Cracking in Soft—Hard Latex Blends: Theory and Experiments

Karnail B. Singh, Girish Deoghare, and Mahesh S. Tirumkudulu*
Department of Chemical Engineering, Indian Institute of Technology-Bombay, Mumbai 400076

Received September 1, 2008. Revised Manuscript Received October 13, 2008

Volatile organic compounds (VOCs) in the traditional paint and coating formulations are an important health and environmental concern, and current formulations are increasingly moving toward water-based dispersions. However, even within the water-based systems, small quantities of organic solvents are used to promote particle coalescence. One route to achieving this goal has been to use mixtures of soft and hard particles, also known as latex blends. We investigate the drying of colloidal films containing mixtures of silica and acrylic particles. Since both the particles deform only slightly at room temperature, this work investigates the cracking behavior of films containing elastic particles of two different elastic moduli. We extend an existing model for the stress versus strain relation for identical particles in a colloidal film to that containing a mixture of equal-sized hard and soft elastic spheres while accounting for the nonaffine deformation. A transition from soft to rigidlike behavior is observed beyond a critical hard particle volume fraction ratio that matches with published results obtained from computer simulations. The model predictions are validated with extensive experimental data on the critical stress and critical cracking thickness for various ratios of hard and soft particle volume fraction.

1. Introduction

Adverse impacts on health and the environment are forcing paint and coating manufacturers to replace the volatile organic compounds in traditional formulations with water-based formulations, also referred to as latex. However, even the water-based formulations are not completely organic solvent-free and contain small amounts of organic compounds to plasticize polymer particles so that a balance between film forming ability and the mechanical properties of the final film can be achieved under ambient conditions. For example, polymers with low glass transition temperatures ($T_g$s) will easily form a film at room temperature but the final film will be tacky with poor mechanical properties. On the other hand, polymers with high $T_g$s have good elastic properties but the final film suffers from the problem of cracking.

To achieve both good film forming ability and excellent mechanical properties from aqueous dispersions without the use of volatile compounds several approaches have been explored. One of these is the use of core/shell latex particles where the core of the particle is a high $T_g$ polymer whereas the shell is a low $T_g$ film-forming polymer. When particles come in contact, the shell coalesces to form a continuous phase whereas the core provides the mechanical strength to the final film. The other approach, which forms the subject matter of this study, is the use of latex blends containing soft (low $T_g$) and hard (high $T_g$) polymer particles. In these blends, soft particles coalesce to fill the voids and the hard ones give mechanical strength to the final film.

While most of the existing literature on the film formation and cracking mechanism in drying colloidal films consider monodisperse spheres with identical mechanical properties, a few have focused on latex blends. Winnik and Feng1 experimented with a latex blend containing a high-$T_g$ polymer [poly(methyl methacrylate), PMMA] and a copolymer of butyl methacrylate and butyl acrylate [P(BMA-co-BA)] with $T_g \leq 10^\circ C$ and found that the films dry at a slower rate than films cast from dispersions containing only one type of particle. They observed that the rate of drying passes through a minimum with increasing hard particle volume fraction with the minimum occurring at a value of $\alpha = 0.56$, where $\alpha$ is the ratio of hard particles volume to the total solid volume. As expected, the ratio of hard to total solid volume was found to strongly affect the film formation behavior of the blend. Martinez and Lewis6 have reported the film formation in blends of latex and silica. In this study, the film shape evolution and the stress development during film formation were studied for a blend of acrylic latex (particle size of 330 nm and $T_g = -6^\circ C$) and silica (particle size of 570 nm). It was found that blends with $\alpha < 0.4$ behaved like pure latex films. However, a

![Figure 1. Particle positions during deformation.](image)


10.1021/la802857q CCC: $40.75 © 2009 American Chemical Society
Published on Web 12/18/2008
A marked transition from a deformable to rigidlike response was observed as the silica volume fraction increased beyond this value (i.e., $\alpha > 0.4$). They measured the stress of the drying film using the well-known cantilever technique and found that the stress peak became sharper as the silica volume fraction in the blend was increased.

Lepizzera et al. have studied the influence of glass transition temperature and relative particle loading on film forming ability and mechanical properties of latex blend films. The hard latex in this study was synthesized from PMMA with particle size and particle glass transition temperature as 210 nm and 105 °C, respectively. Soft particles were based on methyl methacrylate-butyl acrylate-acrylic acid with a size ranging from 55 to 210 nm and a $T_g$ ranging from −1 to 18 °C. It was found that for blends with soft particle $T_g$ less than 0 °C, the maximum weight fraction of hard latex for obtaining crack-free transparent films is constant and equal to $\alpha = 0.55$ irrespective of soft particle $T_g$. On the other hand, an inverse proportionality between hard particle weight fraction and soft particle $T_g$ was observed for films with soft particle $T_g$ greater than 0 °C. Further, irrespective of soft particle $T_g$, all films crack for $\alpha > 0.55$. Some of the studies have also considered the effect of particle size and size ratio on film formation behavior of latex blends. Colombini et al. found that higher the soft/hard particle size ratio, the film cracks at lower values of $\alpha$. The size of the dispersed hard phase also affects the viscoelastic film properties with smaller particles giving mechanically strong films. Tzitzinou and Keddie have also shown the influence of size ratio on film formation behavior. Depending on the concentration of small particles, they can form a connecting network around the larger ones leading to

**Figure 2.** Scanning electron micrograph of the surface of a blend film with $\alpha = 0.5$.

**Figure 3.** Scanning electron micrograph of the cross-section of a blend film with $\alpha = 0.5$.

**Figure 4.** Scanning electron micrograph of the cross-section of a blend film with $\alpha = 0.5$, heated at 70 °C for about half an hour.

**Figure 5.** Scanning electron micrograph of the film—substrate interface of a blend film with $\alpha = 0.5$, heated at 70 °C for about half an hour.

**Figure 6.** Scanning electron micrograph of the surface of a blend film with $\alpha = 0.95$. 
a continuous phase inversion. Feng et al.\textsuperscript{9} have reported the effect of particle size, glass transition temperature, evaporation rate and soft particle volume fraction ratio on morphology and transparency of blend films. At high evaporation rates, they obtained turbid films which was attributed to the insufficient time available for the soft particles to deform and close the void spaces in the film. The turbidity of the film is caused by light scattering from defects that are comparable or larger than the wavelength of light. Turbid films were also obtained when the hard particles aggregated and a nonuniform distribution of hard and soft particles was obtained. On the other hand, decreasing the $T_g$ or increasing the fraction of soft particles improved the transparency of the film. They conclude that the size of the soft particles plays a minor role in determining the transparency of the film.

On the theoretical end, Jagota and Scherer\textsuperscript{10,11} have studied the sintering rates and viscosities of two and three-dimensional random packing of hard and soft spheres of identical size using a numerical model. The particle packing was replaced by a network of points (that represent the center of particles) and

---

**Figure 7.** Dimensionless stress versus dimensionless time, $\bar{t} \equiv \dot{E} t (h_o (1 - \phi_o))$, for various $\alpha$, where $\dot{E}$ is the evaporation rate, $h_o$ is the initial average wet film thickness, $R$ is the radius of the particles, and $\phi_o$ is the initial particle volume fraction. Note that the initial thickness is different in the four cases.

**Figure 8.** Variations of effective shear modulus ($G_{eff}$) with $\alpha$. Note that the shear moduli for different interactions are $G_{HH} = 31$ GPa, $G_{SS} = 0.8$ GPa, and $G_{HS} = 0.8$ GPa.
Further, depending on the type of interaction, the links were either represented by springs or by dashpots. Finally, the deformation of this network was studied to investigate the sintering and deformation of randomly packed spheres. Here, two different cases were considered. In the first (bonded) case, the contact between hard particles resist all the relative velocities as well as spins. In second (sliding) case, the contacts between hard particles can slide and bend but resist interpenetration. In their analysis, force and moment balance equations were solved at each network point assuming that the system is in equilibrium. It was found that the transition from soft to hardlike behavior occurs at a rigidity threshold which coincides with the percolation threshold \((\alpha = 0.32)\) for the bonded case whereas in sliding case, the rigidity threshold was much higher \((\alpha \sim 1)\) than the percolation threshold.

We present both the theoretical and experimental investigations of latex blends containing equal sized elastic spheres of two different shear moduli. The model developed here extends the stress versus strain relation of Routh and Russel\(^\text{14}\) for a drying colloidal film containing identical spherical particles to that containing a latex blend. 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. The model has been successful in predicting not only the stress profile in drying films of both film forming and non-film forming dispersions\(^\text{12}\), but also in predicting the cracking mechanism in the latter.\(^\text{3,5}\)

In the present work, a mathematical model for film formation in latex blends has been developed. Here, we have employed the concepts developed for monodisperse systems and derived the constitutive equation for a blend with soft and hard particles. We account for the nonaffine deformation in the film and predict critical cracking stress and critical cracking thickness (CCT) that are validated with measurements on a blend of acrylic silica particles.

## 2. Model

Consider a drying colloidal film containing equal sized spherical particles of two different shear moduli. When the particles reach close packing, three different types of contacts between a pair

of particles are possible: namely, hard sphere—hard sphere (HH) contact, hard sphere—soft sphere (HS) contact, and soft sphere—soft sphere (SS) contact. The HH and SS contacts for the deformation of a two-particle system have been solved by Routh and Russell. They assumed that the particle pair is subjected to contact forces, \( \mathbf{F} \), that act along the line joining the centers of spheres and the particles deform such that they remain sections of spheres (Figure 1c) throughout the deformation. For the HS contact, we consider a pair of contacting hard and soft elastic spherical particles of equal size acted upon by contact forces, \( \mathbf{F} \), again, acting along the line joining their centers but we assume that the hard sphere is rigid while the soft sphere deforms elastically under the applied forces. Therefore, on complete deformation, the soft sphere engulfs the hard sphere. Figures 1a–c present schematics of the hard—soft particle pair at various stages of deformation.

The strain at the particle pair level is defined as the ratio of the change in the interparticle center to center distance, at any instant to that at complete deformation,

\[
\varepsilon_{HS} = \frac{\text{change in interparticle distance (at time } t\text{)}}{\text{change in interparticle distance at complete deformation}}
\]

(1)

For the present case,

\[
\varepsilon_{HS} = \frac{2R_0 - d_t}{2R_0 - d_f}
\]

(2)

where \( d_t = (2^{1/3} - 1)R_0 \). Here, \( R_0 \) is the original radius of the two particles, \( R_t \) is the radius of the soft sphere after the onset of deformation, and \( d_f \) is the distance between the centers of the hard and soft sphere during deformation, while \( d_t \) is the distance between the spheres at complete deformation. The variable \( \varepsilon' \) denotes the axial distance between the center of the soft sphere and the vertical plane passing through the intersection of the two spheres. The first step toward obtaining the stress—strain relation is to relate the radius of the expanding soft sphere to its original radius and the particle strain. The calculation of \( R_t/R_0 \) involves the volume conservation equation and is presented in Appendix A. Since, the value of \( R_t/R_0 \) is known at \( \varepsilon_{HS} = 0 \), (35) is successively differentiated with respect to \( \varepsilon_{HS} \) to obtain a Taylor series expansion up to \( O(\varepsilon_{HS}^3) \).

\[
\frac{R_t}{R_0} = 1 + \beta \varepsilon_{HS}^2 + O(\varepsilon_{HS}^3)
\]

(3)

As mentioned earlier, the goal is to relate the strain at the particle pair level to the forces acting on the pair. During the deformation, it is assumed that the surface of the soft sphere deforms radially while the surface of the hard sphere translates in the axial direction. Consequently, the surface displacement vector for the soft sphere is given by,

\[
\tilde{S}_1 = (R_t - R_0) \tilde{n}_1 + g(R_0, \varepsilon_{HS}) \tilde{\varepsilon}_z
\]

while that for the hard sphere is given by,

\[
\tilde{S}_2 = -(2R_0 - d_t) \tilde{\varepsilon}_z
\]

where, \( \tilde{n}_1 \) and \( \tilde{n}_2 \) (see Figure 1c) are unit vectors perpendicular to the surface of the soft and hard sphere, respectively, while \( \tilde{\varepsilon}_z \) is the unit vector in the \( z \)-direction. The function, \( g(R_0, \varepsilon_{HS}) \), is introduced to ensure global incompressibility condition. Then, the strain over the volume of the particle pair is given by (Appendix A),

\[
\int_V \varepsilon_{HS} dV = \int_V \frac{1}{2} \left( \nabla \tilde{S} + (\nabla \tilde{S})^T \right) = \int_A \frac{1}{2} (\hat{n} \tilde{S} + \tilde{S} \hat{n}) dA
\]

\[
= \frac{4}{3} \pi R_0^3 \beta \varepsilon_{HS}^2 (\tilde{T} - 3 \tilde{\varepsilon}_z \tilde{\varepsilon}_z) \quad (4)
\]

Since the volume of each sphere is \( (4/3) \pi R_0^3 \), the volume averaged strain over the two particles is

\[
\left\langle \varepsilon_{HS} \right\rangle = \frac{2}{3} \beta \varepsilon_{HS}^2 (\tilde{T} - 3 \tilde{\varepsilon}_z \tilde{\varepsilon}_z) \quad (5)
\]

Next, we determine the volume averaged stress on the particle pair. The volume integral of stress over the particle pair can be transformed to a surface integral by invoking Gauss’s theorem,

\[
\int_V \bar{\sigma} dV = \int_A \hat{n} \cdot \bar{\sigma} \hat{x} dA
\]

(6)

where \( \hat{n} \) is the unit normal from the surfaces of both particles and \( \hat{x} \) is the position vector. Since we neglect van der Waals force and interfacial tension, only the interparticle contact force contributes to stress,

\[
\hat{n} \cdot \bar{\sigma} = -P_0 \hat{n} \cdot \tilde{T} + \frac{F}{2\pi R_0} \delta(z + R_0) \hat{\varepsilon}_z - \frac{F}{2\pi R_0} \delta(z - d_f - R_0) \hat{\varepsilon}_z
\]

(7)

where \( \delta(z) \) is the Dirac-Delta function and \( P_0 \) is the pressure in the surrounding fluid. On substituting (7) in (6), we have

\[
\int_V \bar{\sigma}_{HS} dV = \int_{A_1 + A_2} \hat{n} \bar{P}_0 \tilde{x} dA + \int_{A_1} \frac{F}{2\pi R_0} \tilde{\varepsilon}_z (r \hat{\varepsilon}_r + z \hat{\varepsilon}_z) dA - \tilde{\varepsilon}_z (r \hat{\varepsilon}_r + z \hat{\varepsilon}_z) dA
\]

\[
\int_{A_2} \frac{F}{2\pi R_0} \tilde{\varepsilon}_z (z - d_f - R_0) = -\frac{8}{3} \pi R_0^3 P_0 \tilde{T} - 4F R_0
\]

\[
\left( 1 - \sqrt{\frac{\beta}{2 \varepsilon_{HS}^3}} \right) \tilde{\varepsilon}_z
\]

(9)

where \( A_1 \) and \( A_2 \) represent surface areas of soft and hard surface respectively (see Appendix B). The stress is then averaged over the two spheres to obtain the volume averaged quantity,

\[
\left\langle \bar{\sigma}_{HS} \right\rangle = \frac{1}{V} \int_V \bar{\sigma}_{HS} dV = -P_0 \tilde{T} - \frac{3F}{2\pi R_0} \left( 1 - \sqrt{\frac{\beta}{2 \varepsilon_{HS}^3}} \right) \tilde{\varepsilon}_z
\]

(10)

For the particle pair deforming under the contacting force, the deviatoric stress \( \left\langle \bar{\sigma}_{HS} \right\rangle \) and the strain \( \left\langle \varepsilon_{HS} \right\rangle \) are related to stress relaxation modulus of the material by

\[
\left\langle \bar{\tau}_{HS} \right\rangle = 2 \int_{-\infty}^t G(t - t') \frac{d\left\langle \varepsilon_{HS} \right\rangle}{dt'} dt'
\]

(11)

The deviatoric stress tensor is related to the total stress, \( \left\langle \bar{\sigma}_{HS} \right\rangle \) and the isotropic pressure \( P \) as

\[
\left\langle \bar{\sigma}_{HS} \right\rangle = \left\langle \bar{\tau}_{HS} \right\rangle - \left( P \right) \tilde{T}
\]

(12)

where

---


\[ \langle P \rangle = P_0 + \frac{F}{2\pi R_0^2} \left( 1 - \sqrt{\frac{\beta}{2\epsilon_{HS}}} \right), \]
and
\[ \langle \tau_{HS} \rangle = \frac{F}{2\pi R_0^2} \left( 1 - \sqrt{\frac{\beta}{2\epsilon_{HS}}} \right) \left( T - 3\dot{\epsilon}_0 \dot{\epsilon}_0 \right) \]

On substituting the averaged deviatoric stress and strain tensor in (11), the contact force is related to the particle strain to \( O(\epsilon_{HS}^2) \).

\[ F = \frac{4\pi R_0^2}{3} \beta \int_0^t G(t - t') \frac{d}{dr} \langle \epsilon_{HS}^2 \rangle \, dt' \]  

Note that the trace of the volume averaged stress gives the average isotropic pressure in the particle as well as the equation governing the viscoelastic deformation of two spheres (12).

2.1. Nonaffine Deformation. Recall that Routh and Russell derived the stress–strain relation for a film containing monodisperse identical spheres by assuming affine deformation, where the strain at the particle level is the same as that at the macroscopic level. However, for a latex blend containing equal-sized hard and soft spheres, the strain at the particle pair level will depend on the moduli of the interacting particles and will in general be different from that at macroscopic level. Next, we account for the nonaffinity by assuming that the strain at the particle pair level for the three types of interactions differs from macroscopic strain by a function that, at lower order, is linear in macroscopic strain,

\[ \langle \epsilon_{SS} \rangle - \langle \epsilon \rangle = a(\epsilon) \]
\[ \langle \epsilon_{HH} \rangle - \langle \epsilon \rangle = b(\epsilon) \]
\[ \langle \epsilon_{HS} \rangle - \langle \epsilon \rangle = c(\epsilon) \]

Here \( \langle \epsilon \rangle \) is the macroscopic strain tensor and \( \langle \epsilon_{SS} \rangle, \langle \epsilon_{HH} \rangle \), and \( \langle \epsilon_{HS} \rangle \) are respectively the strain tensors at the particle pair level for soft–soft, hard–hard, and hard–soft interactions. If the fraction of hard particles (total particles) is \( \alpha \), then the probability of finding a pair of hard–hard particles in a representative volume is \( \alpha^2 \), that of a pair of soft–soft particles is \( 1 - \alpha \), and that of a pair of hard–soft particles is \( 2\alpha(1 - \alpha) \).

\[ \alpha^2 \langle \epsilon_{HH} \rangle + (1 - \alpha)^2 \langle \epsilon_{SS} \rangle + 2\alpha(1 - \alpha) \epsilon_{HS} = \langle \epsilon \rangle \]

The constraint equation is therefore

\[ a(1 - \alpha)^2 + b\alpha^2 + 2\alpha(1 - \alpha) = 0 \]

2.2. Orientational Average Stress–Strain Relation. We focus on a single particle in the packing and integrate over the configuration of its neighbors to obtain the volume averaged macroscopic stress,

\[ \langle \sigma \rangle = \frac{1}{V} \int_V \sigma \, dV = \frac{1}{V} \sum_{\text{contacts}} \bar{F} \bar{R} - \int_P \bar{P} \bar{T} \, dV \]

where, \( \langle \bar{F} \rangle \) is the macroscopic stress in a representative volume containing the particles, \( \Sigma \) represents the contribution from all its contacting neighbors, and \( \bar{R} \) is the position vector for the contacting forces (Figure 1d). The averaged stress (indical notation) can be rewritten to highlight the contribution from the two phases,

\[ \langle \sigma_{ij} \rangle = \langle \sigma_{ij} \rangle_{\text{liquid}} - \langle \sigma_{ij} \rangle_{\text{solid}} = \left\{ \begin{array}{ll}
(1 - \phi)P_0\delta_{ij} & \text{if} \quad \phi P_0\delta_{ij} + \frac{1}{V} \sum_{n} \bar{F}_n^i \bar{R}_n^j \end{array} \right\} \]

Since the stress generated in the solid phase arises from all possible interaction, we have

\[ \sigma_{ij} = -(1 + \phi)P_0 \left\{ \phi P_0\delta_{ij} + \frac{1}{V} \sum_{n} \bar{F}_n^i \bar{R}_n^j \right\} \]

\[ \left( \alpha^2(1 + a)^2 G_{SS} + \alpha^2(1 + b)^2 G_{HH} + \left( \frac{8}{3} \beta \right)^2 2\alpha(1 - \alpha)^2 G_{HS} \right) \]

The product of the contact force and its position vector for each of the interactions to the lowest order in respective strain is given by

\[ (F_{R})_{SS} = \frac{\pi R_0^3}{2} \int_0^t G_{SS}(t - t') \frac{d}{dt} \left[ \frac{r_{mm}^\epsilon}{r^2} \right] \epsilon_{mm} \frac{d}{dt} \]

\[ (F_{R})_{HH} = \frac{\pi R_0^3}{2} \int_0^t G_{HH}(t - t') \frac{d}{dt} \left[ \frac{r_{mm}^\epsilon}{r^2} \right] \epsilon_{mm} \frac{d}{dt} \]

\[ (F_{R})_{HS} = \frac{4\pi R_0^3}{3} \int_0^t G_{HS}(t - t') \frac{d}{dt} \left[ \frac{r_{mm}^\epsilon}{r^2} \right] \epsilon_{mm} \frac{d}{dt} \]

where the soft–soft (22) and hard–hard (23) particle contact relations are taken from Routh and Russell and \( G_{SS}, G_{HH}, \) and \( G_{HS} \) are the relaxation moduli for the three contacts. Note that \( G_{HH} \) becomes equal to \( G_{SS} \) when \( G_{HH} > G_{SS} \). Assuming all orientations of the particles to be equally likely, we average over them to obtain,

\[ \sigma_{ij} = -P_0 \delta_{ij} \left\{ \phi P_0 \delta_{ij} + 4\epsilon_{mm} \right\} \]

where, \( \phi \) is the total solid volume fraction and \( M \) is the average number of nearest neighbors. Up to this point, we have assumed the most general form of constitutive relation for the film deformation. In order to determine the values of \( a, b, \) and \( c \), we shall now consider special case of a packing containing hard and soft elastic spheres where the above relation becomes,

\[ \sigma_{ij} = -P_0 \delta_{ij} \left[ \frac{M\phi}{280} \right] \left\{ (1 - \alpha)^2(1 + a)^2 G_{SS} + \alpha^2(1 + b)^2 G_{HH} + \left( \frac{8}{3} \beta \right)^2 2\alpha(1 - \alpha)^2 G_{HS} \right\} \]

Landau and Lifshitz show that for an isotropic elastic material, the elastic energy density up to third order in strain is given by,

\[ \epsilon' = \mu \epsilon + \frac{\kappa}{3} \epsilon + \frac{4}{3} \epsilon \epsilon_{mm} + 4 \epsilon \epsilon_{mm} \epsilon_{mm} + 2 B \epsilon \epsilon_{mm} \epsilon_{mm} + \frac{C}{3} \epsilon_{mm} \epsilon_{mm} \]
The elastic energy for closed packing of a latex blend (in the absence of solvent) to the lowest order in strain can be obtained by substituting values of \( A, B, \) and \( C \) in (27). Next, we hypothesize that the nonaffine strains at the particle level will be such that they minimize the elastic energy of the network. Here we use the standard principle of minimum total potential energy, which states that all displacements that satisfy the boundary conditions of a structural system, those corresponding to configurations of stable equilibrium make the total potential energy a relative minimum. This approach is similar to Hashin’s variational method \(^{14}\) used to determine bounds for the overall shear modulus for composites containing linear elastic phases. Under a given deformation, minimization of \( \gamma \) with respect to nonaffine strains amounts to minimizing the coefficient \( G_{\text{eff}} \) with the constraint given in (17), i.e.

\[
\text{minimize } G_{\text{eff}} \text{ for constraint: } a(1 - \alpha^2) + b\alpha^2 + 2c\alpha(1 - \alpha) = 0 \quad (28)
\]

Using the method of Langrange multipliers, we get

\[
1 + a = \left[ \frac{\alpha^2}{G_{\text{HH}}} + \frac{(1 - \alpha)^2}{G_{\text{SS}}} + \frac{3}{8\beta} \frac{2\alpha(1 - \alpha)}{G_{\text{HS}}} \right] \frac{1}{G_{\text{SS}}}
\]

\[
1 + b = \left[ \frac{\alpha^2}{G_{\text{HH}}} + \frac{(1 - \alpha)^2}{G_{\text{SS}}} + \frac{3}{8\beta} \frac{2\alpha(1 - \alpha)}{G_{\text{HS}}} \right] \frac{1}{G_{\text{HH}}}
\]

\[
1 + c = \left[ \frac{\alpha^2}{G_{\text{HH}}} + \frac{(1 - \alpha)^2}{G_{\text{SS}}} + \frac{3}{8\beta} \frac{2\alpha(1 - \alpha)}{G_{\text{HS}}} \right] \frac{1}{G_{\text{HS}}}
\]

so that the effective shear modulus becomes

\[
G_{\text{eff}} = \frac{1}{\left[ \frac{\alpha^2}{G_{\text{HH}}} + \frac{(1 - \alpha)^2}{G_{\text{SS}}} + \frac{3}{8\beta} \frac{2\alpha(1 - \alpha)}{G_{\text{HS}}} \right]}
\]

Note that the constitutive relation (25) is similar to that derived by Routh and Russel\(^{1}\) for identical spheres except that the shear modulus is replaced by the effective modulus.

Tirumkudulu and Russel\(^{3}\) used their constitutive relation to calculate the stress field in a drying film and determined the critical stress for the film to crack by adopting the well-known Griffith energy balance concept. For the case of a drying film containing latex blends, we can write directly the expression for the critical stress for cracking,

\[
\frac{\sigma_c R_0}{2\gamma} = 0.1877 \left( \frac{2R_0}{h} \right)^{2/3} \left( \frac{G_{\text{eff}} M\phi_{\text{exp}} R_0}{2\gamma} \right)^{1/3} \quad (29)
\]

Here, \( \gamma \) is the liquid–gas interfacial tension, \( h \) is the film thickness, and \( \phi_{\text{exp}} \) is the random close packing volume fraction. The derivation of the above expression can be understood from a simple scaling analysis. According to the constitutive relation, the in-plane tensile stress generated in the film during drying scales with the square of the strain, \( \sigma \sim Ge^2 \). On equating the elastic energy recovered per unit length of crack, \( E_c \sim h^3\sigma_0 \), to the increased surface energy per unit length, \( E_s \sim y/h \), we get the critical stress for cracking, \( \sigma_c \sim G^{1/3}(y/h)^{2/3} \). Note that the critical stress is independent of particle size.

More recently, Singh and Tirumkudulu\(^{4}\) identified two regimes for obtaining crack free films for a drying colloidal film containing identical particles. The strain–limited regime pertains to the case of a drying film containing soft particles where the particles completely deform to fill the pores under the capillary pressure exerted by the menisci at the top of the film. This is possible only when the tensile stress at maximum deformation is less than the critical stress. Thus the critical cracking thickness \( h_{\text{max}} \) below which the films are crackfree is obtained from,

\[
G^{1/3}(y/h)^{2/3} \sim G(1 - \phi_{\text{exp}}) \gamma \quad \text{giving } h_{\text{max}} \sim \gamma G(1 - \phi_{\text{exp}})^{3/2} \quad \text{Alternatively, the stress–limited regime occurs when the particles are hard and the menisci adjust their curvature till the maximum capillary pressure (\( P_{\text{max}} \)) is reached, beyond which they recede into the network resulting in partial deformation. Here the critical thickness is obtained by equating the stress at \( P_{\text{max}} \) to the critical cracking stress, \( \sigma_c \sim G^{1/3}(y/h)^{2/3} \sim -P_{\text{max}} \) giving \( h_{\text{max}} \sim \gamma G^{1/3}(P_{\text{max}})^{3/2} \).

For latex blends, the corresponding critical cracking thickness for the strain–limited regime is given by

\[
h_{\text{max}} = \frac{37\gamma}{G_{\text{eff}} M\phi_{\text{exp}} (1 - \phi_{\text{exp}})^3} \quad (30)
\]

while that for the stress–limited regime is

\[
h_{\text{max}} = 0.64 \left[ \frac{G_{\text{eff}} M\phi_{\text{exp}} R_0}{2\gamma} \right]^{1/3} \frac{(2\gamma)}{P_{\text{max}} R_0}^{1/2} \quad (31)
\]

A single value of the dimensionless capillary pressure, \( -P_{\text{max}}R_0/2\gamma \sim 1.4 \), resulted in a good match between CCT measurements and above predictions over a wide range of particle sizes and rigidities. The same value was used in this study for all values of \( \alpha \).

### 3. Experiments

Experiments were conducted with a blend of silica and acrylic (BX261) particles of same size. Details of the dispersions used in this study are given in Table 1. Although the particle size is the same, there is a significant difference in the particle rigidity. The composition of the blend is described in terms of relative hard particle volume fraction \( \alpha \). The value of \( \alpha \) was varied from 0 to 1 and for each composition, the critical stress for cracking as a function of film thickness and critical cracking thickness (CCT) were measured.

The CCT measurements were performed over a temperature range of 25–28 °C and a relative humidity of 35–40%. Thin films were cast on glass substrates placed on a spin coater (slow rotation rate ~20 rpm) by disbursing small amounts of dispersion. Here, the spin coater was employed to spread the liquid uniformly over a fixed area so as to obtain a nearly circular film. Further, the thickness of the film was varied by disbursing increasing amounts of dispersion over the same area. After the films were cast, they were left to dry under ambient conditions. On complete drying, it was examined under an optical upright microscope (Olympus, BX-60) for cracks at varying magnifications. Finally, the thickness profile of the dry film was obtained using a surface profilometer (Dektak-150). It should be noted that in some cases the entire film was crack free which gave the lower limit for CCT.

The classical cantilever technique was employed to measure the stress in a drying film.\(^{15}\) Here, a thin layer of the dispersion was applied on a thin silicon wafer of dimensions 13 mm (length) by 5

### Table 1. Details of Dispersions Used in the Present Study

<table>
<thead>
<tr>
<th>dispersion</th>
<th>Particle Composition</th>
<th>Particle Diameter (nm)</th>
<th>( T_g ) (°C)</th>
<th>Shear Modulus ( G ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>colloidal silica</td>
<td>silica</td>
<td>330</td>
<td>31</td>
<td>0.8</td>
</tr>
<tr>
<td>acrylic (BX261)</td>
<td>acrylate</td>
<td>353</td>
<td>40</td>
<td>0.8</td>
</tr>
</tbody>
</table>

mm (width) by 0.128 mm (thickness) and clamped on one side. A laser beam is reflected from the free end of the substrate and collected by a position sensitive detector (On-track). The position of the detector is set in such a way that the reflected beam falls normally on the surface of the detector. The entire detector assembly is mounted on a traverse so that the desired positioning can be done with precision. The position data (i.e., the x, y coordinates of the reflected beam) from the detector is directly fed to a computer. As the film dries, the tensile stresses in the drying film bend the substrate that consequently results in the movement of reflected beam on detector surface. Finally, the displacement of the reflected beam is related to the average tensile stress in the film. The details of stress measurement technique and CCT measurements can be found in the work of Tirumkudulu and Russel[12] and Singh and Tirumkudulu,[4] respectively.

We also ensured that the evaporation rate for these experiments was constant throughout the experiment. This was checked by drying films separately under similar conditions on a weigh balance. We also noticed that the drying rate remained constant long after the film cracked. Hence, we could also measure the evaporation rate of the sample used for stress experiments by transferring it to the weigh balance immediately after it cracked and recording its weight change.

In blends, one of the major concerns is the distribution of the constituent soft and hard particles. As reported by Feng et al.,[9] the morphology of blend films is influenced by the distribution of hard and soft particles. Films were examined using scanning electron microscopy to see the particle distribution.

4. Results and Discussion

As shown in Table 1, the blends contain particles of similar size but with a very different shear moduli. In order to see the particle distribution in the final film, dried films were viewed under a scanning electron microscope (SEM). Figure 2 shows the SEM image of the surface of a dried film with \( \alpha = 0.5 \). The hard particles are uniformly distributed in the matrix of soft particles. Further, the soft acrylic particles seemed to have undergone significant deformation at the film surface. In order to see the particle distribution throughout the film, the film was cut and the cross section imaged. Again, the cross section or the interior of the film has a uniform distribution of both the soft and hard particles (Figure 3). Here also, the soft particles can be seen to have deformed significantly. To differentiate between the two types of particles and to ascertain their distribution inside the film, we exposed one of the films to an ambient temperature of 40 °C in an oven for half an hour. Since the glass transition temperature of the soft (acrylic) particles is 40 °C, we expect the particles to fuse completely on heating at such an elevated temperature. Figure 4 shows the SEM image of one such film where the deformed domains confirm that the distribution of soft-hard particles in the blend is indeed uniform. Figure 5 shows the SEM image of the same film close to the film-substrate interface. It appears that the film has a slightly larger number of hard particles at the film-substrate interface compared to the soft particles but this segregation appears to be restricted close to the substrate. We next look at the particle distribution for \( \alpha = 0.95 \) (Figure 6). As can be seen, the hard particles in the film are packed in well-ordered domains. Further, the coalesced soft particles can also be seen at a few locations between the hard particles. This is indeed surprising given that the soft particle fraction is very small which suggests that the hard and soft particles are dispersed well at all volume fractions.

Figure 7 presents the dimensionless stress evolution as a function of the dimensionless time for four different values of \( \alpha \). Once the particle concentration reaches that for random packing, the stress starts to increase, reaches a maximum at which the film cracks, and then decreases. Note that we do not present the full stress relaxation profile after cracking as the samples are removed for measuring the evaporation rate shortly after the crack initiation. For both \( \alpha = 0 \) and 0.5, the increase and the decrease in stress is slow suggesting that the film undergoes viscous deformation. This suggests that even with 50% hard particles, the response is essentially that for soft particles. This observation is in line with the experiments of Martinez and Lewis[6] who did not find any significant variation with hard particle fraction in stress profile for films containing less than 40% hard particles. In contrast to these profiles, those for \( \alpha = 0.9 \) and 1 show that the stress reaches a maximum value within \( \Delta t = 0.01 \) and decreases to a negligible value as quickly. The response here is entirely elastic as the stress relaxes to a negligible value immediately after crack nucleation.

4.1. Comparison with the Model. The dependence of effective shear modulus on \( \alpha \), as predicted by the model, is presented in Figure 8. The effective shear modulus varies little and is close to the shear modulus of the soft particles for \( \alpha < 0.95 \). This suggests that the addition of hard particles into the soft matrix for \( \alpha < 0.95 \) does not significantly contribute to the mechanical properties of the film and hence the blend essentially behaves like the one composed of only soft particles. However, at a value of \( \alpha \) close to 0.95, a steep increase in the effective shear modulus is seen. It implies that the transition from soft to rigidlike behavior takes place at this value of \( \alpha \). The experimental results shown in Figure 6 also point to this type of behavior where the hard particles are packed in a very ordered structure and hence are capable of transmitting the applied load to the entire film. It is interesting to note that the model predictions are in good agreement with the numerical simulations of Jagota and Scherer[11] who showed that the rigidity threshold in a mixture of soft-hard particles with sliding contacts between hard particles is at a site fraction close to 0.95. However, it is important to note that, for cases where the shear moduli for soft-soft (\( G_{ss} \)) and hard-hard (\( G_{hh} \)) interactions are comparable, a more gradual transition from soft to rigidlike behavior will be observed unlike that seen in Figure 8.

The variations in dimensionless critical stress with the dimensionless film thickness over the entire range of volume fraction ratio (\( \alpha \)) are shown in Figure 9. The dependence of dimensionless critical stress on dimensionless film thickness for \( 0 < \alpha < 1 \) is similar to the predicted behavior of \( G_{eff} \) in that a jump in the critical stress is seen for values of \( \alpha \gtrsim 0.95 \). The stress measurements also confirm the transition from soft to rigidlike behavior at \( \alpha \sim 0.95 \). Figure 10 compares the stress measurements with those predicted by the model. Here, the theoretical plots are scaled in such a way that the line for \( \alpha = 1 \) matches with the experiments. The predicted critical stress variation with film thickness matches with all the experiments in that the exponent of two-thirds is close to the observed trend. This confirms the validity of the proposed approach to lump the modulus variations in \( G_{eff} \). However, at lower values of \( \alpha \), the absolute values are lower than the experimental results. The discrepancy can be attributed to the viscous deformation of the soft particles. The energy dissipation reduces the stored elastic
energy in the network thereby requiring higher stresses to crack the film.

The experimental results for critical cracking thickness (CCT) are compared with the theoretical predictions for different values of $\alpha$ in Figure 11. The measured CCT varies almost linearly with $\alpha$ whereas the model shows an abrupt increase in CCT at a value of $\alpha$ close to 0.95. This is somewhat surprising given that the trend for the measured critical stress shows a negligible variation for $\alpha < 0.95$. The model predictions match well with theory for both low and high values of $\alpha$ but exhibit large differences for the intermediate values. One possible reason for the discrepancy could be the following. The critical cracking stress for a thin film varies inversely with film thickness (29). For the measurement of critical stress, we typically apply thick films ($\sim$100–200 $\mu$m) on our substrates and measure the stress at which the film cracks. Since the stresses are low, we would expect small particle deformations in the film and, for higher values of $\alpha$, they would be mostly elastic. On the other hand, we apply thin films ($\sim$5–20 $\mu$m) to determine the critical cracking thickness. Here, the film experiences the highest possible stress that corresponds to the maximum capillary pressure. Consequently, at such large stresses we can expect significant viscous deformation of the particles. It is possible that the simple assumptions made to account for the nonaffine deformation (14)–(16) may not be valid at such large deformations. Thus the large mismatch may be due to the significant viscous deformation of the soft particles although the model assumes them to undergo small elastic deformation in the packing. More work is required to resolve these issues.

5. Conclusion

A mathematical model for film formation in latex blends has been developed. The model captures the main aspects of drying and cracking behavior of the blend films. The model predictions correspond well with the numerical simulations reported in the literature for the transition in soft to rigidlike behavior for blends of hard and soft particles. Further, the model predictions are validated with extensive experimental data. While the predicted critical stresses match well with the measured values, the critical thickness shows a trend different from the experiments. The viscous deformation of the particles in the drying film which has not been accounted for in the model may be the cause for the discrepancy.

Acknowledgment. This work was supported by the Department of Science and Technology, India. The authors thank Dr. Martin Murray of AkzoNobel for discussions and Dr. S. L. Kamath of Metallurgy and Materials Science Department of IIT—Bombay for help with SEM images.

Appendix A: Calculation of $R_i/R_s$ Ratio

Consider the following position of hard and soft spheres. With the origin of the coordinate system fixed at the center of the soft sphere, $R_i$ the radius of the soft sphere, $R_s$ the radius of the rigid sphere at any stage of deformation, and $d_i$ defined as distance between centers of both sphere, the equation for the soft sphere becomes,

$$x^2 + y^2 + z^2 = R_i^2$$

and that for the hard sphere is

$$x^2 + y^2 + (z - d_i)^2 = R_s^2$$

The plane of intersection between two spheres is given by solving (32) and (33) and is at distance $z = \zeta$ from the origin,

$$\zeta = \frac{R_i^2 - R_s^2 + d_i^2}{2d_i}$$

The sectional volumes are shown in Figure 12. The volume of the section of the sphere is given by

$$V_i = \frac{2}{3} \pi h_i (3r_i^2 + h_i^2) \quad i = 1, 2$$

where $V_i$ is the volume enclosed in section ACBA and $V_2$ is the volume of the section ADAB. The height $h_i$ and radius $r_i$ for the sectional volume $V_i$ are, $h_1 = (R_0 - d_i + \zeta)$ and $r_1 = (R_0^2 - (d_i - \zeta)^2)^{\frac{1}{2}}$. Similarly, for the sectional volume of soft sphere, we have $h_2 = (R - \zeta)$ and $r_2 = (R_{\text{soft}}^2 - (R - \zeta)^2)^{\frac{1}{2}}$. The hard and soft spheres are assumed to be initially of equal radii. Enforcing the volume conservation condition, we have

$$4 \pi R_i^3 - V_1 - V_2 = 4 \pi R_s^3$$

Appendix B: Two Particle Coordinate System

The equation of the soft sphere at any time is given by

$$x^2 + y^2 = R_i^2 - z^2 = f_i(z)$$

The equation of the surface is given by

$$F_i = x^2 + y^2 - f_i(z)$$

so that the normal unit vector to the surface of the soft particle is given by

$$\hat{n}_1 = \frac{\nabla F_i}{|\nabla F_i|} = \frac{2x \hat{x} + 2y \hat{y} - f_i'(z) \hat{z}}{\sqrt{4(x^2 + y^2) + f_i'(z)^2}} = \frac{r}{R_i} \hat{r} - \frac{f_i'(z)}{2R_i} \hat{z}$$

where $f_i'(z) = -2z$. Similarly, the normal to the surface of the harder particle is given by

$$\hat{n}_2 = \frac{2x \hat{x} + 2y \hat{y} - f_s'(z) \hat{z}}{\sqrt{4(x^2 + y^2) + f_s'(z)^2}} = \frac{r}{R_0} \hat{r} - \frac{f_s'(z)}{2R_0} \hat{z}$$

where the equation of the second sphere is given by

$$x^2 + y^2 = R_0^2 - (z - d)^2 = f_s(z)$$

The area of the surface element for the first sphere is given by (Figure 13)

$$dA = \frac{\sqrt{f'_i(z)}}{\cos \psi} \, dz \, d\theta = R_i \, dz \, d\theta$$

so that the surface integral of a function $M(z, \theta)$ over the surface of the soft sphere is given by (40)
Integrating the above surface integral for the soft sphere within limits, \( z_1 = -R_0 \) and \( z_2 = z' \), the value of surface deformation is given by

\[
(SI)_1 = \int_0^{2\pi} \int_{z_1}^{z_2} M(z, \theta) R_i \, dz \, d\theta \quad (40)
\]

For the hard sphere, the limit of definite integral becomes \( z_1 = z' \) and \( z = R_0 + d_0 \), and the value of the surface integral then becomes

\[
(SD)_2 = \int_0^{2\pi} \int_{z'}^{R_0 + d_0} \left[ -(2R_0 - d_0) \right] R_0 (\hat{n}_3 \hat{e}_z + \hat{e}_z \hat{e}_{z'}) \, dz \, d\theta \quad (42)
\]

**Calculation of the Trace**

For an incompressible material, the trace of \( \{ f_V \hat{\epsilon}_{IS} \, dV \} \) = 0. The strain integrated over the volume of the two spheres, can be written in terms of the surface integral over surface displacements,

\[
\int_V \hat{\epsilon}_{IS} \, dV = \int V \frac{1}{2} (\nabla \hat{S} + \nabla \hat{S}^T) \, dV = \int_A \frac{1}{2} (\hat{S} + \hat{S}) \, dA \quad (43)
\]

For the soft sphere, the displacement vector is along the outward direction radial from its center,

\[
\vec{S}_1 = (R_i - R_0 \hat{n}_1 + g(R_0, \epsilon_{IS}) \hat{e}_z
\]

The normal \( \hat{n}_1 \) to the surface of soft sphere is given by (37), so that

\[
\hat{n}_1 \hat{e}_1 = \frac{R_0^2}{R_i^2} \hat{e}_r \hat{e}_r + \frac{f_1'(z) \hat{e}_r + f_1'(z) \hat{e}_z}{4R_i^2} \hat{e}_r \hat{e}_z - \frac{1}{2} \frac{R_0^2}{R_i^2} (\hat{e}_r \hat{e}_r + \hat{e}_z \hat{e}_z) \quad (44)
\]

The zero trace condition results in two surface integrals, \( I_1 \) with terms containing \( \hat{e}_r \hat{e}_r \) and \( \hat{e}_r \hat{e}_z \), and \( I_2 \) and \( I_3 \) with terms containing \( \hat{e}_z \hat{e}_z \) for the soft sphere while \( I_2 \) is obtained for the hard sphere,

\[
I_1 = \int_0^{2\pi} \int_{R_i}^{R_0} \frac{R_0^2}{R_i^2} (R_i - R_0) R_0 + (\cos \theta \hat{e}_r + \sin \theta \hat{e}_z) \times
\]

\[
(\cos \theta \hat{e}_r + \sin \theta \hat{e}_z) \, dz \, d\theta
\]

For the hard sphere, the displacement along the \( \hat{e}_z \) direction, so that the surface displacement vector is

\[
\vec{S}_2 = -(2R_0 - d_0) \hat{e}_z \quad (45)
\]

Hence, \( \{ f_V \vec{S}_2 \, dV \} \) is given by

\[
I_4 = \int_0^{2\pi} \int_{z'}^{R_0} \left[ \frac{f_1'(z) \hat{e}_r + f_1'(z) \hat{e}_z}{2R_0} (2R_0 - d_0) \hat{e}_{z'} \hat{e}_{z'} \right] \, dz \, d\theta
\]

The other terms in the trace \( \{ f_V \hat{\epsilon}_{IS} \, dV \} \) go to zero because for the coordinate system defined,

\[
\int_0^{2\pi} \hat{e}_r \hat{e}_r \, d\theta = \int_0^{2\pi} (\cos \theta \hat{e}_r + \sin \theta \hat{e}_r) \, d\theta = 0 \quad (46)
\]

Also, it can be verified that

\[
\int_0^{2\pi} \hat{e}_r \hat{e}_z \, d\theta = \int_0^{2\pi} (\cos \theta \hat{e}_r + \sin \theta \hat{e}_r) \cos \theta \hat{e}_z + \sin \theta \hat{e}_r \, d\theta = \pi (\hat{e}_r \hat{e}_r + \hat{e}_r \hat{e}_z) \quad (47)
\]