Simultaneous Stress and Weight Measurements for Particulate Films Made from Capillary Suspensions

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Introduction

In an increasingly connected world, moving towards the Internet of Things, cheap and flexible electronic devices such as radio frequency identification (RFID) tags have been gaining interest [1]. Printing techniques, for example screen printing, is a well-known and low-cost method to realize electronic circuits. Additives, in the form of surfactants and binders, for instance, are usually added to the paste in order to meet the specific demands of the circuits, such as crack free films, and tune the rheological properties for better printing results. To prevent agglomeration of the suspended particles, surfactants that sterically stabilize the particles are added. Binders on the other hand, adjust the flow properties and prevent cracking. The drawback of these additives is the fact that a conductive circuit requires a connected, flocculated network. Therefore, another processing step is required to remove the additives after drying as well as partially sintering the particles together. High temperature curing represents a conventional technique accomplishing the task at hand. This crucial step can be limited in temperature, however, by the use of polymeric substrates that have low glass transition temperatures. Different conductive ink formulations can drastically change the curing temperature to relatively low levels [2].

One approach to tackle cracking and particle mobility during the drying of hard particle suspensions is by using capillary suspension-based formulations [3]. In the pendular state, the preferentially wetting secondary fluid forms capillary bridges between the particles. The capillary force from such bridges induces the formation of a sample-spanning particle network [4, 5], which limits the direction of particle motion during film drying. This capillary bridging force also counters the capillary force within pores generated by evaporation. Crack-free films can be produced at thicknesses much greater than the critical cracking thickness for a suspension without capillary interactions, and even persists after sintering [3]. This method is applicable to a broad range of materials and can be easily implemented using well-established industrial methods. Additionally, the advantage of this approach is that organic additives are not needed to prevent cracking or tune the flow properties of the pastes. The phenomenon of reduced film cracking is attributed to lower drying stresses. This work focuses on the simultaneous stress and weight measurements of capillary suspension films at various drying conditions.

Experimental

The underlying mechanisms of coating drying is a complex process influenced by various factors. In order to reduce the complexity, boundary conditions need to be imposed. We achieved this by designing and building a temperature and humidity controlled chamber. Humidity is a factor that influences the steady state drying conditions and thus the drying velocity of the films. Humidity is controlled by mixing the saturated stream with the required ratio of dry air to attain the desired relative humidity in the drying chamber. To keep the influence on enhanced drying through air flow to a minimum, a low total flow rate of 8 liters per minute was used throughout the experiments. Different techniques exist to measure the stresses in films. Our custom built stress measurement apparatus uses the cantilever deflection method to determine stresses within the tape cast film [6]. As sketched in **Figure 1,** the cantilever fixture is suspended from an analytical balance, which makes the drying rate of the same film accessible in a simultaneous measurement. The film shrinks as a result

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of the stresses during the drying process and the adhesion of the particles to the cantilever substrate cause it to bend. This deflection is measured using a position sensing detector (PSD).

The capillary suspensions in this paper were prepared using Al_2O_3 particles, 1-heptanol as the bulk phase, and water as secondary phase. Additionally, to change the vapor pressure ratio of the bulk and the secondary liquid, glycerol is substituted for water. The shear moduli of the pastes were varied by modifying the secondary fluid content. Experiments were carried out under different temperatures and relative humidities.

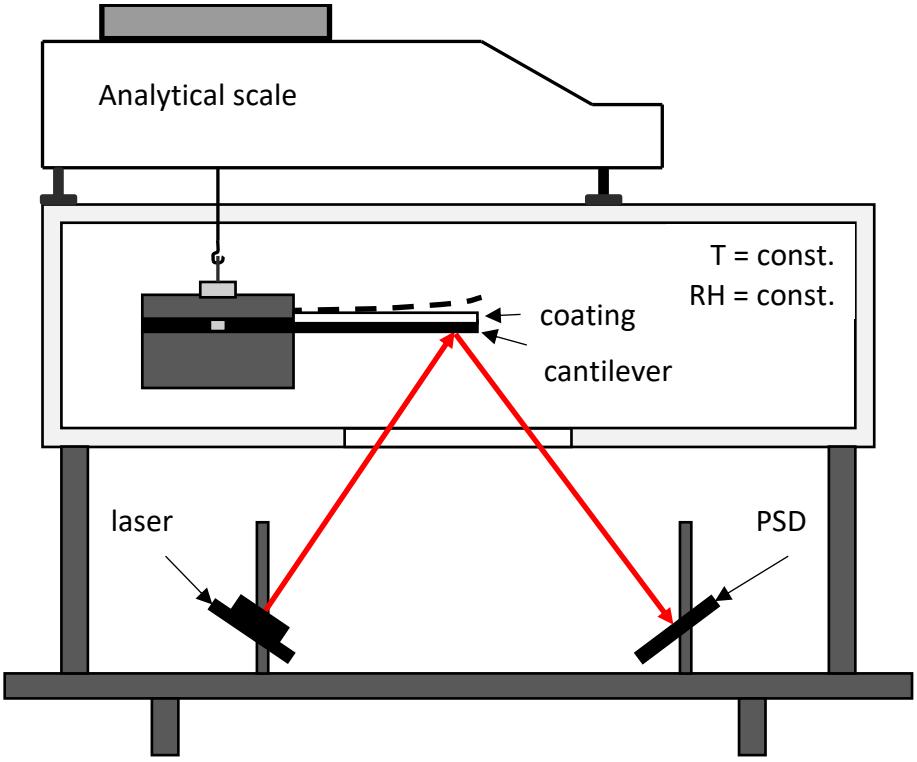

Figure 1: Temperature (T) and humidity (RH) controlled chamber. The fixture with the coating is attached to an analytic scale. Simultaneous stress and weight measurement of the same sample are achieved in situ using this apparatus.

Results

Pure alumina suspensions without any added water (ϕ_{sec}= 0) show a lower peak stress at a drying temperature of 40 °C compared to 30 °C, as shown in **Figure 2a**. An increase in the chamber's relative humidity (RH) to 10% lowers the maximum stress at 30 °C to the same approximate value as that for both humidities at the higher temperature. Alternatively, this higher peak stress at 1% RH and 30 °C can be reduced when water is added to the suspension (ϕ_{sec}= 0.015). The stress for this sample is reduced to the same lower level shown for the pure suspension at the higher humidity or higher temperature. Higher humidities and temperature have no significant effect on the peak stress while drying for the ϕ_{sec}= 0.015 samples. The further addition of water to ϕ_{sec}= 0.025 has no influence on the stress at the low humidity and 30 °C, but does for the other conditions tested. The maximum stress of the coating decreases, well beyond the values without any added water, to approximately the same level for the higher humidity and temperature. On average, the maximum stress for the capillary suspension drops by 0.12 MPa compared to that of the pure suspension. When substituting water for glycerol with lower vapor pressure, the drying stresses are further reduced. This significant decrease, especially for the 2.5 vol% glycerol sample, is attributed to the lower vapor pressure of the glycerol, which remains trapped in the particle network structure throughout the drying process.

Simultaneous weight measurement of the coating allows the particle volume fraction to be calculated. The fluid evaporates during drying, thus increasing the particle content in the coating, typically until random close packing is reached. This coincides with the stress approaching its maximum value [7]. **Figure 2b** depicts the particle volume fraction at the peak stress for the various suspensions.

If it is assumed that the packing does not further decrease after the stress peak, then it appears the films made from samples at ϕ_{sec}= 0 have a higher density at the higher temperature. A small decrease in density occurs by increasing the RH. The intermediate water content samples show an increase in the porosity at each condition when compared to the pure suspension. By further increasing the secondary fluid content to 2.5% by volume, the porosity of the films increases even further. Augmenting the RH at 40 °C results in a much lower film density than was observed for a relative humidity of 1%. Looking at the lower vapor pressure glycerol samples it can be seen, that the porosity level is at about the same level of the 2.5% water sample. This is important to note because the 1.5% and 2.5% glycerol sample have almost identical porosities but significantly different peak stresses. That means, that a change in film porosity is not the only cause for a peak stress reduction during drying of particulate coatings.

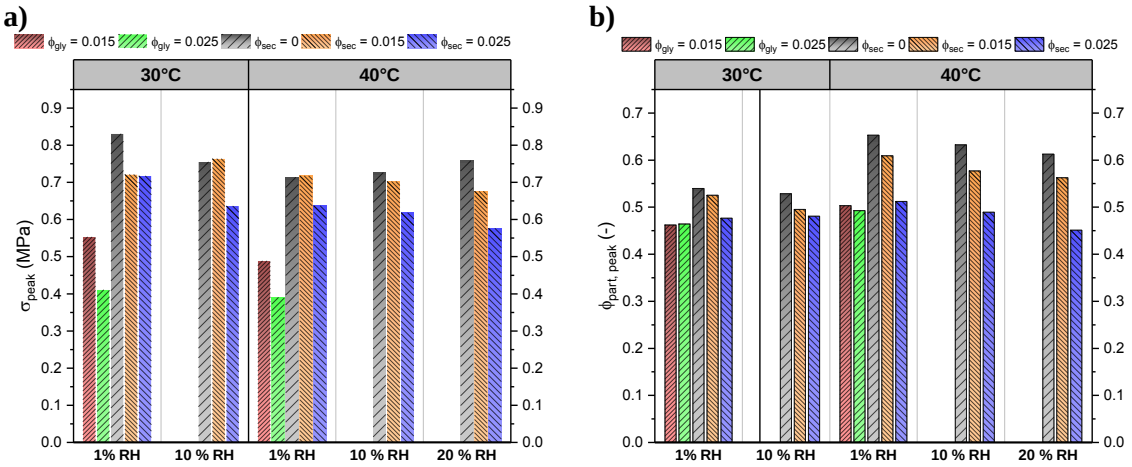

Figure 2: a) the maximum stress during drying and b) the calculated particle volume fraction at the peak stress for various suspensions as a function of relative humidity and temperature.

Conclusions

We performed simultaneous weight and stress measurements in a temperature and humidity controlled chamber as demonstrated for pure alumina suspensions as well as capillary suspensions. While a reduction in the peak stresses is demonstrated with temperature and humidity for normal suspensions, a significant reduction in the peak stress occurs upon the addition of a secondary fluid. This reduction in stress should be tied to crack prevention when using capillary suspensions making them an ideal candidate as a precursor for the Internet of Things.

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References

1 Gubbi J, Buyya R, Marusic S et al. Internet of Things (IoT): A vision, architectural elements, and future directions. Future Generation Computer Systems 2013; 29 (7): 1645–1660

2 Perelaer BJ, Laat AWM de, Hendriks CE et al. Inkjet-printed silver tracks: Low temperature curing and thermal stability investigation. J. Mater. Chem. 2008; 18 (27): 3209

3 Schneider M, Maurath J, Fischer SB et al. Suppressing Crack Formation in Particulate Systems by Utilizing Capillary Forces. ACS Appl Mater Interfaces 2017; 9 (12): 11095–11105

4 Bossler F, Koos E. Structure of Particle Networks in Capillary Suspensions with Wetting and Nonwetting Fluids. Langmuir 2016; 32 (6): 1489–1501

5 Koos E, Willenbacher N. Capillary Forces in Suspension Rheology. Science 2011; 331 (6019): 897–900

6 Payne JA, McCormick AV, Francis LF. In situ stress measurement apparatus for liquid applied coatings. Review of Scientific Instruments 1997; 68 (12): 4564–4568

7 Guo JJ, Lewis JA. Aggregation Effects on the Compressive Flow Properties and Drying Behavior of Colloidal Silica Suspensions. Journal of the American Ceramic Society 1999; 82 (9): 2345–2358