

FACTORS AFFECTING THE DRYING BEHAVIOR OF CERAMIC FILMS

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ABSTRACT

Drying behavior of PMN films were investigated using a cantilever deflection based device and scanning probe microscope. Drying stress of the films was measured as a function of suspension composition. Results showed that hydroxypropyl methycellulose (HPMC) has some influence on the stress formation due to its effect on the surface tension of the suspension. On the other hand roughness measurements showed that HPMC has insignificant effect on the roughness of the films and roughness is mainly depended on the binder content of the suspensions.

Keywords: Tape Casting, Ceramic Suspensions, Drying Stress, Roughness.

1. INTRODUCTION

Tape casting is a technique which is commonly used for the fabrication of ceramic sheets. The technique consists of deposition of a thin layer of a suspension on a carrier surface, generally using the doctor blade technique. After drying, a flexible green sheet is obtained with a thickness ranging from about 10 μ m to 1 mm [1, 2]. Aqueous tape casting suspensions generally composed of ceramic powder, dispersant, binder, plasticizer and water. In some cases, a wetting agent can be used in the formulations to enhance the spreading of the suspension on the carrier film [3, 4]. Latexes form films upon drying when the water evaporates. At a certain stage the particles coalesce and form polymeric network [5].

Drying of ceramic films is a complex process. After casting the film is in a super-saturated state which means that there is excess water to fill the pores between the particles. Therefore, ceramic particles move freely in the liquid phase under the influence of the Brownian motion and capillary flow [6-8]. The aim of the current study is to investigate the effect of ceramic suspension formulations on the drying stress formation and roughness of the lead magnesium niobate films in green state produced by aqueous tape casting.

2. EXPERIMENTAL

2.1. Materials

Lead magnesium niobate powder (average particle size, d_{50} , 1.8 μ m and BET surface area of 1.168 m^2/g) was produced by combustion spray pyrolysis provided by the Praxair Inc. USA. PAA/PEO comb polymer was employed as the dispersant to prepare highly concentrated stable PMN suspensions. The binder used in the study was an aqueous based nonionic acyclic latex emulsion, Rhoplex B-60A (Rohm and Haas Co, Philadelphia, PA). In the study hydroxypropyl methycellulose (Methocel F4M, DOW Chemicals Co., Midland MI) with a molecular weight of 3500 g/mol was used as the wetting agent. Details about the PMN slurry preparation for tape casting can be found elsewhere [9].

2.2. Method

A cantilever deflection based device was used for measuring the drying stress in tape-cast films (see Figure 1). The device uses cantilever deflection method for measuring stress. When the applied coating dries, a bending moment on the cantilever is created due to the stress transferred from the stress in the coating to the substrate at the interface [10,11].

The stress evolution of PMN tape cast layers was monitored as a function of drying time. The cantilever deflection was determined as a function of drying time using an optical lever consisting of a 3 mW HeNe laser, position sensitive photodiode and appropriate optics. The deflection data were recorded by a data acquisition computer. A steel substrate was mounted onto a movable sample holder fixed at one end. Then suspensions were deposited onto the substrate with a syringe. This assembly was then moved towards the doctor blade at a constant speed of 1 cm/s to create a film with a thickness of 300 μm . Stress in coating causes cantilever to bend. It is related to the deflection by the following equation:

$$\sigma = \frac{dEt^3}{3cl^2(t+c)(1-\nu)} \quad (1)$$

Where c is the final coating thickness, d is the cantilever deflection, E is the elastic modulus, ν is the Poisson's ratio, t and l are the thickness and the length of the cantilever, respectively [10].

Roughness of the green films was analyzed using scanning probe microscope (Digital instruments, MMSPM Nonoscope IV).

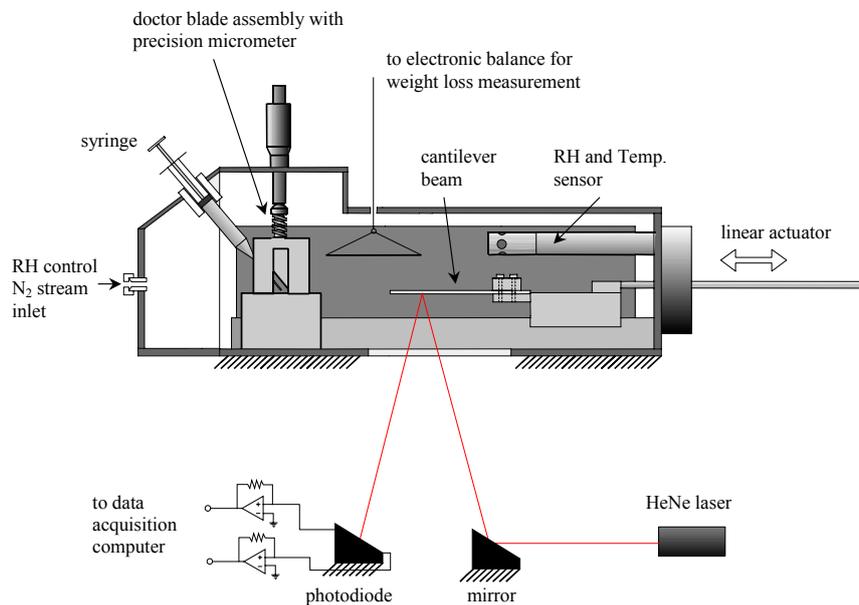


Figure 1. Schematic illustration of the drying stress measurement device (from ref. [12]).

3. RESULTS AND DISCUSSION

3.1. Drying Stress of the PMN Films

Drying stress in PMN films were investigated using cantilever deflection method as a function of drying time and the hydroxypropyl methycellulose (HPMC) concentration. Figure 2 show the effect of HPMC concentration on the stress formation of the PMN films. All layers exhibited a rapid period of rise in tensile stress followed by a maximum stress and stress decay to a final residual stress. A decrease was observed in stress formation as the HPMC concentration increase. This may be attributed to the decrease in surface tension in the presence of HPMC.

In all films, the drying stress evolution displayed three distinct regions: stress rise (σ_{rise}), stress maximum followed by relaxation, and secondary stress rise ($\sigma_{\text{secondary}}$) followed by the presence of a residual stress (σ_{residual}). During the stress rise period evaporation leads an increase in solids concentration [12]. Chiu and Cima found that stress maximum occurs when the network does not shrink further in other words when the 100% saturation is reached. Further evaporation causes $\sigma_{\text{secondary}}$ as the water evaporates from within the pore network. Residual stress occurs due to strength of the particle network that consist binder and polyelectrolyte [6].

Stress rise period is directly proportional to the surface tension of the liquid phase and inversely proportional to the particle size. It is given by the Laplace equation: [7, 10]

$$P_{cap} = \frac{2\gamma}{r_p} \quad (2)$$

Where γ is the liquid/vapor surface tension and r_p is is the pore radius. The pore radius can be approximated by the following equation:

Chiu and Cima also showed that the maximum drying stress, σ_{max} , is proportional to the surface tension of the liquid phase and inversely proportional to the particle size. Therefore, in this study the observed reduction in the σ_{max} may be attributed the reduction in the surface tension in the presence of HPMC [6].

The secondary stress rise observed for the PMN/latex films, was attributed to latex coalescence. Latex coalescence involves the particle consolidation caused by evaporation, deformation of the lattices. The transition to a continuous organic film results in contraction of the binder phase and increased compressive force on the PMN network, resulting in a secondary stress rise in the dry film [5,12]. The behavior observed in PMN/latex films during secondary stress period is a general characteristic of the films that contain powder and organic phase. It was reported that in binder free films (contain only the powder) the stress relaxas after the maximum stress period. Martinez showed that initially during drying both latex and rigid particles behave similarly. But the main difference is the slope of the stress rise [13].

To summarize, during drying of the gels solvent is transported from the interior of the film to the surface. This behavior induces compression in the particle network. The drying body would like to shrink in three dimensions but since it is constrained by the substrate it can only shrink in the z-direction. But it is kept in tension in the x-y plane [13, 8, 1]. This solvent induced tension in the particle network is what drives the drying stress measured in the study [7].

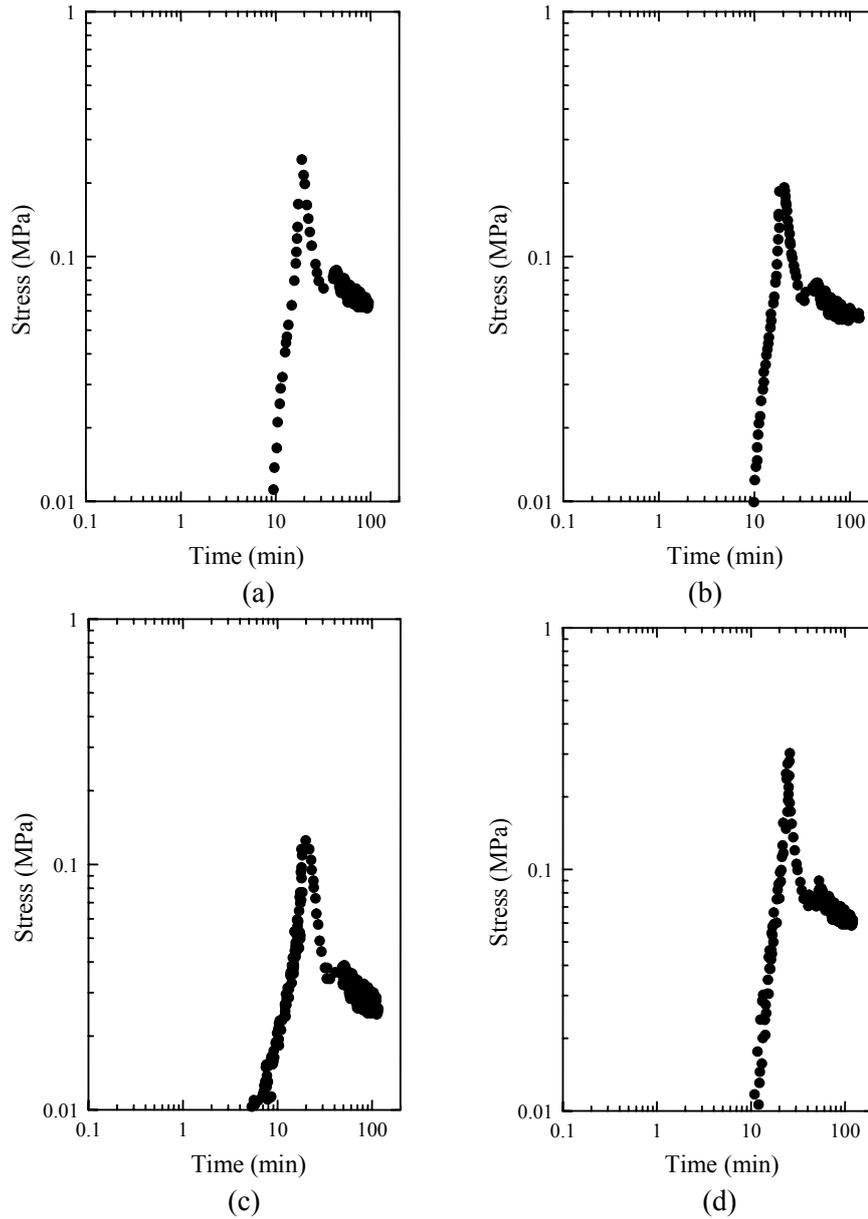


Figure 2. Drying stress of PMN films containing a) 3.5 mg/ml cellulose, b) 5 mg/ml cellulose c) 7 mg/ml cellulose d) no cellulose ; ϕ : 0.55.

3.2. Roughness of the PMN Films

Surface morphology of the PMN green tapes (casting thickness of 300 μm) were analyzed using atomic force microscope with contact mode. Figure 3 show the effect of HPMC concentration on the roughness of the PMN films. Roughness values are also tabulated in Table 1. Results showed that there is no significant difference between the roughnesses of the films as a function of HPMC content. On the other hand, the scanning area was very small (100 μm) during the AFM analysis therefore, some small local heterogeneities may effect the results in a great extend.

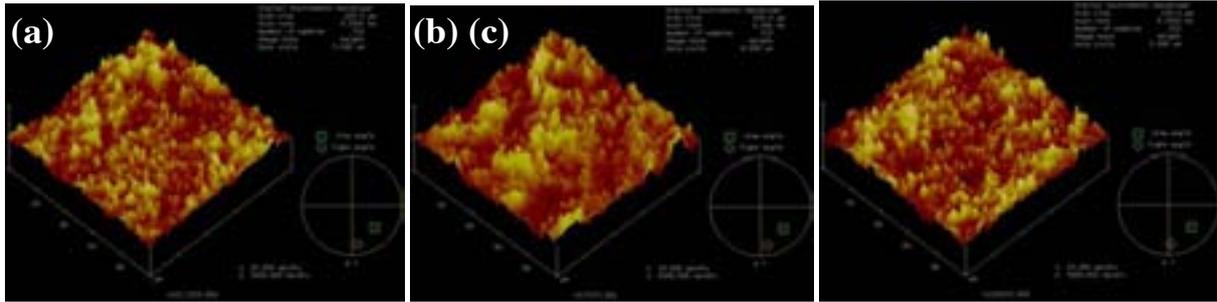


Figure 3. AFM images of the PMN films having different HPMC concentration a) 3.5mg/ml b) 7 mg/ml, c) 10 mg/ml.

Table 1. Roughness values PMN films as a function of HPMC concentration.

HPMC (mg/ml)	Average Roughness (nm)
3.5	488.96
7.0	650.35
10	542.33

Figure 4 presents the effects of binder concentration (PMN:binder ratio) on the roughness of the green tapes. AFM pictures reveal that roughness of the films decreases as the binder content decreases. This may be an indication of the possible PMN powder and latex particle interactions. Roughness values are also tabulated in Table 2.

Table 2. Effect of PMN:binder ratio on the roughness of the PMN films.

PMN film composition	Avg. Roughness (nm)
R1	650.35
R1.5	313.16
R2	266.39

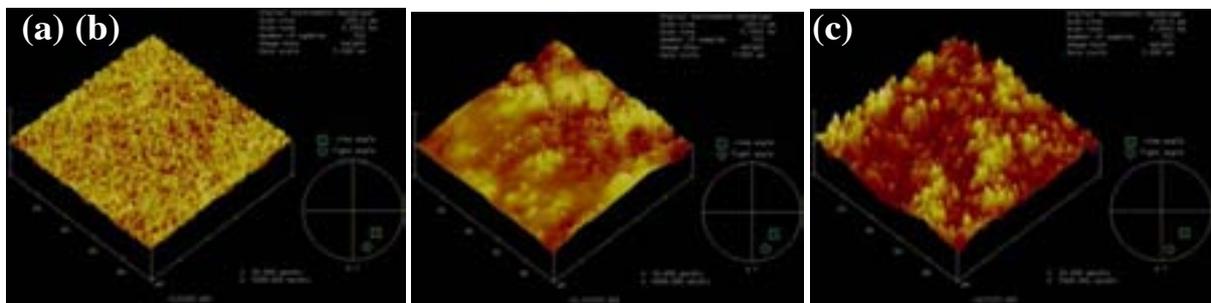


Figure 4. AFM images of the PMN films having different PMN: binder ratios(R) a) R2 b) R1.5 c) R1.

4. CONCLUSIONS

A cantilever deflection based device was used for measuring the drying stress in tape-cast films. The stress evolution of PMN tape cast layers was monitored as a function of drying time. A decrease was observed in stress formation as the HPMC concentration increase. This was attributed to the decrease in surface tension in the presence of HPMC. In all films, the drying stress evolution displayed three distinct regions. Surface morphology of the PMN green tapes were analyzed using atomic force microscope with contact mode. Results showed that there is no significant difference between the roughness of the films as a function of HPMC content. Results also showed that roughness of the films decreases as the binder content decrease.

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