50 %).

The arbitrary viscosity was found to approach the actual viscosity of the PVS/cyclohexane solution (3.2 mPa s) at high withdrawal speeds, indicating a decreased effect of evaporation phenomena as expected. μ_{arb} increases with decreasing withdrawal speeds and reaches the range of the viscosity of the solvent-free PVS component at a withdrawal speed of 10 mm min^{-1}.
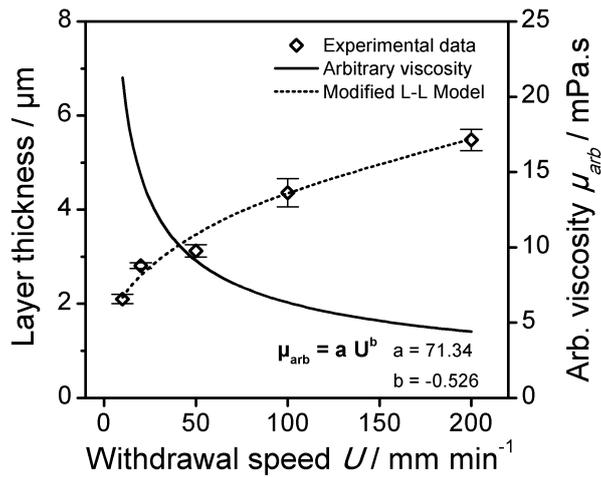
Fig. 5: Experimental and model data of the layer thickness of cross-linked PVS layers from PVS/cyclohexane solutions (50 Vol.%) as a function of withdrawal speed. An arbitrary viscosity term was introduced to modify the Landau-Levich model to account for withdrawal-speed dependent phenomena such as evaporation.

Up to this point, only the thickness of cross-linked preceramic polymer films has been considered. Several further considerations have to be taken into account when converting the deposited polymer films into ceramic coatings through pyrolysis. A combination of mass loss and density increase causes significant shrinkage of the preceramic polymer during pyrolytic conversion. In the case of the PVS used, linear shrinkages of up to 25 % have been observed [20]. As a result, the layer thickness can be expected to significantly decrease during pyrolytic conversion. Furthermore, the preparation of filler-free polymer-derived ceramic coatings is limited to a critical thickness of a few micrometers, above which crack formation can be observed as a result of internal stress build-up [10]. Thicker coatings have been achieved by the introduction of inert or active filler particles [6,7].

Dip-coating on porous substrates. The coating behavior of PVS films on porous substrates was investigated with commercially available ceramic filters as base materials. The filters, consisting of a TiO_2/ZrO_2 composite, show an asymmetric pore structure (Fig. 6 a and b). A base layer with coarse pores acts as mechanical support, and is covered with an intermediate layer with pores in the size range of 1 μm to 2 μm, as well as a top-layer with a nominal pore size of 0.2 μm and a thickness of 5 μm.

Based on the dip-coating characteristics discussed in the previous chapter, withdrawal speeds were selected to achieve a film thickness of 4-5 μm in cross-linked state, assuming a dense substrate. This corresponded to withdrawal speeds of 20 mm min^{-1} for pure PVS and 100 mm min^{-1} for the PVS/cyclohexane solution, respectively.

Dip-coating of the porous substrates resulted in the formation of an interpenetrating composite layer consisting of the formerly porous top layer of the filter and the PVS-derived ceramic compound (Fig. 6 c-f). Instead of forming an isolated film on top of the substrate, the porous structure was infiltrated by the coating solutions. The infiltration depth was higher for samples coated with PVS/cyclohexane, reaching up to 20 μm. A possible explanation is the significantly lower viscosity of the PVS/cyclohexane solution, promoting infiltration. Even though small cracks and pores can be found in the formed composite layer, no continuous cracks across the coating can be observed, resulting in a densified top layer.

If required by the intended application, several methods can potentially be applied to facilitate the formation of an isolated coating on top of the porous substrate. Increasing the coating solution viscosity may deter infiltration phenomena. Furthermore, the application of masking techniques, using a fugitive pore filler such as wax before coating, have been applied successfully [21].
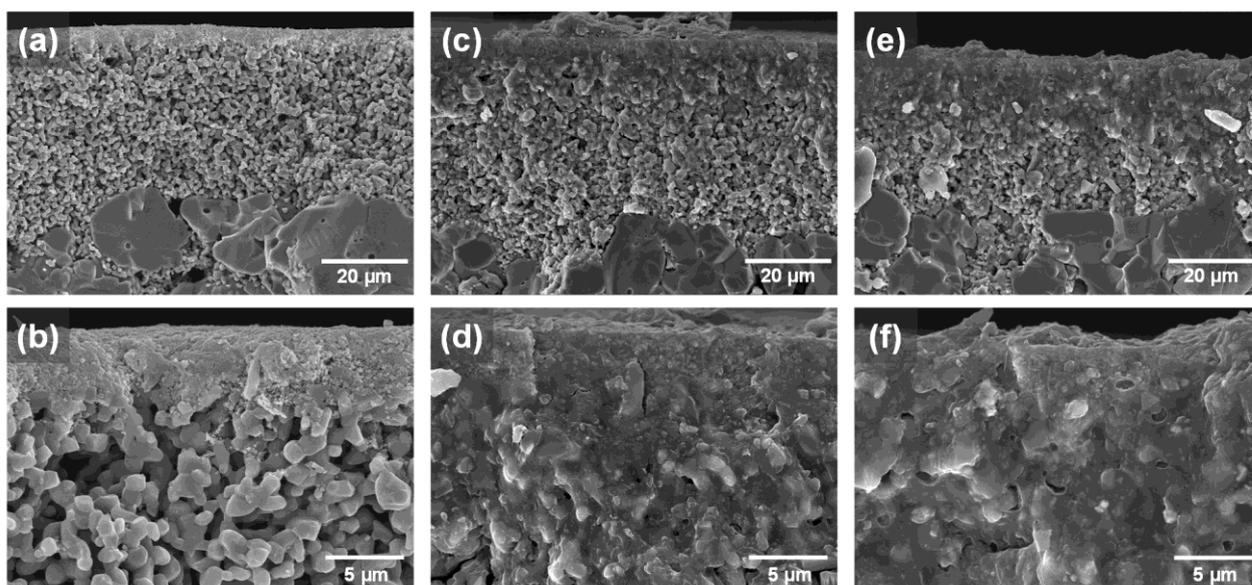
Fig. 6: Cross-sections of porous substrates before coating (a,b), and of substrates coated with PVS (c,d) or PVS/cyclohexane (e,f) after pyrolytic conversion. The infiltration of the porous top layers by the PVS component is clearly visible.

Conclusions

The experimentally measured coating liquid characteristics such as surface tension and viscosity can be used to adequately predict the coating thickness of polyvinylsilazane-based films on dense substrates. A good correlation between experimentally determined coating thicknesses and thicknesses predicted by the Landau-Levich model is observed for the pure polymer. However, solvent evaporation has to be taken into account when modelling the dip-coating process for solvent-containing coating solutions, specifically when using solvents with high vapor pressure such as cyclohexane. In this case, the deviation from the Landau-Levich model was found to be inversely related to the withdrawal speed. Low withdrawal speeds resulted in thicknesses significantly higher than expected. The introduction of a correction factor was found to suitably describe the deviation behavior, thus facilitating prediction of the coating thickness within the range of experimental investigation.

When considering the coating of porous substrates, substrate infiltration was found to result in significantly different coating morphologies. If the formation of isolated, dense films on top of the porous base materials are desired, precautions have to be taken to inhibit the flow of the coating liquid into open pores during and after the coating process. Possible approaches for this include increasing the coating liquid viscosity, or using masking techniques to fill the substrate pores with easily removable filler (e.g. wax).

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