A Model for Gel Drying

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Synopsis

A theoretical model for drying of a thin gel film is presented. The model is based upon the premise that as solvent is removed from any portion of a gel structure which is permeable by the solvent, the structure shrinks locally to fill the voids left by the solvent. The diffusion coefficient of solvent through the gel film is assumed to be an exponential function of concentration and temperature. The governing equations for the model indicate that for nonisothermal drying, the results of drying and shrinkage rates are functions of 13 independent dimensionless system variables. These results are obtained with the help of a computer solution of the proposed model. The computer results indicate that, except under extreme temperature conditions, the drying and shrinkage rates are most influenced by dimensionless groups M, P, and $\overline{P}$, defined by eq. (9) of the paper. Furthermore, the drying and shrinkage rates are essentially independent of groups M and P for the values of M and P greater than approximately 100 and 10, respectively. The effect of variable solvent diffusivity on approximate time to achieve the steady-state drying and shrinkage rates is approximately handled by defining a dimensionless time variable $\bar{\tau}$ in terms of average solvent diffusivity. Finally, some experimental data on drying and shrinkage rates of isothermal drying of lyphogel film under natural convection condition are obtained. These data are found to be in qualitative agreement with similar computer predictions by the proposed model.

INTRODUCTION

It is a commonly observed phenomenon that evaporation of a solvent from a gel structure causes a considerable shrinkage in the gel. This shrinkage either causes loss in solvent permeation characteristics of the gel or it makes the gel brittle and sometimes creates fractures in it. From a practical standpoint, both of these phenomena are undesirable. A theoretical model which could predict the drying and shrinkage rates of a gel structure under a wide variety of drying conditions is therefore needed.

The present paper describes a theoretical model for drying of a gel structure. Even though the model is developed mainly for a *thin film* geometry such as the one illustrated by Figure 1, a very similar model can be easily obtained for other shapes of gel such as an infinite cylinder, etc. The predictions of the model are tested against experimental data on isothermal drying of lyphogel film. The model should be applicable to the processing

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of all materials which shrink and either rupture or loose their physical properties during drying.

THEORETICAL

The theoretical model developed here is based upon the premise that as solvent is removed from any portion of a gel structure which is premeable by the solvent, the structure shrinks locally to fill the voids left by the solvent. Therefore, any concentration gradients of solvent in the gel will create differences in local shrinkage, which in turn cause the loss in physical properties of the gel and the development of local stresses within the gel structure. If these stresses exceed the yield stress of the gel, it ruptures.   The gel and solvent can be assumed to behave as a regular solution.

Consider a thin film of gel (very long in the other two directions) depicted in Figure 1, with initial solvent content X_0 (lb_m solvent/lb_m of solvent-free gel), temperature T_0, and thickness L_0, suddenly immersed in a gas stream at temperature T_G and solvent partial pressure P_G.   At some time t after immersion, the gel has assumed a transverse concentration and temperature profile governed by the rates of mass and heat transfer at the surface and within the structure.   In addition, the gel thickness has been reduced because of shrinkage due to solvent loss.   If one assumes a basis of one unit mass of solvent-free gel, the local density of the structure is given by

$$\rho(y,t) = [1 + X(y,t)]\Big/\left[\frac{1}{\rho_g} + \frac{X(y,t)}{\rho_s}\right] \tag{1}$$

where ρ_g and ρ_s are solvent-free gel density and solvent density, respectively.   The rate of mass transfer of solvent from the surface, W, is given by

$$W = \left[D \exp\left([\gamma_1 + \gamma_2(T - T_0)]\left\{X\Big/\left(\frac{1}{\rho_g} + \frac{X}{\rho_s}\right)\right\}\right)\frac{\partial}{\partial y}\right.$$
$$\left.\times \left\{X(y,t)\Big/\left[\frac{1}{\rho_g} + \frac{X(y,t)}{\rho_s}\right]\right\}\right]_{y=L} = M_s K_G(P_V - P_G)$$
$$= M_s K_G \left[\frac{KX(y,t)P_s(L,t)}{\rho_s\left[\frac{1}{\rho_g} + \frac{X(y,t)}{\rho_s}\right]} - P_G\right] \tag{2}$$

where the vapor pressure of the solvent at the surface, P_s, is

$$P_s(L,t) = P_0 \exp\left[\frac{M_s\lambda(T(L,t) - T_0)}{R_G T_o T(L,t)}\right] \tag{3}$$

In eq. (2), D is the diffusion coefficient of solvent through gel at zero solvent concentration; M_S is the molecular weight of the solvent; K_G is the gas-phase mass transfer coefficient; K is Henry's law constant; P_G is the partial
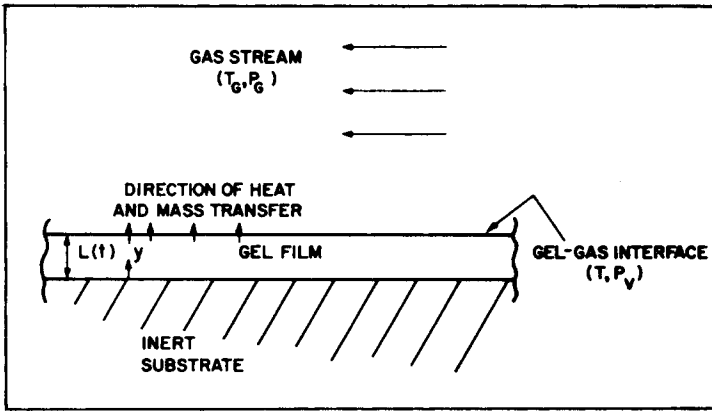
Fig. 1. Schematic of a gel drying process.

pressure of solvent in the bulk gas phase, and γ_1 and γ_2 are the coefficients which take account of concentration and temperature dependence of solvent diffusivity. In eq. (3), P_0 is the vapor pressure at initial temperature T_0; λ is the heat of vaporization; and R_G is the universal gas constant. X, T, and L in eqs. (2) and (3) are the time-dependent local solvent concentration, the temperature, and the thickness of gel, respectively; and y in eq. (2) is the distance from the inert support (see Fig. 1). Equation (2) assumes that diffusivity is an exponential function of concentration and the temperature.[1,2]

The assumption that the solvent pressure at the surface of the gel, P_V, obeys Henry's law[3] is made because the gel has attraction for the solvent so that the actual vapor pressure is the pure component vapor pressure less the pressure due to the attractive forces between the gel and the solvent. Thus,

$$P_V = P_s(L,t) - P_a. \tag{4}$$

Since the adsorption pressure P_a is proportional to the fraction of gel surface that is free of solvent and to the vapor pressure of the solvent, one may write

$$P_a = (1 - f_a)P_s(L,t) \tag{5}$$

where the fugacity f_a is given by

$$f_a = K f_v = \frac{KX}{\rho_s \left[\dfrac{1}{\rho_g} + \dfrac{X}{\rho_s} \right]}. \tag{6}$$

Hence,

$$P_V = P_g(L,t) - P_a = \frac{KX P_s(L,t)}{\rho_s \left[\dfrac{1}{\rho_g} + \dfrac{X}{\rho_s} \right]} \tag{7}$$

in which f_v is the fugacity in the vapor phase.[3]   The internal rate of mass
transfer by diffusion is governed by the equation

$$\frac{\partial}{\partial y}\left[De^{[\gamma_1 + \gamma_2(T-T_0)][X/(1/\rho_g + X/\rho_s)]}\frac{\partial}{\partial y}\left(\frac{X}{\left[\frac{1}{\rho_g} + \frac{X}{\rho_s}\right]}\right)\right] = \frac{\partial}{\partial t}\left(\frac{X}{\left[\frac{1}{\rho_g} + \frac{X}{\rho_s}\right]}\right).$$

(8)

In general, the temperature distribution within the gel will be functions
of both distance y and time t.   However, since the model is developed here
primarily for a thin film of gel, it is assumed that, at any given time, the
temperature of the entire gel structure is uniform with distance.   Thus, in-
tegral heat balance on gel drying will give

$$h_G(T_G - T) + W(\lambda + C_{SV}(T_G - T)) = \frac{d}{dt}[L \, \bar{C}_{p \, \text{avg}} \, \rho_{\text{avg}} T]$$ (9)

where

$$L(t)\bar{C}_{p \, \text{avg}} = \int_0^{L(t)} \left\{\left(\frac{X}{1+X}\right)C_{SL} + \left(\frac{1}{1+X}\right)C_G\right\}dy$$ (10)

and

$$L(t)\,\rho_{\text{avg}} = \int_0^{L(t)} \rho \, dy.$$ (11)

In the above equations, h_G is the gas-phase heat transfer coefficient, and C_G,
C_{SV}, and C_{SL} are temperature-independent specific heats of solvent-free gel,
solvent vapor, and solvent liquid, respectively.

The shrinkage is given by a material balance on the solvent-free gel.
Thus,

$$L_0 = \int_0^{L(t)} \frac{\left[\frac{1}{\rho_g} + \frac{X_0}{\rho_s}\right]}{\left[\frac{1}{\rho_g} + \frac{X(y,t)}{\rho_s}\right]} dy.$$ (12)

Finally, it is assumed that there is no mass transfer across the interface of
gel and the porous support (or substrate).
Thus,

$$\frac{\partial}{\partial y}\left\{\frac{X(y,t)}{\left(\frac{1}{\rho_g} + \frac{X(y,t)}{\rho_s}\right)}\right\} = 0, \text{ at } y = 0$$ (13)

Dimensionless Form of Equations

Defining the parameters

$$C(y,t) = \frac{X(y,t)}{\left[\dfrac{1}{\rho_g} + \dfrac{X(y,t)}{\rho_s}\right]}; \quad \psi = \frac{C(y,t)}{C_0}; \quad \theta = \frac{T_G - T(t)}{T_G - T_0}; \quad M = \frac{K_G L_0 M_s P_0}{D C_0};$$

$$E = \frac{M_s \lambda}{R_G T_0}; \quad P = \frac{K C_0}{\rho_s}; \quad H = \frac{\lambda}{C_{SV}(T_G - T_0)}; \quad \bar{T} = \frac{T_G}{(T_G - T_0)};$$

$$\bar{P} = \frac{P_G}{P_0}; \quad \alpha_1 = \frac{\rho_g \rho_s}{(\rho_g - \rho_s)C_0}; \quad \alpha_2 = \frac{\rho_s}{C_0}; \quad \bar{B} = \frac{D C_{SL} C_0}{L_0 h_G \alpha_1};$$

$$\bar{C}_{PG} = C_G / C_{SL}; \quad \bar{A} = \frac{M_s K_G P_0 C_{SV}}{h_G}; \quad \bar{\alpha}_1 = \gamma_1 C_0; \quad \text{and} \quad \bar{\alpha}_2 = \gamma_2 C_0 (T_g - T_0),$$

$$(14)$$

the governing equations for the transport of mass and heat through a thin film of gel can be written into the following dimensionless forms:

Mass Transport:

$$\frac{\partial}{\partial \eta}\left[e^{[\bar{\alpha}_1 + \bar{\alpha}_2(1-\theta)]\psi} \frac{\partial \psi}{\partial \eta}\right] = \xi^2 \frac{\partial \psi}{\partial \tau} \tag{15}$$

$$\frac{\partial \psi}{\partial \eta}(0,\tau) = 0 \tag{16}$$

$$-e^{[\bar{\alpha}_1 + \bar{\alpha}_2(1-\theta(\tau))]\psi(1,\tau)} \frac{\partial \psi}{\partial \eta}(1,\tau) = \xi M\left[\psi P \exp\left\{\frac{E(1-\theta)}{T - \theta}\right\} - \bar{P}\right] \tag{17}$$

and

$$\psi(\eta,0) = 1. \tag{18}$$

Heat Transport:

$$\theta - \bar{A}\left[\psi P \exp\left\{\frac{E(1-\theta)}{\bar{T} - \theta}\right\} - \bar{P}\right][H + \theta]$$

$$= \bar{B}\frac{d}{d\tau}\left\{ \xi(\bar{T} - \theta)\left[\int_0^1 (\alpha_1 - \psi)d\eta\right]\left[\int_0^1 \left\{\left[\frac{\psi}{1 - \psi/\alpha_1}\right]\right.\right.\right.$$

$$\left.\left.\left. + \bar{C}_{PG}\frac{\alpha_1 \alpha_2}{\alpha_1 - \alpha_2}\left[\frac{1 - \psi/\alpha_2}{1 - \psi/\alpha_1}\right]\right\}d\eta\right]\right\} \tag{19}$$

and

$$\theta(0) = 1.0. \tag{20}$$

In the above equations, ξ is defined by

$$\xi(\tau) = \frac{\alpha_2 - 1}{\int_0^1 [\alpha_2 - \psi] d\eta}. \tag{21}$$

The local strain ϵ, at a point initially at y_0 and at y at a later time t is given by

$$\epsilon(y,t) = \frac{y}{y_0} - 1 = \frac{\xi\eta}{\eta_0} - 1. \tag{22}$$

If the film is of finite length and width and if the edges of the film are clamped, then the maximum bending stress σ_{max} on the film is[4]

$$\sigma_{max} = \frac{G}{(1 - \mu)}(\xi - 1) \tag{23}$$

where G is Young's modulus and μ is Poisson's ratio. If σ_{max} exceeds yield stress of the film, then the film will crack. Since the strain will be the largest at the gel surface, fissures would first open there; and then they would propagate to some equilibrium plane away from the bottom of the gel. It is worth pointing out that if the gel is an infinite cylinder, the local stresses would be both radial and tangential. Thus, for this type of gel,[4]

$$\sigma_r(\eta,\tau) = \frac{G}{(1 - \mu)} \left\{ -\frac{1}{\eta^2} \int_0^\eta \epsilon\ (\eta',\tau)\eta' d\eta' + \int_0^1 \epsilon(\eta,'\tau)\eta' d\eta' \right\} \tag{24}$$

and

$$\sigma_t(\eta,\tau) = \frac{G}{(1 - \mu)} \left\{ \frac{1}{\eta^2} \int_0^\eta \epsilon(\eta,'\tau)\eta' d\eta' + \int_0^1 \epsilon(\eta,'\tau)\eta' d\eta' - \epsilon(\eta,\tau) \right\}. \tag{25}$$

In this case, if radial or tangential stress (i.e., σ_r or σ_t) exceeds the yield stress, the gel will rupture. The maximum values of σ_r and σ_t will be at the gel surface.

Solution of Equations

It is obvious that the system of eqs. (15) to (21) is not easily solvable by standard analytical techniques. In the present study, eq. (15) coupled with eqs. (19) and (21) was solved numerically on the computer. A highly stable, two-step, linearized, η-centered finite-difference technique similar to the one proposed by Douglas[5] was used. In the first step, a backward finite-difference equation was written for eqs. (15), namely.

$$e^{[\bar{\alpha}_1 + \bar{\alpha}_2(1-\theta)]\psi_{i,j}} \left\{ \left[\frac{\psi^*_{i,j+1} - 2\psi^*_{i,j} + \psi^*_{i,j-1}}{\Delta\eta^2} \right] + \left[\frac{\psi^*_{i,j+1} - \psi^*_{i,j-1}}{2\Delta\eta} \right] \right.$$
$$\left. \times [\bar{\alpha}_1 + \bar{\alpha}_2\ (1 - \theta)] \left[\frac{\psi_{i,j+1} - \psi_{i,j-1}}{2\Delta\eta} \right] \right\} = \xi^2(\psi^*_{i,j} - \psi_{i,j}) \bigg/ \frac{\Delta\tau}{2}$$
$$0 < j < J \quad (26)$$

where $J\Delta\eta = 1$.

The finite difference equations for $\psi_{i,j}$ at $j = 0$ and $j = J$ were obtained by taking material balances on last half-slices of the film and making use of the boundary conditions eqs. (16) and (17). The centers of these formulations are taken at quarter-slices from each end. Thus, for $j = 0$,

$$e^{[\bar{\alpha}_1 + \bar{\alpha}_2(1-\theta)]\psi_{i,0}} \left[\frac{2}{\Delta\eta^2} \left(\psi^*_{i,j} - \psi_{i,0} \right) \right] = \xi^2 (\psi^*_{i,0} - \psi_{i,0}) \Big/ \frac{\Delta\tau}{2} \quad (27)$$

and for $j = J$,

$$\left(e^{[\bar{\alpha}_1 + \bar{\alpha}_2(1-\theta)](\psi_{i,J} + \psi_{i,J-1})/2} \frac{2}{\Delta\eta^2} - \xi^2 \frac{0.5}{\Delta\tau} \right) \psi_{i,J-1}$$

$$- \left(\frac{2}{\Delta\eta} \xi MP \exp \left\{ \frac{E(1-\theta)}{\bar{T}(-\theta)} \right\} + e^{[\bar{\alpha}_1 + \bar{\alpha}_2(1-\theta)][\psi_{i,J}+\psi_{i,J-1}]/2} \frac{2}{\Delta\eta^2} + \xi^2 \frac{1.5}{\Delta\tau} \right)$$

$$\times \psi_{i,J} = - \xi^2 (0.75\psi_{i,J} + 0.25\psi_{i,J-1}) \Big/ \frac{\Delta\tau}{2} - 2M \xi \bar{P}/\Delta\eta. \quad (28)$$

In eqs. (26) to (28), the variable $\psi_{i,j}$ is the value of ψ at $\tau_i = i\Delta\tau$ and $\eta_j = j\Delta\eta$; and the variable $\psi_{i,j}$ is the value of ψ at $\tau_i = i\Delta\tau + \Delta\tau/2$ and $\eta_j = j\Delta\eta$.

Equations (26) and (28) are the standard backward difference equations with half-steps in the time increment ($\Delta\tau/2$). They form a tridiagonal matrix which can be easily solved for $\psi^*_{i,j}$. Once $\psi^*_{i,j}$ are obtained, the new values (at time $\tau_i = i\Delta\tau + \Delta\tau/2$) of dimensionless film thickness and the film temperature, namely ξ^* and θ^*, are obtained from eqs. (21) and (19), respectively. The integration in eq. (21) and the similar integrations in the right-hand side of eq. (19) were carried out using Simpson's rule of integration.[6] Equation (19) was solved for θ^* by a fourth-order Runge-Kutta method.[6]

With the knowledge of $\psi^*_{i,j}$, ξ^*, and θ^*, the second step for the solution of eq. (15) was taken. The finite-difference formulation for the second step is very similar to the first one. In this case, the full time step ($\Delta\tau$) is taken. For this step, the finite-difference equations similar to eqs. (27) to (29) are.

$$e^{[\bar{\alpha}_1 + \bar{\alpha}_2(1-\theta^*)]\psi^*_{i,j}} \left\{ \left[\frac{\psi_{i+j,j+1} - 2\psi_{i+1,j} + \psi_{i+1,j-1}}{\Delta\eta^2} \right] \right.$$

$$\left. - \left[\frac{\psi_{i+1,j+1} - \psi_{i+1,j-1}}{2\Delta\eta} \right] [\bar{\alpha}_1 + \bar{\alpha}_2(1 - \theta^*)] \left[\frac{\psi^*_{i,j+1} - \psi^*_{i,j-1}}{2\Delta\eta} \right] \right\}$$

$$= \xi^{*2} (\psi_{i+1,j} - \psi_{i,j})/\Delta\tau \quad 0 < j < J \quad (29)$$

$$e^{[\bar{\alpha}_1 + \bar{\alpha}_2(1-\theta^*)]\psi^*_{i,0}} \left[\frac{2}{\Delta\eta} \left(\psi_{i+1,1} - \psi_{i+1,0} \right) \right] = \xi^{2*} (\psi_{i+1,0} - \psi_{i,0})/\Delta\tau$$

$$\text{for } j = 0 \quad (30)$$

and

$$\left(e^{(\bar{\alpha}_1 + \bar{\alpha}_2(1-\theta^*))(\psi^*_{i,J} + \psi^*_{i,J-1})/2} \frac{2}{\Delta\eta^2} - \frac{0.25}{\Delta\tau} \xi^{*2} \right) \psi_{i+1,J-1}$$

$$- \left(\frac{2}{\Delta\eta} \xi^* MP \exp\left\{ \frac{E(1-\theta^*)}{(\bar{T}-\theta^*)} \right\} + e^{(\bar{\alpha}_1 + \bar{\alpha}_2(1-\theta^*))(\psi^*_{i,J} + \psi^*_{i,J-1})/2} \right.$$

$$\left. \frac{2}{\Delta\eta^2} + \xi^{*2} \frac{0.75}{\Delta\tau} \right) \psi_{i+1,J} = -\xi^{*2}(0.75\psi_{i,J} + 0.25\psi_{i,J-1})/\Delta\tau$$

$$- 2\xi^* M\bar{P}/\Delta\eta \qquad \text{for } j = J \quad (31)$$

Equations (29) to (31) once again form a tridiagonal matrix which can be solved to obtain $\psi_{i+1,j}$ (the values of ψ at time $\tau_i = (i+1)\Delta\tau$). With the knowledge of $\psi_{i+1,j}$, the value of ξ and θ at time $\tau_i = (i+1)\Delta\tau$ can be obtained from the integrations of eqs. (21) and (19), respectively.

RESULTS AND DISCUSSION

From a practical standpoint, the two parameters of most significance in drying of a gel are the drying rate and the shrinkage of the gel as functions of time. The conditions under which a gel will crack can be evaluated with the knowledge of these parameters, if the data for Young's modulus G, Poisson's ratio μ, and the yield stress as a function of solvent concentration are available. All the results and discussions are therefore aimed here toward the behavior of drying and shrinkage rates under a variety of drying conditions. The results will be presented in two sections. First, the effects of various systems parameters on the drying and the shrinkage rates will be analyzed with the help of numerical results generated by the computer solution of the proposed theoretical model. The main objective of this type of analysis is to assess the importance of each of the above mentioned dimensionless variables. Secondly, the drying rate predictions of the present model will be compared with experimental data of isothermal drying of lyphogel film.

Effects of System Parameters on the Drying and Shrinkage Rates

The results of drying rate can be presented in terms of a quantity F, which is defined as

$$F(t) = \frac{[\text{lb of solvent/lb of solvent} + \text{gel}]_{t=t}}{[\text{lb of solvent/lb of solvent} + \text{gel}]_{t=0}} \times 100$$

$$= \frac{\int_0^{L(t)} \frac{X(y,t)/(1 + X(y,t))}{X_0/(1 + X_0)} \times 100 \, dy}{L(t)} . \quad (32)$$

Thus, $F(t)$ is numerically equal to the percentage of average initial solvent concentration retained in the gel at time t.
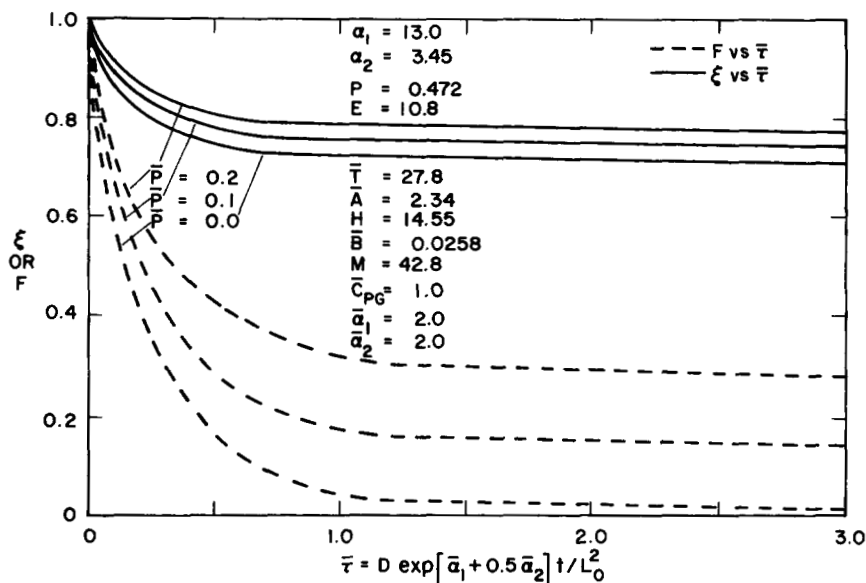
Fig. 2. Drying and shrinkage rates as functions of $\bar{P}$.

There are 13 independent dimensionless variables, namely, P, α_1, α_2, H, E, $\bar{T}$, M, $\bar{A}$, $\bar{B}$, C_{PG}, $\bar{\alpha}_1$, $\bar{\alpha}_2$, and $\bar{P}$. A given gel–solvent system at some initial concentration of solvent in the gel fixes the parameters P, α_1, α_2, $\bar{\alpha}_1$, $\bar{\alpha}_2$, and C_{PG}. Furthermore, the parameters H, $\bar{A}$, and $\bar{B}$ mainly affect the time dependence of temperature of the film. Thus, effects of these parameters on drying and shrinkage rates are only indirect and in many instances only of secondary importance. The dimensionless parameters M, E, $\bar{T}$, and $\bar{P}$ are thus of primary importance, and hence their effects on drying and shrinkage rates are first outlined here.

The effect of $\bar{P}$ on drying rate is obvious. An increase in $\bar{P}$ should reduce the drying and shrinkage rates, as shown in Figure 2. The value of M indicates the magnitude of relative resistances of the gas and gel films during drying. The larger the value of M, the smaller the resistance of the gas film. For a typical set of system conditions, the effects of variations in M on drying and shrinkage rates are illustrated in Figure 3. These results indicate that for the value of M greater than approximately 100, the drying and shrinkage rates become essentially independent of M.

The typical effects of variations in $\bar{T}$ on drying and shrinkage rates are shown in Figure 4. Even though these effects are not as pronounced as those described in Figure 3, they indicate that an increase in $\bar{T}$ (or decrease in gas temperature for a given initial gel temperature) will decrease the drying rate.

A large value of E indicates a strong dependence of vapor pressure of solvent on the temperature. Thus, for a given set of gas and initial film temperatures, the drying and shrinkage rates should be increased with an in-
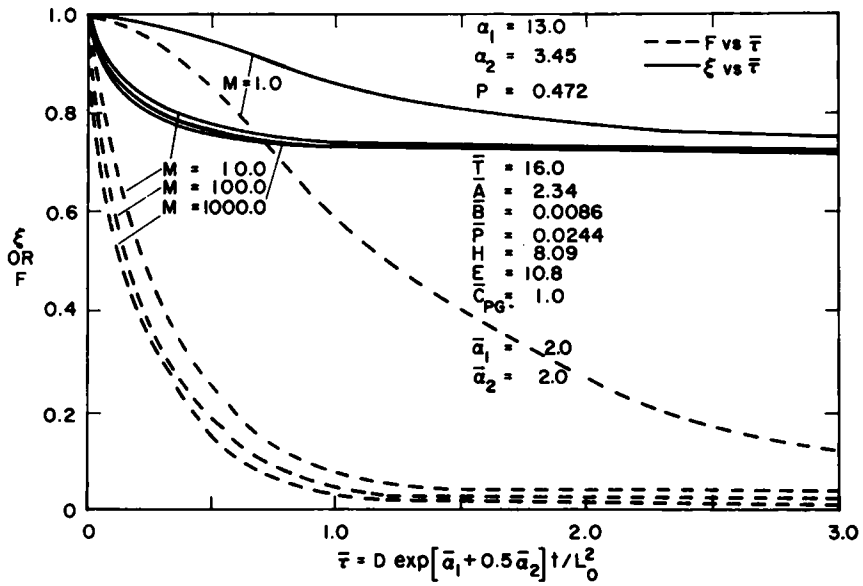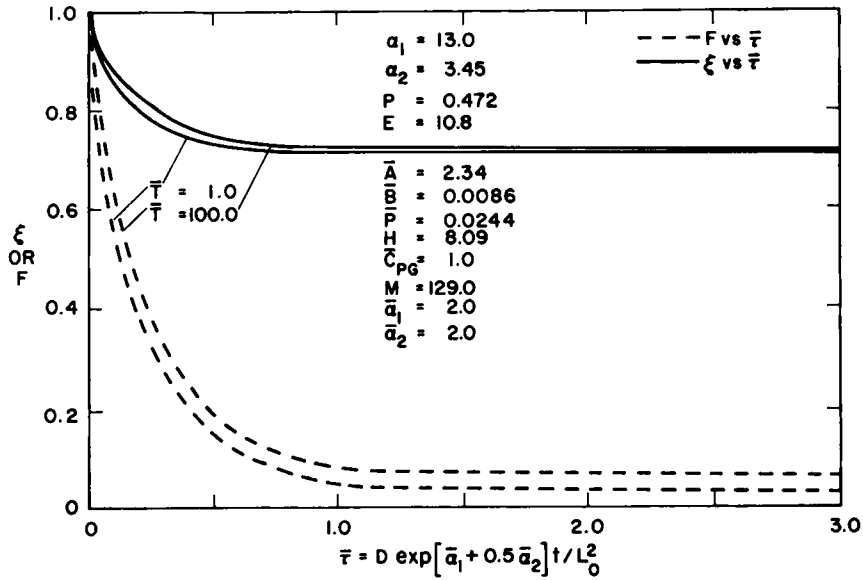
Fig. 3. Drying and shrinkage rates as function of M.

Fig. 4. Drying and shrinkage rates as functions of T.

crease in value of E. This is illustrated in Figure 5 for a typical set of conditions.

For few typical system conditions, the effects of variations in $\bar{A}$, $\bar{B}$, and H on drying and shrinkage rates were also examined. These effects were found to be very small. It should be noted that the effects of variations in
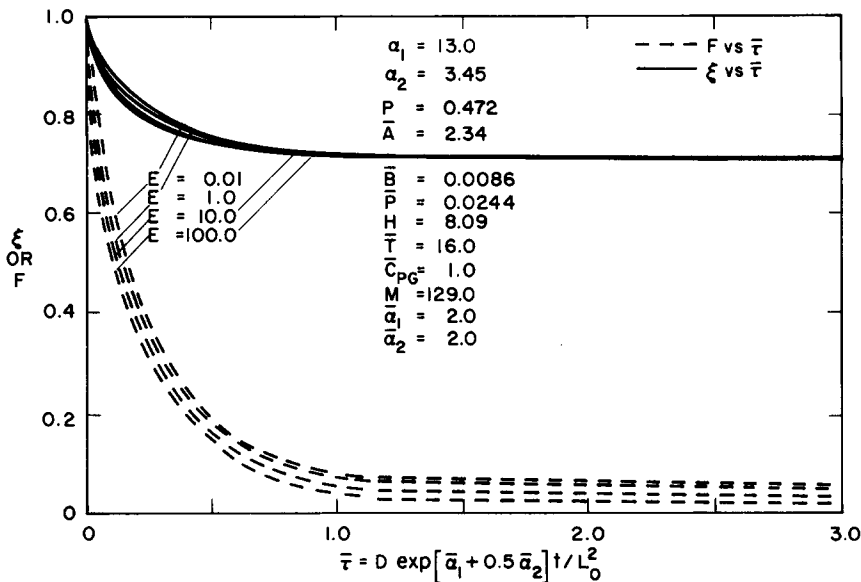
Fig. 5. Drying and shrinkage rates as function of E.

$\bar{A}$, $\bar{B}$, and H are most prominent only in the initial phase of drying when the temperature of the gel is changing rapidly with time. During this time, the increase in $\bar{A}$ and H and a decrease in $\bar{B}$ should increase the drying and the shrinkage rates. Once the temperature of the gel achieves an equilibrium with the gas temperature, the variations in $\bar{A}$, $\bar{B}$, and H should have no effect upon the drying and shrinkage rates.

For a fixed initial concentration of solvent in the gel, a variation in P indicates the variation in Henry's law constant. The effect of variation in P on drying and shrinkage rates were obtained for a typical set of system conditions. These results are shown in Figure 6. The results indicate that an increase in P (or Henry's law constant) increases the drying and shrinkage rates; although the increment is very small for the values of P greater than 1.

For a fixed initial solvent concentration in the gel and the fixed solvent and gel densities, the effect of density differences between gel and the solvent on the drying and the shrinkage rates can be examined by varying α_1 and keeping all other system conditions unchanged. This effect is illustrated in Figure 7 for a typical set of system conditions. The results indicate that an increase in α_1 (or the decrease in density difference between gel and the solvent) will decrease the drying rate with a relatively little change in the shrinkage rates.

Finally, two general points should be noted about the results shown in Figures 2 to 7. The maximum shrinkage of the gel is determined by the value of α_2. Thus, $\epsilon_{min} \rightarrow 1 - 1/\alpha_2$ when $\tau \rightarrow \infty$. Secondly, the abscissa of each of these figures is defined in terms of diffusion coefficient evaluated
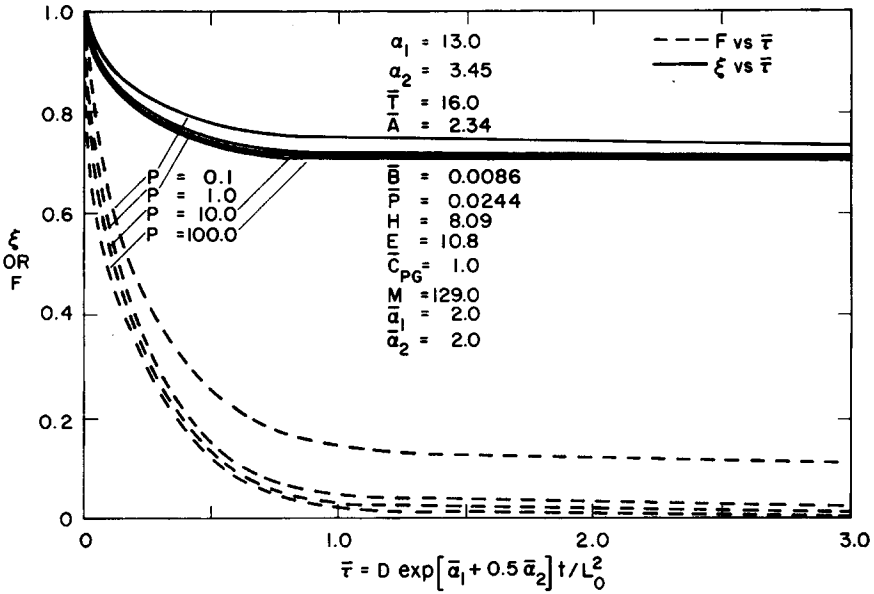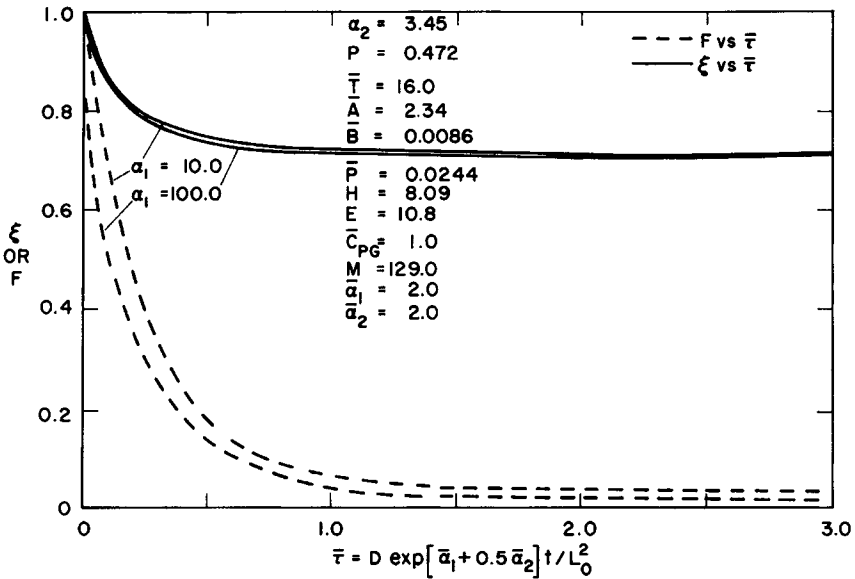
Fig. 6. Drying and shrinkage rates as functions of P.

Fig. 7. Drying and shrinkage rates as functions of α_1.

at the approximately arithmetic averages of initial and final temperatures and concentrations. This type of abscissa coordinate was chosen to indicate that time required for approximate leveling of drying and shrinkage rates is related to $\bar{\alpha}_1$ and $\bar{\alpha}_2$ through only $\bar{\tau}$.

Comparison of Theoretical Predictions with Experimental Measurements

In order to verify the validity of the theoretical model, some measurements on drying of Lyphogel film were carried out. Lyphogel is a polymeric gel supplied by Gelman Instrument Company, Ann Arbor, Michigan. This gel is extremely hygroscopic, and in the swollen state it carries water approximately five times its weight. Unfortunately, even though it dries and shrinks considerably, it also cracks up very easily, thereby making the measurements of drying and shrinkage rates rather difficult and inaccurate. In the present study, the measurements of drying and shrinkage rates on this film were carried out only under very mild conditions of drying where no severe cracking was observed for a long period of time.

The experimental results were obtained for isothermal and natural convection condition (at room temperature of approximately 75°F) in a constant-humidity chamber. Three humidity values, namely, 65% R.H., 73% R.H., and 85% R.H., were examined. Various film thicknesses were examined. The other two dimensions of the film were approximately 4 in. by 4 in. The results of this study are summarized in Figure 8. Since there are no data available for diffusion coefficient as a function of concentration and Henry's law constant, the theoretical model is not directly applicable to the evaluation of these results. However, as illustrated in Figure 2, the results of Figure 8 also indicate that initial drying rate is approximately a
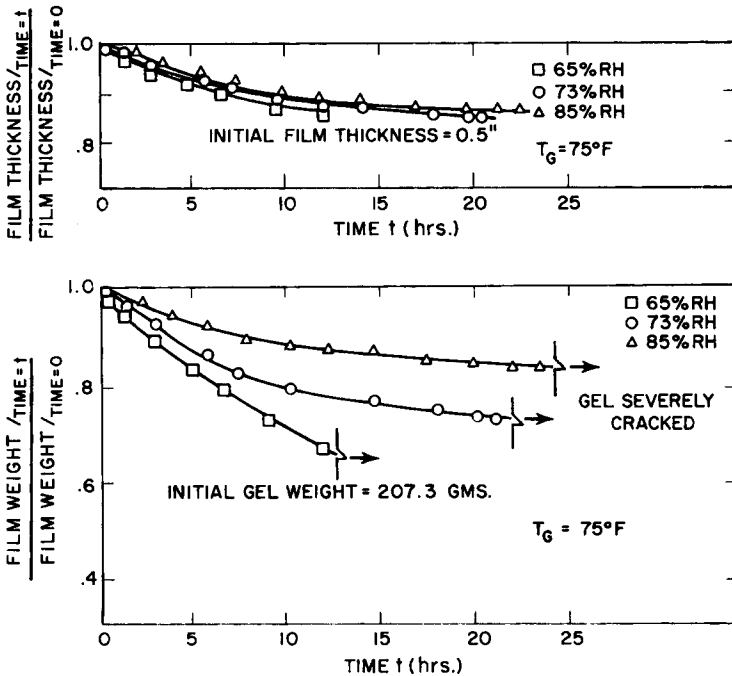

Fig. 8. Drying and shrinkage rates of Lyphogel. Isothermal drying in natural convection conditions.

logarithmic function of gas-phase humidity. Furthermore, the nature of the experimental drying and shrinkage rates plots are qualitatively very similar to the theoretical plots shown in Figures 2 and 7. The similar results were obtained at other film thicknesses. Attempts were also made to measure the drying and shrinkage rates at higher temperatures and under forced convection conditions. The latter measurements were carried out in a tray dryer. The preliminary data showed that, as predicted by the model, an increase in gas temperature as well as air flow rate increases the drying and shrinkage rates. However, due to severe cracking of the gel in early stages of drying, these measurements are believed to be of only qualitative significance, and their quantitative values will not be reported here.

CONCLUSIONS

It is concluded from the present study that

1. The drying and shrinkage rates will be essentially independent of air flow rate and Henry's law constant as long as dimensionless quantities M and P are greater than approximately 100 and 10, respectively. Except under extreme temperature conditions the drying and shrinkage rates are most influenced by the dimensionless groups M, P, andd $\bar{P}$ defined in this paper.

2. The effect of concentration and temperature dependence of diffusion coefficient upon the time required for approximate leveling of drying and shrinkage rates can be approximately handled by defining a dimensionless time variable $\bar{\tau}$ in terms of average diffusion coefficient, as shown in Figures 2 to 7.

3. The predictions of the theoretical model are in qualitative agreement with the experimental data on isothermal drying of Lyphogel film under natural convection conditions.

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