Drying and Consolidation in Drying Colloidal Dispersions

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Abstract

When a thin film of wet paint or coating containing suspended submicron sized colloidal particles is dried on a substrate, evaporation of the solvent concentrates the particles. The drying and consolidation process leads to the formation of space filling particle networks and in many cases gives rise to tensile stresses in the network. Drying and consolidation process builds up stresses in the colloidal packing while packing flaws such as voids and dislocations nucleate cracks thereby compromising the mechanical integrity of such materials. An understanding of the fluid-solid phase transition for varying particle size, shape and chemistry (inter-particle interaction), followed by prediction of particle packing as a function of the said parameters in the presence of external fields is critical to industries as diverse as electronics, paints, coatings, ceramics, and agriculture. The paper presents some of our recent work on the film formation and cracking phenomenon in wet films formed from colloidal dispersions.

Keywords: compressive yield stress; plastic deformation; colloid

1. Introduction

The process of consolidating suspended particulate solids in liquids under the application of load like gravitational force, centrifugal force or a pressure load in a filter is a problem of widespread practical and theoretical importance. The compaction of particulate suspensions is used in solid-liquid separation processes, fabrication of ceramic materials and in drying of colloidal dispersion to create particulate solids or continuous polymer film. Compaction of colloidal particles is affected by a number of parameters such as particle size, shape, and inter-particle potential and is dependent on a balance of three forces—the external driving force such a gravity or centrifugal force, the viscous drag force and a particle or network stress developed due to direct particle-particle interactions.

When a thin film of a colloidal dispersion containing soft polymer particles, such as a wet paint, is applied on a nonporous surface, evaporation of the solvent concentrates the particles into a close packed array. Further evaporation is accompanied by stresses in the wet film that deform the particles so as to close the pores. When the particle glass
transition temperature is sufficiently lower than the ambient temperature, polymer chains diffuse across contacting interfaces to fuse the particles, ultimately resulting in a homogeneous film. The film generally binds to the underlying substrate, generating shear stresses that resist deformation in the transverse plane and giving rise to transverse tensile stresses. When the magnitude of the tensile stress exceeds a critical value, cracks nucleate, thereby compromising the mechanical integrity of the film. Recent developments in the understanding of the film formation process have shown the drying and particle deformation mechanisms to be rather complex.

Holl et al. distinguishes three different modes of drying in a wet film where the first mode corresponds to homogeneous drying where the water concentration is spatially homogeneous and all parts of the film dry at the same rate. The second mode of drying occurs when the particle diffusivity is negligible, allowing evaporation to concentrate particles at the liquid-air interface. The resulting sheet of packed particles at the surface grows in thickness as the vertical convection induced by the negative capillary pressure draws in more particles. Here, the capillary pressure is caused by the liquid menisci between the particles at the air-film interface. Finally, the third mode involving propagation of lateral fronts occurs when the nonuniform thickness of the film causes the particles to reach close packing first at the edge. Here, in contrast to the previous case, the low pressure caused by the liquid menisci at the edge draws water laterally from the bulk and deposits particles at the front.

The evaporation of solvent leads to a film of close packed particles where stresses generated during drying can cause particle deformation. The earliest theory of deformation for spheres in contact, proposed by Hertz relates the change in the center to center distance between two touching spheres to their elastic modulus and the external force squeezing them together. Alternatively, the viscous sintering of two spheres, proposed by Frenkel, balances the interfacial tension, which minimizes the particle surface area, against viscous forces resisting deformation, resulting in a simple relation between rate of strain, the internal viscosity of the particle, and interfacial tension. Finally, the JKR theory balances the surface energy and elastic response to predict the strain as a function of the interfacial tension and the shear modulus. Routh and Russel derived a constitutive relation relating the macroscopic stress to macroscopic strain in a drying film. They considered the viscoelastic deformation of a pair of identical particles due to contact and interfacial forces and related the strain at the particle level to these forces. Next, they volume averaged the forces over all orientations to arrive at the macroscopic stress versus strain relationship for a drying film. In the absence of particle-solvent interfacial tension, the expression for the macroscopic stress tensor for identical elastic spheres reduces to

\[ \sigma_{ij} = \delta_{ij} \left\{ -P - \frac{GM\phi_{rcp}}{140} (\epsilon_{mm}^2 + 2\epsilon_{nm}\epsilon_{mn}) \right\} - \frac{GM\phi_{rcp}}{35} (\epsilon_{mm}\epsilon_{ij} + 2\epsilon_{im}\epsilon_{mj}) \]  

where, \( \epsilon_{ij} \) is the macroscopic strain, \( P \) is the capillary pressure, \( \phi_{rcp} \) is the random close packing concentration, \( G \) is the shear modulus of the particles and \( M \) is the number of contacting neighbors. The constitutive equation is an improvement over the traditional poroelasticity models as the former accounts for the nonlinear deformation at the particle level and the influence of particle size, modulus and packing characteristics on the macroscopic deformation field. The model has been successful in predicting not only the stress profile in drying films of both film forming and cracking systems, but also in predicting many aspects of the cracking mechanism in the latter.

Specifically, an analysis based on the Griffiths criterion wherein a balance between elastic energy released during crack propagation and the increased surface energy determines the critical stress at which a drying thin film cracks,

\[ \frac{\sigma_c R}{2\gamma} = 0.1877 \left( \frac{M\phi_{rcp}}{N^2} \right)^{1/3} \left( \frac{GR}{2\gamma} \right)^{1/3} \]  

Here, \( \sigma_c \) is the critical stress at which the film cracks, \( N \equiv h/(2R) \) is the thickness rendered dimensionless with particle diameter. The experiments from Cima’s lab have shown that irrespective of particle size and rigidity there exists a critical cracking thickness (CCT) below which films do not crack. Proceeding with expression for the critical stress, Singh and Tirumkudulu showed that for dispersions containing hard particles (stress-limited regime), particle deformation is negligible, and the CCT increases with particle size as well as particle rigidity whereas for soft particles where the particles completely deform to close the pores (strain- limited regime) the CCT decreases with increasing particle rigidity but is independent of particle size. The CCT \( h_{max} \) for the stress-limited regime is obtained by equating the tensile transverse stress at the maximum attainable capillary pressure \( (P_{max}) \) to \( \sigma_c \),

\[ h_{max} = 0.64 \left[ \frac{GM\phi_{rcp}R^3}{2\gamma} \right]^{1/2} \left[ \frac{2\gamma}{P_{max}R} \right] \]
and it agrees well with measurements over a wide range of particle properties. Furthermore, the model also suggests that the cracking behavior is influenced by the final packing volume fraction.

Russel et al.\textsuperscript{32} improved on the constitutive relation for drying colloidal packings by adopting the Hertzian contact mechanics at the particle pair level. The final constitutive relation is also non-linear with the stress varying as three halves power of the strain. Using this relation, they determine the capillary pressure necessary either to open an infinite crack in a flawless film or to extend pre-existing flaws of finite lengths. Their results suggest that flaws which are a fraction of the film thickness are sufficient to initiate cracks that would propagate across the sample at pressures modestly greater than obtained from the energy argument. In a related study Man and Russel\textsuperscript{33} demonstrate experimentally the role of flaws in nucleating a crack and show that the critical stress obtained from the energy argument only gives the lower bound.

In a more exact treatment of the effect of flaws on cracking, Sarkar and Tirumkudulu\textsuperscript{34} determined the stress field near a crack tip along with the shape of the crack present in a two dimensional particle packing saturated with solvent. The flaw was embedded inside the colloidal packing and the size of the flaw was assumed to be much smaller than any other dimensions of packing. These flaws may be attributed to micro-cracks, grain boundaries between the clusters of ordered packing of mono-dispersed particles, dissimilar pores inside the colloidal bed etc. Nucleation of a crack under these circumstances changes the stress field close to the crack with stress concentration at the crack tip. The stress and strain fields were linearized about the pre-crack state to determine the disturbance displacement field immediately after the opening of a mode-I crack. These results also yield the stress intensity factor for the two dimensional elastic field which was then related to the surface energy using the well known Griffiths criterion for equilibrium cracks. The calculated quantities are then compared with the numerical solution of the full problem. The calculations show that the dimensionless critical capillary pressure required to open a crack varies inversely with the crack length to the two thirds power and depends on a dimensionless parameter that measures the ratio of the elastic modulus of the packing and $e_o$ is the characteristic strain in the packing, the elastic energy recovered on the opening of a crack of length $a$ in a packing of unit thickness is, $\sigma e_o a^2$. Equating this to surface energy ($\gamma a$) and noting that the capillary pressure is linearly related to the stress, gives the critical capillary pressure for opening the crack, $\frac{\rho R}{2\gamma} \sim A \left( \frac{f}{\gamma} \right)^{2/3} \left( \frac{ER}{\gamma} \right)^{1/3}$, where $\gamma$ is the surface tension of the solvent, $R$ is the radius of the particles, and $A$ is a constant and is determined by solving the boundary value problem.

All the aforementioned work has focused on colloidalally stable suspensions where the particles come into contact at random close packing so that particle deformation occurs without rearrangement of their positions. However, in case of unstable or flocculated dispersions, particle networks form well below the random close packing concentration. In the flocculated case, the particles are strongly aggregated with a potential minimum being much greater than the thermal energy, $-\phi_{min}/kT \geq 20.19$. Therefore, once the inter-particle contacts are created the particles cannot be separated by thermal agitation. Here, the particle network in the aggregated dispersion percolates the entire volume above the gelation volume fraction and an compressive stress during drying is applied externally on the network. The particulate network along with the particles themselves undergo elastic deformation for small loads so that upon removing the load, the network and the particles get back to their respective pre-stress configuration. When the stress is greater than a critical value, known as the compressive yield stress, the particles start rearranging so that the network deforms plastically, and compacts irreversibly to a new volume fraction. At this point, if the load is removed only part of the total strain, which is the elastic component of the total strain, is recovered while the rest is not recovered due to plastic deformation. The compressive yield stress increases with the packing fraction as the number of contacts per particle goes up and consequently the particle network is expected to sustain higher loads. The compressive yield stress is also a function of the size and shape of the particles and the inter-particle potential. Eventually, the compressive yield stress diverges at the random close packing volume fraction. At this point, the particles cannot no longer rearrange and all of the stress is used in deforming the particles. The entire strain is recovered on removing the load provided the particles are purely elastic.

Our recent work has focused on developing constitutive relation for deformation of networks and particles in flocculated packings. The goal is to account for the processes at the particle level in terms of both elastic strain in the particles and the plastic strain due to particle re-arrangement. To this end, we proceed using ideas from the solid mechanics literature where constitutive relations for the deformation of the dense granular networks have been studied in detail.
Fig. 1. (a) A two dimensional coordinate system showing the orientation of a contact point, $S$, on the circumference of the particle. The origin of coordinate system is at the center of a particle. Here, $\hat{e}_r$ and $\hat{e}_\theta$ are the unit vectors in radial and theta direction. (b) Inter-particle forces acting between two disks in contact for the colloidal case. Here, $P$ and $U$ represent, respectively, the radial contact forces due external stress and inter-particle attraction, while $T$ is the contact force in the tangential direction.

In this paper, we present the outlines of a two dimensional model that takes into account the inter-particle colloidal forces while describing the plastic events in the form of rolling/sliding during the deformation along with elastic deformation (details will be presented elsewhere). The theory yields a compressive yield stress which is a function of area fraction of the colloidal packing, the coordination number, the inter-particle potential, coefficient of friction and the normal and tangential stiffness coefficients. The predicted yield stress follows a linear scaling with area fraction for low area fractions, and diverges at random close packing. Yield stress increases with the normal stiffness coefficient or the friction coefficient. Overall stress is contributed by both elastic and plastic deformation for stresses greater than the compressive yield stress.

2. Theory

We consider a two dimensional space filling aggregate of discs, each of diameter $D$, with an average particle density of $N/A$ in an area, $A$ (Figure 1). It is assumed that the deformation is affine, i.e. the strain at the particle pair level is the same as that of macroscopic applied strain. This allows us to write the displacement of a contact point in terms of the macroscopic strain. The displacement has normal and a tangential component, each leading to an inter-particle force directed normally and tangentially to the particle. An additional normal force arises from the inter-particle attraction. The critical angle for the onset of rolling/sliding ($\theta_r$) can be found from a tangential force balance that accounts for the Coulomb’s law of friction,

$$\frac{D}{2} e_o \sin(\theta_r) \cos(\theta_r) = \mu_r D e_o \cos^2(\theta_r) + \frac{\mu U}{k_t}$$

where $\mu_r = \mu k_n/k_t$ is the modified friction coefficient for sliding/rolling, $U$ is the inter-particle potential, $e_o$ is the macroscopic strain, and $k_n$ and $k_t$ are the normal and tangential force coefficients. For fixed values of parameters $(D, \mu_r, U, k_t)$, the above equation gives real solutions only above a critical value of the applied strain. In other words, no slip/roll is possible for strains below the critical strain so that the entire deformation is elastic in nature. The expression for the critical strain is found by imposing the condition that the roots of equation (4) be real,

$$e_c = \frac{4\mu U}{k_t D \left(-\mu_r + \sqrt{\mu_r^2 + 1}\right)}$$

(5)
For applied strains greater than the critical strain, equation (4) gives the critical angle, $\theta_r$, beyond which a neighboring particle in contact will roll or slide. As the particles are in adhesive contact due to inter-particle attractive forces, negligible contact loss during the deformation is assumed. The average stress tensor is given in terms of contact orientation distribution, contact forces, contact density and branch vector joining the center of two particles,

$$\sigma_{ij} = -\frac{4D N_z}{A} \int_0^{\pi/2} E(\theta) F_i \alpha_j d\theta$$

$$= -\frac{4\phi_z}{\pi^2 D} \int_0^{\pi/2} F_i \alpha_j d\theta$$

where $E(\theta)$ is the contact orientation, $F_i$ is the contact force, $\phi$ is the area fraction, $z$ is the coordination number, while $\alpha_j$ is the unit vector connecting centers of two neighboring particles. Assuming the contact orientational distribution is isotropic throughout the deformation and substituting the expression for the contact force (obtained from the displacements) gives the stress contribution resulting from the elastic deformation of the network and that due to the plastic deformation (rolling/sliding),

$$(\sigma_{22})^{\text{elastic}} = \frac{4\phi_z}{\pi^2 D} \left[ \frac{3\pi k_n D e_o}{8} + \frac{U\pi}{4} + k_t De_0 \left( \frac{\theta_r - \sin(4\theta_r)}{4} \right) \right],$$

$$(\sigma_{22})^{\text{plastic}} = \frac{4\phi_z}{\pi^2 D} \left[ \frac{\mu r k_n D e_o}{8} \cos^4(\theta_r) + \frac{\mu r U}{2} \cos^2(\theta_r) \right].$$

The compressive yield stress is equal to the the stress developed at the critical strain ($e_c$), since the total stress is only due to the elastic contribution,

$$\bar{P}_Y \equiv \frac{DP_Y}{U} = \frac{\phi_z}{\pi} \left[ 1 + \frac{\bar{e}_c}{8} \left( 1 + 3 \frac{k_n}{k_t} \right) \right],$$

where $\bar{P}_Y$ is the dimensionless yield stress. From above expressions, it can be seen that the dimensionless yield stress is a function of only four quantities, namely, the area fraction, the coordination number, the ratio of the normal to tangential stiffness coefficient, and the friction coefficient. To close the problem, we need to relate the average coordination number to the area fraction. We obtained the $z$ versus $\phi$ relation by fitting the data obtained computationally for two dimensional packing by Seto et al$^{35}$,

$$z = 3.732\phi^2 - 0.382\phi + 1.984$$

Substituting (10) in (9) gives an explicit expression between the yield stress and the area fraction.

3. Results and Discussion

The main and important outcome of our theory is that the dimensionless yield stress depends only on the particle packing characteristics (coordination number and volume fraction) and the particle contact parameters. The absolute value of course will be dependent on the inter-particle force and the particle size.

In figure 2 the dimensionless yield stress value as a function of the area fraction is plotted. At very low $\phi$, $\mu \approx \mu_{ro}$ so that $\bar{e}_c$ is not dependent on $\phi$. As a result, the dimensionless stress scales as, $ar{P}_Y \sim z\phi$. As in this limit, $z \rightarrow 2$, we have $\bar{P}_Y \sim \phi$. At large values of $\phi$ the functional dependency of $\mu_r$ on $\phi$ increases the power law exponent yielding in a steeper rise in $\bar{P}_Y$ with $\phi$. While the above plot shows the yield stress, it is also important to investigate how the elastic and the plastic stress vary as a function of axial strain for a given initial packing fraction. Figure 3 shows the two contributions along with the total stress for an initial volume fraction of $\phi_{in} = 0.30$. It is seen that the total stress is solely due to elastic deformation of the network up to the critical strain. Above the critical strain, particles roll/slide to give a finite value for the plastic contribution to the total stress. With the increasing strain, both the area fraction and the coordination number increase yielding in an increase in the contribution from both plastic and elastic stresses to the total stress.
0.25 0.5
φ

Fig. 2. Dimensionless yield stress vs area fraction: Here, \( \mu_{ro} = 0.15 \) and \( k_n/k_t = 5/2 \).

Fig. 3. Non-dimensionalized stress vs area fraction: elastic, plastic and total stress. Here \( k_n/k_t = 3 \) and \( \mu_{ro} = 0.15 \).

4. Conclusion

In this paper, we have derived a constitutive relation to explain the consolidation behavior of flocculated colloidal dispersion. The model incorporates the inter-particle forces, particle and contact deformation, and plastic events such as rolling/sliding during the deformation process. The particle network experiences pure elastic deformation up to a yield stress above which both elastic and plastic deformation occur in the network. At very low area fractions, the compressive yield stress changes linearly with area fraction whereas at high area fraction the rise is steeper, with divergence taking place at random close packing. The derived constitutive relation is dependent on a few parameters which can be measured independently. Consequently, now the deformation of strongly aggregated colloidal dispersions in complex geometries can be solved. As a future work, the analysis will be extended to three dimensional aggregated colloidal systems.
References