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PORE EVOLUTION AND SOLVENT TRANSPORT DURING DRYING OF GELLED SOL-GEL COATINGS: PREDICTING 'SPRINGBACK' *

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ABSTRACT

This paper reports predictions of drying phenomena in deformable porous gel coatings (i.e. a porous solid elastic network filled with air or solvent). Initially, a gelled coating is *saturated* with solvent, but as it dries, liquid-vapor menisci begin to recede into larger pores and the gel becomes *a partially-saturated* porous medium. The tensile capillary pressure in the liquid causes a compressive deformation on the solid skeleton and a consequent reduction in thickness and pore-size of the coating. A theory coupling the large deformation of the solid skeleton to capillary pressure in the interstitial liquid is used to predict the course of drying of dip-coated porous gel coatings. The theory predicts a 'springback' effect in late stages of drying as the effects of capillary pressure diminish, which matches with experimental observations.

INTRODUCTION

The sol-gel method is a convenient method for producing ceramic coatings with a wide range of properties and for a wide range of applications. Brinker and Scherer (1990) have shown that the properties of the ceramic coatings are sensitive to the processing conditions used to coat the film onto a substrate and drying conditions used to remove solvents from the gelled coating. This

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paper develops a theory to describe fully-coupled, multiphase transport in a deformable, unsaturated porous media and shows how the final properties of a gelled film can depend upon the processing conditions.

In general, inorganic gels produced from the sol-gel route are viewed as composed of a solid network whose pores are filled with liquid or gas. Bulk gels and gel coatings have been produced from the sol-gel method with a wide range of porosity (up to 99.5%) and a wide range of pore-sizes (Brinker and Scherer 1990, Scherer 1992). Some measurements suggest that the pore-radius in gels can be on the order of several angstroms, i. e. on the same order as the size of the solvent molecules. An issue is whether a medium with such small pores can really be called porous or whether the volume contained in the pores is merely free volume in a continuous medium. Another issue is whether molecules confined in pores of molecular dimensions have properties similar to the same molecules in bulk liquid. In gels with larger pore-sizes (on the order of several nanometers) experiments show that they behave like porous media (supercritical drying enables the retention of the initial wet gel porosity by the elimination of the main driving force for shrinkage, interfacial tension in the pores, and reversible springback of gels also indicates existence of a capillary stress that vanishes as the material nears dryness). In this paper, we treat the gel as a porous body with a distribution of pore sizes and assume that the solvent in the pores has the same properties as bulk liquids. This model is not specific to gels produced from particulate or polymeric sols and should qnalitatively be valid in both cases. We also assume there is no molecular adsorption onto the pore walls and that the liquid remains in the pores even under extraordinarily large capillary pressures. These assumptions become more valid in gels with larger pore-sizes (> 10 nm), but in this paper we apply the theory over the whole range of pore-sizes.

The model developed in this paper is composed primarily of four parts: 1) a macroscopic description of flow in an unsaturated porous media, 2) a simple, microscopic, pore-scale model to obtain the parameters for the macroscopic model, 3) a solid-mechanics model of the interaction between capillary pressure and solid network deformation (including the saturation effect), and 4) a lumped parameter (mass transfer coefficient) model for solvent vapor removal from the coating surface. The model predicts the evolution of moisture (or liquid) content, stress, porosity (fraction of medium volume occupied by pores), and pore-radius during drying of a gelled coating. Under appropriate conditions, a drying gel coating can exhibit all the drying stages shown in Figure 1; this figure depicts drying of a gel coating during continuous low-speed dip-coating with a solvent (coating liquid). Initially, the gel is saturated with solvent and has an entrained layer of bulk the gel can expand back to its original volume, i. e. 'springback'. The rate *of springback is* determined primarily by diffusion of solvent vapor through the gas in the pores and through the external gas phase. The final coating thickness is determined by the physical properties of the gel

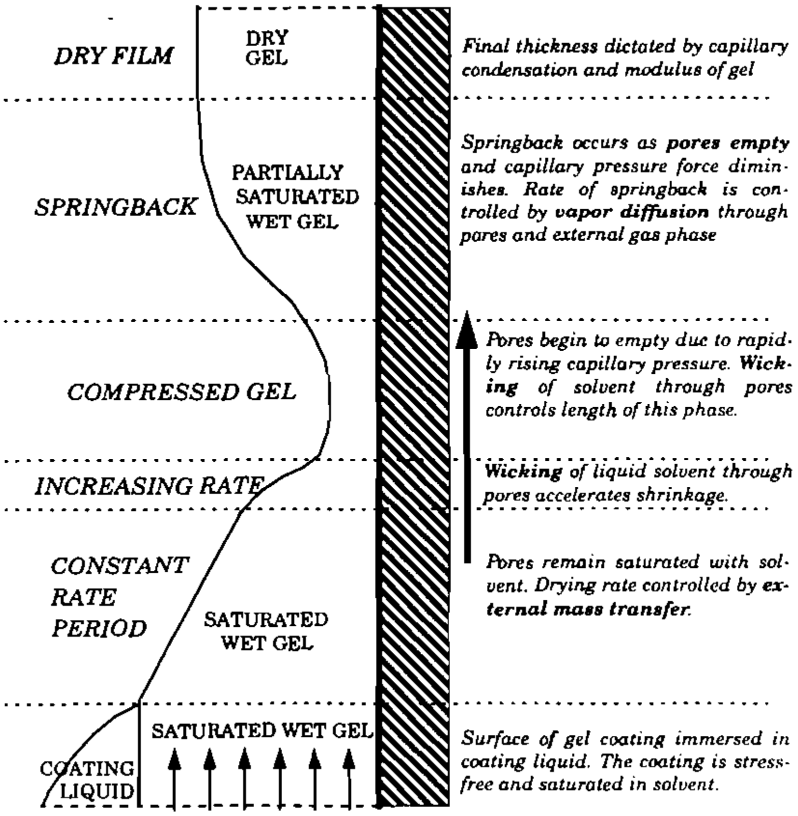


FIGURE 1. Stages of drying of dip-coated, porous, gel films which exhibit a 'springback' phenomenon.

(modulus and pore-radius) and the solvent content of the drying gas. This paper shows how all these stages can be predicted from theory.

SOLVENT MASS CONSERVATION

An example of steady-state, low-speed dip-coating of a porous gel coating is depicted in Figure 1. We use the approach of Martinez (1995) to describe twophase flow in a partially-saturated porous medium. The steady-state equation of mass conservation of solvent in both the liquid and gas phases is:

$$-\nabla\bullet\left(F_l + X_\upsilon F_g + J_\upsilon\right) + C_l \nabla\bullet \upsilon_s = 0 \tag{1}$$

F_l, and $X_v F_g$ are the convective mass fluxes of solvent in the liquid (liquid is assumed to be pure solvent) and gas phases relative to the motion of the solid porous network, v_S. J_V is the diffusion flux of solvent vapor in the gas phase. C_l is the bulk concentration of solvent in both phases per unit volume of porous medium; so the last term represents the convective flux of solvent moving with the porous solid. The convective flux in the gas phase is negligible because pressure gradients in the gas phase are small under the conditions explored in this paper. The convective flux in the liquid is calculated using Darcy's law for multi-phase flow porous media and accounts for the reduction in permeability of the liquid phase as the saturation decreases. The diffusion flux of vapor is calculated using Fick's law. The pore liquid and solvent vapor are assumed to be in local equilibrium by the Kelvin equation. More detail on these equations is given in Cairncross et al. (1996).

MICROSTRUCTURE MODEL OF POROUS MEDIUM

In partially saturated coatings, the physical properties and the saturation depend upon the pore structure (porosity, pore-radius, and pore-size distribution) and the capillary pressure of the liquid; when the capillary pressure is zero, the porespace is saturated (filled) with solvent, but as the capillary pressure rises the saturation falls to zero. There are many empirical correlations for liquid on its surface; at this point the coating *is stress free.* When the bulk liquid evaporates, the gel coating is exposed to air and begins drying and shrinking. Initially the drying rate is nearly constant because the gel is saturated with solvent and changes in the porosity and solvent partial pressure are small. Later, as the capillary pressure in the liquid starts to rise rapidly, the rate of coating shrinkage increases, and the coating enters its most compressed state. As the capillary pressure rises, the largest pores in the media empty and the gel becomes *partially saturated.* In a partially saturated gel. the capillary pressure force, which causes the gel to shrink, decreases and the dependence of physical properties of porous media in a variety of materials. We used a simple pore microstructure model to determine the properties as a function of the capillary pressure and porosity of the medium. The simple model treats the pore-space as a bundle of randomly oriented capillary tubes with a distribution of pore-sizes (Bear and Bachmat 1990). The pore-size distribution used in this paper follows a weighted exponential probability density function about a mean pore-size, where the mean pore-size is a function of the porosity (Cairncross et al. 1996). The saturation, permeability, and relative permeability are all calculated from this pore-size distribution function.

THEORY OF STRESS IN POROUS COATINGS

Sol-gel films are deformable. The extent of deformation is determined by conservation of the elastic energy in the solid network subject to the forces imparted on it from external sources and from the interstitial fluid. Because the coatings are thin and the rate of deformation is small, gravitational and inertial forces are neglected to get a quasi-static momentum equation:

$$\nabla \bullet T_{tot} = 0 \tag{2}$$

Here T_{tot} is the total stress tensor for the medium including both the stress in the solid porous network and in the interstitial fluids.

In an unsaturated porous medium, the total stress is a sum of the partial stresses in all the phases plus any additional momentum due to action along the interfaces between the three phases.

The stresses in the interstitial fluids are normally isotropic and represented by the capillary pressure,. $p_c \equiv p_g - p_l$. The gas pressure is assumed to be ambient pressure everywhere, and the liquid pressure is tensile (lower than atmospheric) for wetting liquids. This tensile capillary stress causes the solid network to be in compression. Normally, the total stress is split into an "effective stress" or "drained network stress" and an isotropic pressure stress (Biot and Willis 1957, Zienkiewicz et al.1990):

$$T_{tot} = \sigma_{eff} - \left(1 - \frac{K_n}{K_s}(1-\phi)\right) S p_c I \tag{3}$$

This is the effective stress law for partially-saturated porous media in which the bulk modulus of the porous network (K_n) may be close to that ot the solid material (K_s); this relationship has good theoretical foundations for saturated porous media (S = 1) and is normally also used in partially saturated porous media.

The effective stress relates the solid network stress to the state of strain in the network. We use a large-strain constitutive equation:

$$T_{tot} = 2G_n E^* + K_n e^* I - \left(1 - \frac{K_n}{K_s}(1-\phi)\right) S p_c I \tag{4}$$

G and K_n are the elastic shear and bulk moduli of the porous gel, respectively, E^* is a dilation-free large-deformation strain tensor (Segalman et al. 1992) $e^* = 3\left(\det|F|^{1/3} - 1\right)$ is the large-deformation dilation of the porous medium with F the deformation gradient. This equation reduces to a standard NeoHookean constitutive equation in the limit of small strains. The bulk modulus of the porous medium varies in a power law with the porosity of the medium as shown by Scherer,1989. The porosity varies with the dilation of the porous medium:

$$\det|F| = \frac{1-\phi_0}{1-\phi} \tag{5}$$

ϕ_0 is the porosity of the medium in the undeformed state (when F = I)

Because the coating is in steady-state motion, the porous medium convects through the domain and deforms as it passes through the domain. The velocity ofthe porous solid is related to the velocity that the solid would have if it were undeformed, v_0, and to the state of deformation (Oden and Lin 1986):

$$\nu_s = \nu_0 \bullet F \tag{6}$$

Thus, the deformation gradient maps the velocity from the stress-free-state to the deformed state. This relationship is used to calculate the bulk convection term in the mass balance equation (1).

EVAPORATION CONDITION FOR FREE SURFACE

At the free surface of drying coatings, the rate of internal solvent transport to the surface equals the external mass transfer rate. In this paper, we treat the mass transfer in the external phase by a lumped-parameter mass transfer coefficient model. Thus, we get a flux boundary condition at the free surface:

$$n \bullet \left[F_l + X_\nu F_g + J_\nu - C_l \nu_s = K_G\left(\rho_\nu - \rho_\infty\right)\right] \tag{7}$$

The left-hand side of equation (7) represents the normal mass flux of solvent to the surface of the coating, and the right-hand side represents the mass flux of solvent away from the surface on the gas side. n is a unit normal to the surface, K_G is a mass transfer coefficient based on a gas phase concentration driving force, ρ_v is the concentration of solvent vapor in the gas at the surface of the coating and ρ_∞ is the concentration of solvent in the gas phase far away from the coating. In this paper, the mass transfer coefficient is treated as a constant along the free surface. The solvent vapor density is related to the capillary pressure by the Kelvin equation and the ideal gas law.

RESULTS

The theory described in this paper was solved using the finite element method as described elsewhere (Schunk et al.1995, Cairncross et al.1996). The equations are solved on subdomains (elements) in a mesh as pictured in Figure 2a. Because the coating is thin (< 5μm), gradients in properties through the coating depth are small, and only two elements through the thickness of the coating were needed to obtain accurate results; however, the gradients in properties parallel to the substrate are steep, requiring fine discretization in that direction. The results compare well with experimental data of Samuel et al. 1996 and Prakash et al. 1995.

Figure 2 shows a prediction of drying of a low-speed dip-coated gel film using standard values of the physical properties (see Cairncross et al. 1996). This prediction reproduces all the stages of drying shown in Figure 1 and qualitatively matches the experimental data of Prakash et al.1995. Initially the decrease in film thickness is nearly linear, corresponding to a constant-rate period (see Figure 2b); nearly constant-rate drying rates are often observed in during early removal of wetting liquids from porous media (Sherwood 1929). At a distance of about 0.5, the rate of shrinkage increases; this acceleration in shrinkage coincides with a rise in the capillary pressure. The rising capillary pressure creates a pressure gradient parallel to the substrate that drives liquid flow through the pores, a phenomenon commonly referred to as *wicking*. At a distance of about 0.5, the saturation begins to decrease as solvent empties out of the largest pores. When the saturation falls, the capillary-induced stress in the coating is reduced, and the coating expands. The rate of expansion is dictated primarily by the drying conditions and diffusion of solvent vapor through the pore-space; more rapid diffusion results in slower springback. Some additional calculations have shown that solvent vapor diffusion in the external gas phase can also delay springback, which would make the predictions match better with the experimental data of Prakash et al.1995.

Figure 3 compares predictions of springback over a range of coating properties. The plots show the minimum thickness of the coating as it dries, the final thickness of the coating, and the ratio of final thickness to minimum thickness, which we call the springback ratio. In gels with small pores or gels with high modulus, the springback ratio approaches one, i.e. there is no springback under these conditions. In the small pore case, the coating does not springback because the pores are small enough that the liquid never empties out of them. In the high modulus case, the coating is so stiff that the shrinkage is negligible. The springback ratio exhibits a maximum with respect to both pore-radius and modulus, but due to computational difficulties we could not obtain results showing the springback ratio returning to one in the cases of large pores and low modulus. In the large pore case, springback is sudden because the saturation falls rapidly over a short range of capillary pressure, and the steep gradient of this sudden springback is difficult to capture in our computations. In the low modulus case, the shrinkage at the start of drying is very sudden and causes similar numerical difficulties to the large pore case.

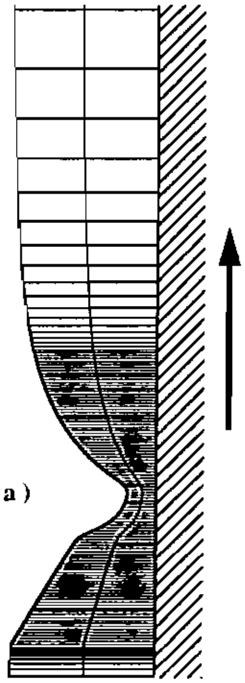
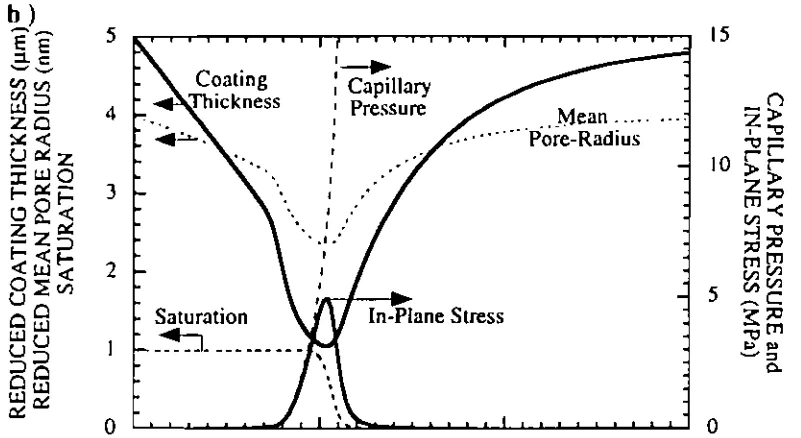


FIGURE 2. Prediction of a drying dip-coated gel film with rp = 4 nm, □o = 0.99, Ko= 8 GPa, RH = 0.0001, KG = 0.25 cm/s. a) Mesh expanded 100x horizontally showing coating thickness profile. b) Properties along the free surface showing that 'springback' coincides with a peak in stress and a fall in saturation.

Figure 2b shows a rapid rise in the capillary pressure at the point where the gel becomes partially saturated. The product of the capillary pressure and the saturation roughly correspond to the in-plane (or bending) stress experienced by the gel. The in-plane stress goes through a maximum during drying, and the value of the maximum stress depends strongly on the physical properties of the gel. In gels with smaller pore-radius, the maximum stress during drying increases because the fall in saturation is delayed. This result implies that gels with smaller pores are more likely to crack than coatings with larger pores.



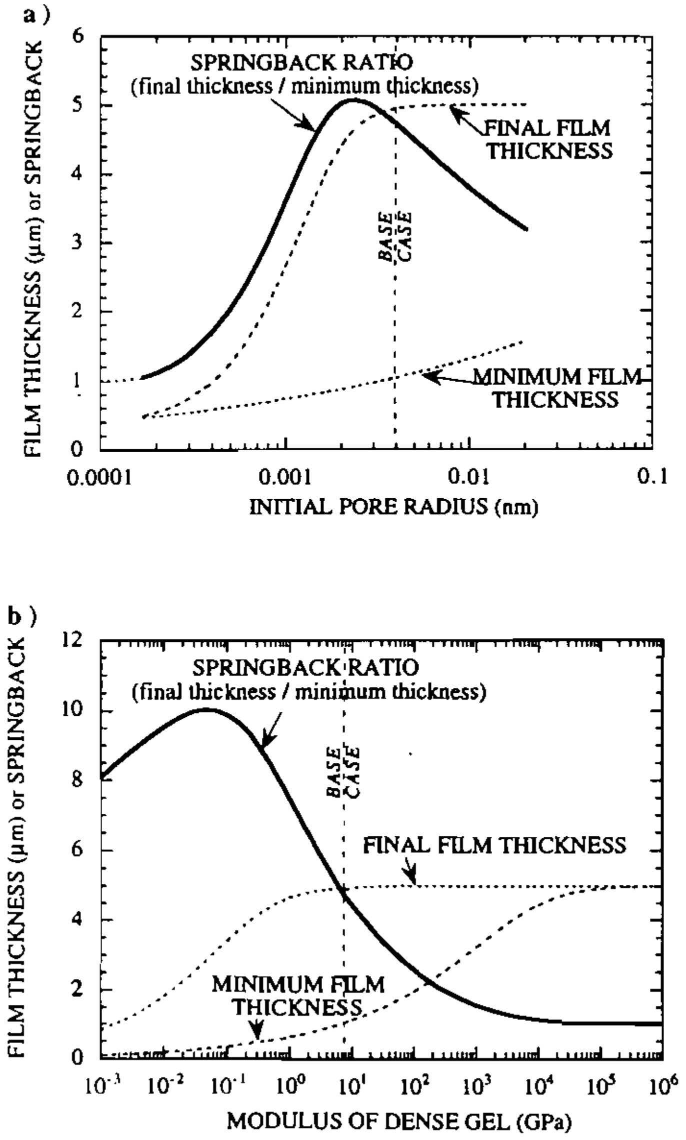


FIGURE 3. Predictions of minimum thickness, final thickness, and springback as functions of a) initial pore-radius, and b) initial modulus. Springback does not oc- cur in coatings with small pores or in stiff coatings.

CONCLUSIONS

The theory presented in this paper is able to predict stress development, shrinkage, and springback in porous coatings which qualitatively reproduces experimental data. The magnitude of the *maximum* bending (tensile) stress in the coating is sensitive to the processing parameters and physical properties of the solvent and the porous network. In coatings with smaller pores, the maximum and residual stresses are higher. In coatings with larger pores (> 1 nm) a `springback' phenomenon is predicted where the stress rises initially but then falls as the pores empty, resulting in a final coating with higher porosity, lower stress, and larger pores.

NOTATION

Cl	Bulk concentration of solvent in porous medium	kg/m^3
E*	Large-deformation, dilation-free strain	-
e*	Dilation	-
F	Deformation gradient tensor	-
F_g	Darcy convection flux of gas in pores	$kg/m^2/s$
F_l	Darcy convection flux of liquid in pores	$kg/m^2/s$
G_n	Shear modulus of porous network	$kg/m/s^2$
Jv	Diffusion flux of solvent vapor in gas phase	$kg/m^2/s$
K_G	Mass transfer coefficient for transport through external gas phase	m/s
K_n	Bulk modulus of porous network	$kg/m/s^2$
K_n	Bulk modulus of dense solid material	kg/m/s
n	Unit normal to surface	-
p_c	Capillary pressure of liquid in pores	$kg/m/s^2$
S	Saturation (fraction of pore-space filled with liquid)	-
T_{tot}	Total stress tensor for gell	$kg/m/s^2$
v_0	Velocity of solid in stress-free state	m/s
v_S	Velocity of solid phase	m/s
X_v	*Mass* fraction of solvent in vapor phase	-
ϕ_0	Porosity of medium in stress-free state	-
ρ_v	Density of solvent vapor at surface of gel	kg/m^3
ρ_∞	Density of solvent vapor in drying gas	kg/m^3

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