Model of Liquid Permeability in Swollen Composites of Superabsorbent Polymer and Fiber

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ABSTRACT: The liquid permeability of composites of fiber and superabsorbent polymer (SAP) is critical to the proper performance of absorbent hygiene products such as infant diapers. Previous work has focused on empirically improving performance of absorbent composites by modifying the components, but a systematic study of the parameters affecting permeability of these systems has not been published. A good model of permeability would aid our understanding of the complex phenomenon of liquid permeability of pads that change in volume and porosity during swelling. In the present work, a mathematical model of liquid permeability in both gel beds and composites of fiber and gel is developed. The model uses a Carman–Kozeny approach with added calculation of the porosity and specific surface area that result upon swelling of the SAP, as well as subsequent compression of the swollen composite. The model incorporates ten parameters that are necessary to determine the permeability of the system. The implications of the model for improving permeability in absorbent composites are explored. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4075–4084, 2006

Key words: gels; hydrogels; hydrophilic polymers; networks; modeling

INTRODUCTION

The liquid permeability of composites of fiber and superabsorbent polymer (SAP) is critical to the proper performance of absorbent hygiene products such as infant diapers. Liquid must wick into the composite when it is dry and also flow through it when the composite is in a partially or fully saturated and swollen state. The permeability of wet and compressible fiber mats has been studied and modeled,[1–5] and numerous patents describe SAPs that provide for better permeability in absorbent cores of diapers.[6–11] A simplistic, empirical model of permeability in swollen gel beds has previously been discussed.[12] However, scant work has been reported on the systematic study of parameters affecting the permeability of such swellable, composite absorbent systems.[13] This is no doubt partly because it is difficult to measure precisely the permeability of complex, mixed systems made of materials that vary widely in particle size, shape, and size distribution; the noise in the measurement obscures the signal. Therefore, it is clear that a good model of permeability would help our understanding of the complex phenomenon of liquid permeability in pads that change in volume and porosity during swelling. In this work, a geometrical model of permeability in both gel particle beds and composites of fiber and gel is developed, and the implications of the model are explored.

DEVELOPMENT OF THE MATHEMATICAL MODEL

Darcy's law and the Carman–Kozeny model

The liquid permeability k of a porous medium is defined as the proportionality constant between the pressure drop and flow rate of the liquid moving through the medium, according to Darcy's law:[14]

$$\Delta q = \frac{k}{\eta} \Delta p \qquad (1)$$

The variable Δq is the flow rate per unit cross-sectional area of the porous medium, Δp is the pressure drop per unit length of the porous medium, and η is the viscosity of the fluid. Darcy's law holds for one-directional flow at low and steady flow rates, which may be present in diapers when the structure is rewet in the swollen state, but is not likely to be present in initial stages of wetting from the dry state. The permeability depends on the structure of the pores and the interconnecting channels in the porous medium, and can be mathematically related to specific pore structural features only if a model of the pore structure is used. Perhaps the simplest model is the parallel, straight-capillary bundle model, where the pores are imagined as capillary tubes that extend from one end

of the sample to the other, and which is fundamentally based[15] on the Hagen–Poiseuille law of capillary fluid flow. In this case, the semi-empirical Carman–Kozeny[16] equation gives the permeability as shown in eq. (2):

$$k = \frac{1}{2S_0^2} \frac{\phi^3}{(1-\phi)^2} \tag{2}$$

The variable S_0 is the specific surface of the pores, and ϕ is the porosity (volume fraction of interconnected pores) of the sample. For the capillary bundle theory, the specific surface can be stated in terms of the radius and length of the cylindrical capillaries, which results in the numerical factor of 2 in the denominator of eq. (2). The actual length of a capillary tube may be longer than the length of the sample because the tube can snake through the sample in a tortuous path. Depending on the ratio of true capillary length to the sample length (the tortuosity of the capillaries), the numerical factor can be > 2. Because the porosity of air-laid pads can be quite large, flow paths through the sample may be relatively nontortuous. Therefore we use the simple cylindrical capillary model. The application of the Carman–Kozeny model to systems of high porosity, although contraindicated earlier,[4] has recently been shown to be acceptable.[15] In the case of absorbent pads composed of fibers and granules of SAP, the specific surface can be calculated in terms of the fiber and granule dimensions. To model the permeability in a swelling porous medium, we must derive expressions for the specific surface and the porosity of the swollen system, as discussed in the following sections.

Specific surface in a swelling medium

The specific surface is the ratio of the surface area to the volume of the particles making up the composite, in the present case where the particles are mixed together but unconsolidated. Absorbent pads are made up of two kinds of particles: fibers and polymer granules. The shape of the fibers is approximated as a cylinder, and the shape of the polymer granules is approximated as a sphere. For our model, we further assume a uniform fiber size described by a fiber radius r_f and a fiber length l_f. We also assume a uniform granule size described by the granule radius r_s. The specific surface of a mixture of the fibers and granules is then given by

$$S_0 = \frac{A_{particles}}{V_{particles}} = \frac{A_{fiber} + A_{granules}}{V_{fiber} + V_{granules}}$$
$$= \frac{n_f a_f f_1(Q_f) + n_g a_g f_1(Q_g)}{n_f v_f f_2(Q_f) + n_g v_g f_2(Q_g)} \tag{3}$$

where n_f and n_g are, respectively, the number of fibers and the number of granules in the assembly; a_f and a_g

are, respectively, the surface area of a fiber and a granule, and v_f and v_g are, respectively, the volume of a fiber and of a granule. The variables Q_f and Q_g are, respectively, the swelling extents of the fiber and the granule. The scaling factors $f_1(Q_f)$ and $f_1(Q_g)$ are, respectively, the surface area scaling terms for a swelling fiber and a swelling granule. The factors $f_2(Q_f)$ and $f_2(Q_g)$ are, respectively, the volume scaling terms for a swelling fiber, and a swelling granule. These factors will be determined later.

In constructing a composite of SAP granules and fibers, the mass of each component may be stated in terms of the total mass of the dry composite and the mass fraction of each component. The sum of the mass fractions of the dry components must, of course, equal 1, yielding the following equation for the total mass in terms of the mass fraction of only the SAP component:

$$m_T = m_g + m_f = m_T f_g + m_T(1 - f_g) \tag{4}$$

The number of fibers is determined from the ratio of total fiber mass to the mass per fiber according to eq. (5):

$$n_f = \frac{m_f}{v_f \rho_f} = \frac{m_T(1 - f_g)}{v_f \rho_f} \tag{5}$$

where the variable m_T is the total mass of the dry assembly of fibers and granules, f_g is the mass fraction of granules in the assembly, and ρ_f is the dry density of the fiber substance. The number of polymer granules is determined from the ratio of total granule mass to the mass per granule according to eq. (6), wherein ρ_g is the dry density of the granule substance:

$$n_g = \frac{m_g}{v_g \rho_g} = \frac{m_T f_g}{v_g \rho_g} \tag{6}$$

The surface area per fiber (neglecting the area of the fiber ends) is given by

$$\frac{a_f}{v_f} = \frac{2\pi r_f l_f}{\pi r_f^2 l_f} = \frac{2}{r_f} \tag{7}$$

and the surface area per spherical granule is given by

$$\frac{a_g}{v_g} = \frac{4\pi r_g^2}{(4/3)\pi r_g^3} = \frac{3}{r_g} \tag{8}$$

The scaling functions for the surface areas after swelling, based on the geometries of the particles, are given by eqs. (9) and (10):

$$f_1(Q_f) = \frac{a_{f-swollen}}{a_f} = \frac{2\pi r_{f-s} l_f}{2\pi r_f l_f} = \frac{r_{f-s}}{r_f} \tag{9}$$

$$f_1(Q_g) = \frac{a_{g-swollen}}{a_{g-dry}} = \frac{4\pi r_{g-s}^2}{4\pi r_g^2} = \left(\frac{r_{g-s}}{r_g}\right)^2 \quad (10)$$

The scaling functions for the particle volumes after swelling, based on the geometries of the particles, are given by eqs. (11) and (12):

$$f_2(Q_f) = \frac{v_{f-swollen}}{v_f} = \frac{\pi r_{f-s}^2 l_f}{\pi r_f^2 l_f} = \left(\frac{r_{f-s}}{r_f}\right)^2 \quad (11)$$

$$f_2(Q_g) = \frac{v_{g-swollen}}{v_{g-dry}} = \frac{(4/3)\pi r_{g-s}^3}{(4/3)\pi r_g^3} = \left(\frac{r_{g-s}}{r_g}\right)^3 \quad (12)$$

In comparing eqs. (9)–(11) and (10)–(12), note that $f_1(Q_f) = [f_2(Q_f)]^{1/2}$ for the fibers and $f_1(Q_g) = [f_2(Q_g)]^{2/3}$ for the granules. In addition, the volume scaling functions can be written in terms of the volumes of the components as follows:

$$f_2(Q_f) = \frac{v_{f-swollen}}{v_{f-dry}} = \frac{V_f + V_{saline-absorbed}}{V_f} = 1 + Q_f\left(\frac{\rho_f}{\rho_s}\right) \quad (13)$$

$$f_2(Q_g) = \frac{v_{g-swollen}}{v_{g-dry}} = \frac{V_g + V_{saline-absorbed}}{V_g} = 1 + Q_g\left(\frac{\rho_g}{\rho_s}\right) \quad (14)$$

Equations (9) and (11) may be combined to yield an expression for the swollen-to-dry radius ratio of the fiber in terms of the swelling extent Q_f of the fiber. Similarly, eqs. (10) and (12) may be combined to yield an expression for the swollen-to-dry radius ratio of the granule in terms of the swelling extent Q_g of the granule. Substituting eqs. (4)–(14) into eq. (3) yields eq. (15) for the specific surface:

$$S_0 = \frac{\frac{2(1-f_g)}{r_f\rho_f}\left[1 + Q_f\left(\frac{\rho_f}{\rho_s}\right)\right]^{1/2} + \frac{3f_g}{r_g\rho_g}\left[1 + Q_g\left(\frac{\rho_g}{\rho_s}\right)\right]^{2/3}}{\frac{(1-f_g)}{\rho_f}\left[1 + Q_f\left(\frac{\rho_f}{\rho_s}\right)\right] + \frac{f_g}{\rho_g}\left[1 + Q_g\left(\frac{\rho_g}{\rho_s}\right)\right]} \quad (15)$$

Porosity of swollen, absorbent composites

An equation of the porosity of a swollen composite must account for the construction parameters, the effects of swelling of the components, and the resulting expansion of the composite system. It is also desirable to account for the change in porosity resulting from compression of the composite.

Swelling effect on porosity

The porosity of the absorbent composite is the volume fraction of pores in the composite according to

the following equation, where V_c is the bulk volume of the composite, and V_p is the volume of the pores:

$$\phi = \frac{V_p}{V_c} = \frac{V_p}{V_g + V_f + V_p} \quad (16)$$

The volume of the gel component V_g is given by the volume of the polymer and the volume of any liquid absorbed according to the following equation:

$$V_g = \frac{m_g}{\rho_g} + \frac{m_g Q_g}{\rho_s} = m_g\left(\frac{1}{\rho_g} + \frac{Q_g}{\rho_s}\right) \quad (17)$$

The volume of the fiber component V_f is similarly given by the volume of the dry fiber plus the volume of any liquid absorbed according to

$$V_f = \frac{m_f}{\rho_f} + \frac{m_f Q_f}{\rho_s} = m_f\left(\frac{1}{\rho_f} + \frac{Q_f}{\rho_s}\right) \quad (18)$$

The sum of V_g and V_f is the volume of solids in the pad, given by eq. (19):

$$V_g + V_f = m_T\left[f_g(0.6 + Q_g) + (1 - f_g)(0.67 + Q_f)\right] \quad (19)$$

When the swelling of the SAP and fiber are both zero, the volume of dry solids in the pad is given by the following equation:

$$(V_g + V_f)_{dry} = m_T\left[0.6f_g + 0.67(1 - f_g)\right] \quad (20)$$

The pore volume of the dry pad is determined from the dry porosity and the volume of the dry solids according to

$$V_{p-d} = (V_g + V_f)_{dry}\left(\frac{\phi_0}{1 - \phi_0}\right)$$
$$= m_T\left[0.6f_g + 0.67(1 - f_g)\right]\left(\frac{\phi_0}{1 - \phi_0}\right) \quad (21)$$

Now, substituting eqs. (17) and (18) into eq. (16), and using eq. (4) to state the masses of the components in terms of the total dry mass of the composite and the mass fraction of SAP, and then substituting in the values of the density of SAP granules ($\rho_g = 1.67$ g/cm³), the density of dry cellulose fiber ($\rho_f = 1.50$ g/cm³), the density of 0.9% NaCl solution ($\rho_s = 1.00$ g/cm³), and the measured value of $Q_f = 1$ g/g, we obtain eq. (22) for the porosity of a composite containing SAP swollen in 0.9% NaCl solution (can be used for general swelling if appropriate density of liquid is substituted):

$$\phi = \frac{V_p}{V_p + m_T\left[f_g(0.6 + Q_g) + (1 - f_g)1.67\right]} \quad (22)$$

The pore volume of swollen absorbent composites, although easy to measure, is not amenable to exact mathematical treatment due to the complex nature of the frictional and elastic interactions of the components. We rely therefore on a semi-empirical model based on the special case of affine expansion of the composite.

In affine expansion, only the scale of the geometric figure changes. In a porous solid undergoing an affine expansion, the pore volume increases with the increasing size, but the porosity remains constant. Using eqs. (16)–(22), we write an expression for the ratio of porosities between the swollen and dry state as follows:

$$\frac{\phi}{\phi_0} = 1 = \frac{V_P}{\{V_P + m_T[f_g(0.6 + Q_g) + 1.67(1 - f_g)]\}}$$

$$\frac{\{V_{p-d} + m_T[0.6f_g + 0.67(1 - f_g)]\}}{V_{p-d}} \quad (23)$$

After expanding the terms in braces by their respective pre-factors, collecting like terms, and then canceling the parameter m_T from numerator and denominator, we obtain the following expression for the ratio of the pore volume in the swollen pad to that in the initial dry pad (for the affine expansion case):

$$\frac{V_P}{V_{p-d}} = \frac{[f_g(0.6 + Q_g) + 1.67(1 - f_g)]}{[0.6f_g + 0.67(1 - f_g)]} \quad (24)$$

As an example, if a pad containing a mass fraction of SAP equal to 0.5 swells affinely with the SAP absorbing 25 g/g, then the pore volume will increase by a factor of 21.47.

To generalize this equation to non-affine pad swelling, we introduce a scaling factor q to the numerator of the right-hand side of eq. (24), as shown in eq. (25):

$$\frac{V_P}{V_{p-d}} = \frac{[f_g(0.6 + Q_g) + 1.67(1 - f_g)]^q}{[0.6f_g + 0.67(1 - f_g)]} \quad (25)$$

In the case of affine swelling, the value of q is 1. In the (probably unrealistic) case in which the pore volume increases with swelling more than in the affine case, the scaling factor q would be > 1. And in the case in which pore volume increases more slowly than the affine case, q will be < 1. Pore volume will always change less than the affine case ($q < 1$) whenever there is slippage between the components or deformation of the components in the pad. Therefore, q may be thought of as a "component interaction parameter," or perhaps as a slippage or friction parameter between the components.

Substituting the expression for V_{P-d} from eq. (21) into eq. (25) yields an expression for the pore volume of a swollen composite in terms of the dry porosity of the composite and the functions for swelling and mass fractions. Substituting the obtained expression for the pore volume of a swollen composite V_P into eq. (22) then finally yields the following equation for the porosity in the swollen pad. The swollen pad porosity thus depends on the initial dry porosity, the mass fraction f_g of SAP in the pad, the swelling extent Q_g of the SAP and the scaling, or interaction, factor q:

$$\phi = \frac{1}{\left\{1 + \left(\frac{1-\phi_0}{\phi_0}\right)[f_g(0.6 + Q_g) + 1.67(1 - f_g)]^{(1-q)}\right\}} \quad (26)$$

Compression effect on porosity

The bulk volume of the composite depends on the same parameters as the mass of the composite, plus additional parameters due to the interactions of the components, as noted above. The bulk volume of the composite in compression is made up of two parts: swollen solids (granules and fibers) and pores. Under moderate compression, the solids may be taken to be incompressible; therefore, any compression of the composite results in a reduction of the pore volume. We therefore define a compressive strain ε of the composite as the ratio of the change in pore volume under compression to the remaining pore volume. And we define a compression modulus E_c of the composite system as the ratio of the pressure P applied to the composite to the strain ε. The relationship of these quantities is given by

$$\varepsilon = \frac{P}{E_c} = \frac{\Delta V_{\text{pores}}}{V_{\text{pores}}} = \frac{V_{0-\text{pores}} + V_{\text{solids}} - V_c}{V_c - V_{\text{solids}}} \quad (27)$$

The denominator of the left-hand side of eq. (27) is moved to the right hand side and multiplied out by P/E_c; then terms of V_c and V_{solids} are collected to yield eq. (28) for the volume V_c of the composite in compression:

$$V_c = V_{\text{solids}} + \frac{V_{0-\text{pores}}}{(1 + P/E_c)} \quad (28)$$

Using eq. (28) and a similar math manipulation to that shown in eqs. (16)–(25) yields an expression for the porosity of a compressed, swollen composite pad according to eq. (29). Note the similarity to eq. (26), which is the porosity for the uncompressed pad. However, we have introduced another quantity E_c needed to characterize the compressibility of the

composite. An expression for this new quantity will be derived in the next section:

$$\phi = \frac{1}{\left\{ 1 + \left(1 + \frac{P}{E_c} \right) \left(\frac{1 - \phi_0}{\phi_0} \right) \left[f_g(0.6 + Q_g) + 1.67(1 - f_g) \right]^{(1-q)} \right\}} \quad (29)$$

Compression modulus of the composite

The compressibility of the composite is characterized by the compression modulus, which is defined in eq. (27). The compression modulus of the pad should relate to the amounts and the moduli of the individual components. We use a simple mixing rule, relating the compression modulus of the composite E_c to the volume-fraction weighted average of the gel compression modulus E_g and fiber pad compression modulus E_f, according to eq. (30), where v_g, v_f, and v_p are, respectively, the volume fractions of gel, fiber and pores:

$$E_c = E_g v_g + E_f v_f + E_p v_p \quad (30)$$

Neglecting the compression modulus of the pores yields an equation in terms of the volume fractions of fiber and gel and the moduli of those components. The volume fractions of the two components can be obtained from eq. (19), where the sum in square brackets is the total volume increase of the components and is composed of the individual volume increases of each component. The gel component is indicated by the term containing f_g and the fiber component is indicated by the term containing $(1 - f_g)$. The volume fraction of gel is proportional to the quotient F_g of the gel-only term and the sum of the terms, whereas the volume fraction of fiber is proportional to the quotient F_f of the fiber-only term and the sum of the terms, according to the following two equations. The term $(1 - \phi)$ accounts for the pore volume in the composite:

$$v_g = (1 - \phi) \frac{f_g(0.6 + Q_g)}{f_g(0.6 + Q_g) + 1.67(1 - f_g)} = (1 - \phi)F_g$$

$$(31)$$

$$v_f = (1 - \phi) \frac{1.67(1 - f_g)}{f_g(0.6 + Q_g) + 1.67(1 - f_g)} = (1 - \phi)F_f$$

$$(32)$$

Substituting eqs. (31) and (32) into eq. (30), and recognizing that $F_g + F_f = 1$, yields eq. (33) for the compression modulus of the composite in terms of the moduli of the components and the gel fraction of the total solids. The calculated value of E_c can be used in eq. (29) to calculate the porosity of the composite under compression:

$$E_c = (1 - \phi)(E_g F_g + E_f F_f)$$
$$= (1 - \phi) \left[E_g F_g + E_f(1 - F_g) \right] \quad (33)$$

An experimental value for E_c could also be obtained from thickness compression measurements. An expression for the strain ε can be derived in terms of thickness measurements, from eq. (27) as follows.

In eq. (27), the sum of $V_{0\text{-pores}}$ plus V_{solids} is just the uncompressed volume of the composite V_0. Making this substitution in eq. (27), then dividing both the numerator and denominator by V_0, yields eq. (34) for the strain:

$$\varepsilon = \frac{\left(1 - \frac{V_c}{V_0} \right)}{\left(\frac{V_c}{V_0} - \frac{V_{\text{solids}}}{V_0} \right)} \quad (34)$$

For a flat pad, where the in-plane dimensions are much larger than the thickness, the compression V_c/V_0 is also given by the change in thickness h_c/h_0. Thus the thickness change in a composite pad versus applied pressure may be plotted according to eq. (27) to determine the compression modulus of the pad experimentally.

General model for permeability in swollen composites

A general geometrical model for liquid permeability in swollen composites is now constructed by substituting eq. (27) (porosity) and eq. (15) (specific surface) into eq. (2) (Carman–Kozeny). The necessary parameters are (1) radius of the dry fiber, (2) radius of the dry SAP granule, (3) mass fraction of dry SAP in the dry composite, (4) swelling extents of the SAP and fiber, (5) dry density of the fiber and SAP, (6) density of the swelling liquid, (7) compressive stress (pressure), (8) compression modulus of the swollen gel and the wet fiber, (9) component interaction parameter q, and (10) the dry porosity of the pad.

For the model, a single particle radius is used. The model could be adapted to include a mean particle radius of a size distribution. The mean particle radius of a sample of SAP is obtained easily by sieving analysis, from which the median particle radius is calculated. The radius of the fibers is known. The mass fraction of SAP in any composite is known from the composition used to make the composite. The dry porosity is calculated from the dry dimensions of the pad and from the mass composition. The dry dimensions are used to calculate the bulk volume of the composite. The mass composition of the pad and the chemical densities of the compo-
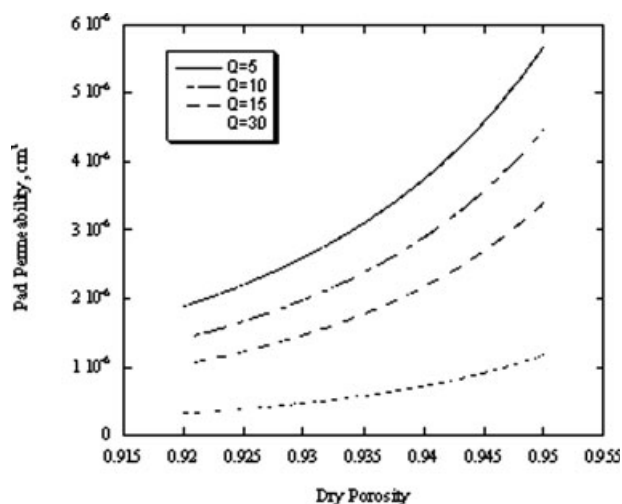
Figure 1 Sensitivity of pad permeability to the porosity imposed in the dry state (44% SAP load).

nents are used to calculate the volumes of the components. After swelling, the dimensions of the pad are used to calculate the wet bulk volume. Blotting the pad under a load will allow the measurement of the effective swelling extent of the polymer in the pad.[17] From the wet dimensions at zero compression, the swelling extent of polymer (and fiber) and the dry porosity, the value of q ''component interaction parameter'' may be calculated. The pad compression and compression modulus may be determined from measurements of the dimensions of the wet pad at different compressive loads.

There are several assumptions and simplifications in the model: (1) the fibers are simple, long cylinders, (2) the SAP granules are spheres, (3) average radii for fibers and spheres are adequate representations of particle distributions, (4) the area of the ends of the fiber cylinders is neglected, (5) all interparticle interactions are subsumed into the ''component interaction parameter'' q, (6) simple scaling of the swollen volume of the composite via the parameter q, (7) under moderate compression the swollen solids are incompressible, and (8) a simple, mixing rule is used for compression modulus of blend with no particle interaction.

MODELING THE PERMEABILITY CHARACTERISTICS OF COMPOSITES

Non-SAP factors in pad permeability

From the set of equations developed in the present study, pad porosity and permeability depend on several factors not related to SAP properties: the initial porosity of the dry composite, the fraction of SAP in the dry composite, the density of the fiber component, and the size of the fibers and on their ability to absorb liquid. The fiber properties are more or less fixed for

cellulose fiber, but can be significantly different for synthetic fibers (for example), which are generally less dense and swell less than cellulose fiber. Cellulose fiber absorbs ~ 1 g liquid per dry gram of fiber. The present model predicts that the wet pad permeability is quite sensitive to the dry density that is set during the pad manufacturing process.

Figure 1 shows how the permeability of the wet pad depends on the dry porosity. The curve is sharply changing over the range of 0.92–0.95, which is a typical range of dry porosity in absorbent pads. This has implications for measurements on diapers because of the variability of the dry density during manufacture, and the changes in dry density that may occur on shipping and handling.

Figure 2 shows the dependence of pad permeability on the fraction of SAP in the pad, in the absence of compression. The permeability increases with SAP loading because the granules have a smaller surface-to-volume ratio than that of the fibers they replace. However, compression effects can obscure this relationship, as discussed later. Figure 3 shows the effect of polymer swelling on pad permeability. The reduction in pad permeability as swelling increases is very significant and is discussed more in the next section.

Superabsorbent properties effect on pad permeability

Permeability vs swelling extent

The model predicts that the permeability of a pad decreases sharply as the swelling extent increases. This effect is shown for a pad with 44% SAP in Figure 4. Permeability in the pad depends on both its porosity and the surface-to-volume ratio of the components of the pad. Both porosity and the surface-to-volume ratio
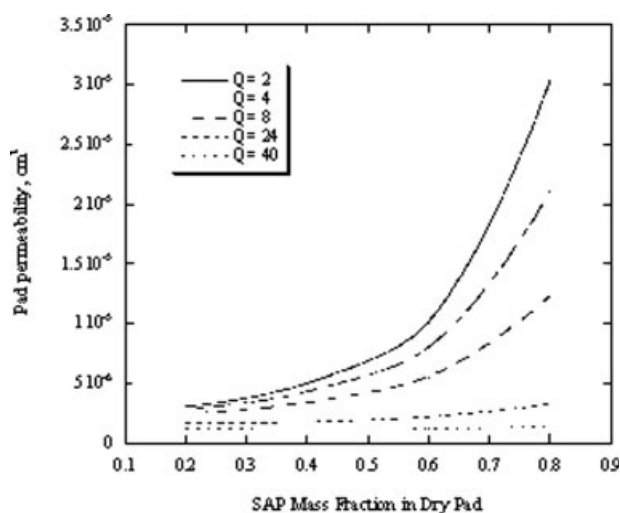

Figure 2 Pad permeability as a function of SAP loading in pad at various swelling extents (no compression).
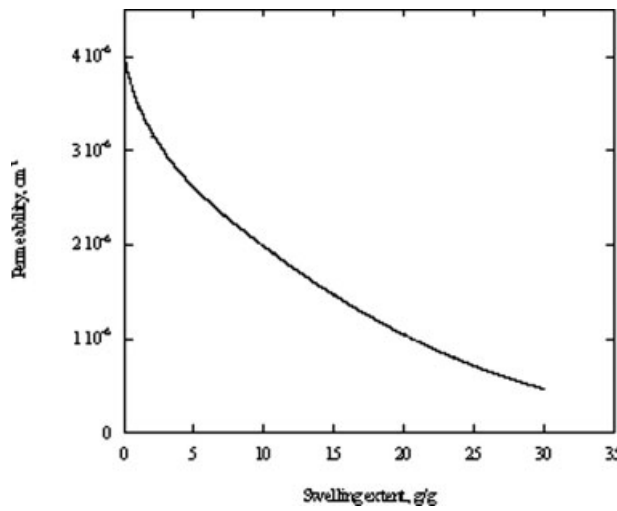
Figure 3 Permeability change with swelling at 44% SAP loading; no compression.

Figure 5 Pad permeability as a function of SAP particle radius at different swelling extents 40% SAP loading.

decrease with increasing swelling, as shown graphically in Figure 5. Permeability decreases with decreasing porosity but increases with decreasing surface-to-volume ratio. The steeper decline in porosity compared with the surface-to-volume ratio means that permeability generally decreases with increased swelling (porosity effects dominate). In Figure 6, the effect of polymer particle size on permeability is demonstrated as a function of the swelling extent. The surface-to-volume ratio decreases as the dry particle radius increases, which results in larger permeability. However, the porosity of the swollen pad declines with increasing swelling, even though the particle size increases during swelling. The overall, combined effect is that the permeability declines with swelling from an initial permeability that is larger for larger dry polymer particles.
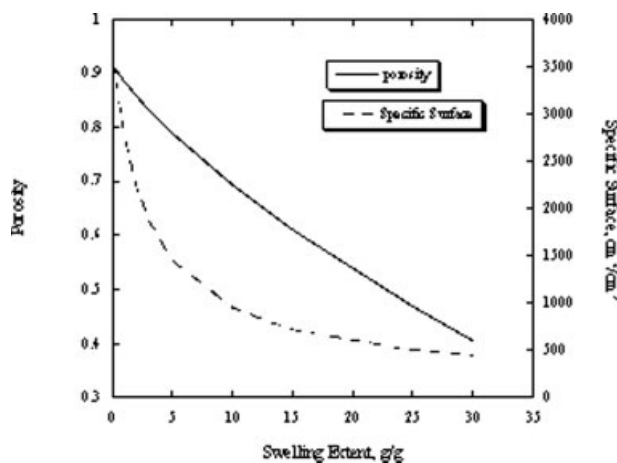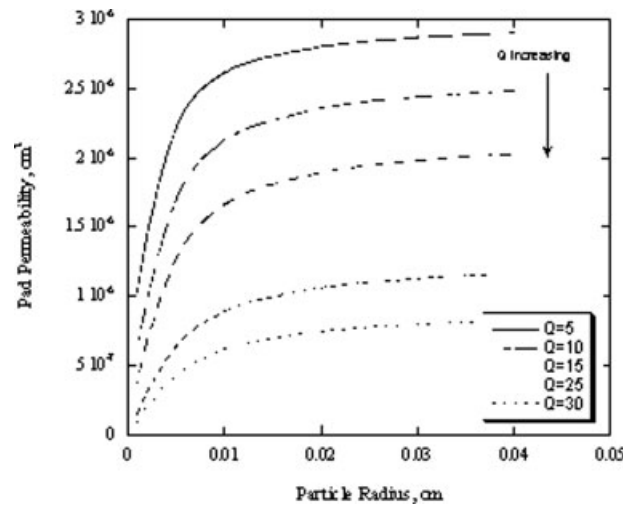
Pad permeability vs SAP bed permeability

The present model cannot definitively predict whether the permeability of pads containing SAP should correlate well to the permeability of gel beds of the same polymer. This is because the porosity equation contains the empirical parameter q, the component interaction parameter. At present there is no way to link the value of q for a pad to that of a gel bed. Although it seems that there should be a relationship between the permeability of a gel bed and the permeability of a composite pad containing the same gel, the model suggests that this cannot be a universal conclusion. The packing relationship of the gel particles in a bed of only gel particles (governed by a particle interaction parameter q for gel particle interaction) will in general not be the same as the packing relationship of those

Figure 4 Changes in porosity and specific surface area as swelling proceeds.
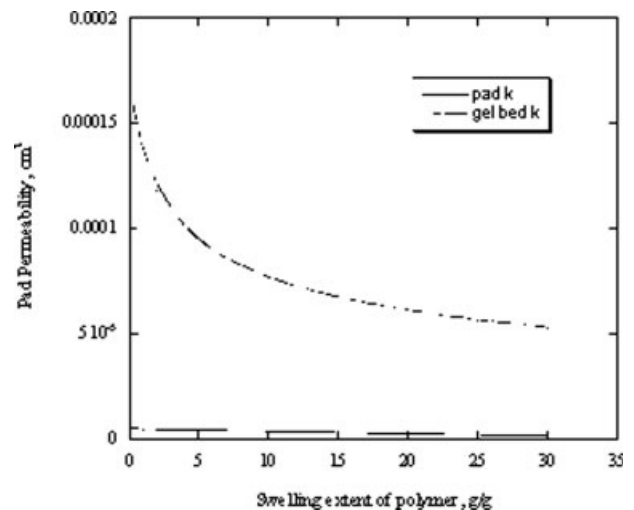

Figure 6 Comparison of permeabilities for a gel bed and a 47% SAP pad vs swelling extent of the polymer. No compression of either gel bed or pad.

same gel particles in the presence of co-mingled fibers (governed by a different value of q). However, from the model we can gain some insight into the conditions under which the pad permeability can be correlated to the gel bed permeability.

A gel bed is simulated by setting the fraction of SAP to 1, and choosing a value of the dry porosity that is consistent with packing of granular materials. The dry porosity of SAP beds is easily determined by measuring the bulk density (and by knowing the true density of the polymer). A typical value of the poured bulk density of a commercially available SAP powder is 0.685 g/cm^3, equivalent to a porosity of 0.590. If the gel bed swells affinely, the value of the component interaction parameter q is unity. If, however, the porosity of the bed decreases with increasing swelling, the value of q must be less than one. The porosity of the swollen gel bed can be experimentally determined from the difference between the free swell capacity of the polymer and its centrifuged retention capacity,[18] with the difference being the pore volume in the gel bed that is filled with liquid in the free swell capacity test. For a typical granular SAP, this difference yields a gel bed porosity of 0.276 at a swelling value of 29 g/g (author's measurement). The change in porosity of the bed upon swelling is governed by q. Within the model, the calculated value of swollen bed porosity is matched to the measured gel bed porosity by iterating q (using the measured dry porosity as the starting point). The change in bed porosity for a commercial sample, from 0.59 to 0.28, results in a value of $q = 0.62$. This value could be compared with q for a pad containing the same polymer.

The bulk density of a pad made with 47 wt% of a commercial SAP was measured in both the dry and swollen state. The wet and dry porosities were calculated from the bulk density and the swelling extent of the polymer. From these values the value of q for the pad was determined to be 0.01, far smaller than that for the gel bed. Using these values of q in the permeability model yields the permeability vs SAP swelling extent for both pad and gel bed. A plot of the pad permeability vs the gel bed permeability for this case is shown in Figure 6 above. The comparison shows that both the pad permeability and the gel bed permeability decrease with increasing swelling of the polymer, as expected. Let us compare this with a different hypothetical polymer.

Our new hypothetical polymer has an improved particle interaction parameter $q = 0.85$; that is, the gel bed expands more affinely as a result of some surface treatment, resulting in a more porous gel bed. Let us further speculate that the q value in the pad increases also, as a result of the surface treatment. We shall scale the q value in the pad by the ratio of the q values in the pad containing a commercial sample of SAP, as discussed above. In the earlier case, the ratio of $q_{(pad)}$
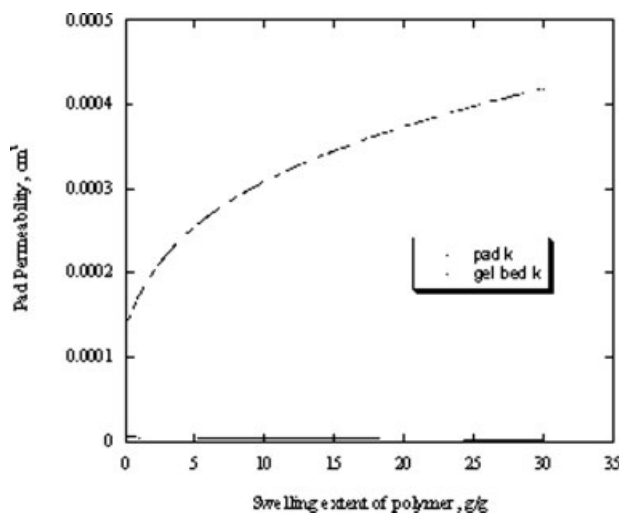

Figure 7 Permeabilities of hypothetical gel bed and pad with proportionately larger values of q (cf. Fig. 6).

to $q_{(gel\ bed)}$ was 0.016. Therefore, the value of $q_{(pad)}$ for our hypothetical case is equal to $0.85 \times 0.016 = 0.014$. Using these q values, the permeabilities of the gel bed and pad are calculated as a function of swelling, and the results are plotted in Figure 7. In this case, the gel bed permeability increases with increasing swelling extent whereas the pad permeability decreases with increased swelling – just the opposite behavior from the first example. Taken with the results from the first example, this second example illustrates the danger in assuming that the gel bed permeability is predictive of the permeability in a pad.

Permeability vs SAP stiffness and pad compression

Pad permeability generally decreases with compression because the pore volume is reduced. During the swelling process, the gel fraction in the pad increases while the modulus of the gel decreases. The resulting effect on pad permeability is seen in Figure 8, where each curve represents a different swelling extent for the polymer. As swelling increases the permeability vs compression curve is shifted to lower permeability.

According to the model, the stiffness or modulus of the SAP affects pad permeability only in compression. With no compression, the pad permeability can increase with increasing polymer loading at a fixed swelling extent (Fig. 2). However, upon compression this effect disappears, as shown in Figure 9. The results shown in Figure 9 are for pads made with a polymer with low modulus swollen to 25 g/g. The permeability rise at high polymer loading in the absence of compression is not seen in the permeability under compression at either 0.3 or 0.6 psi.

The compression modulus of the pad is affected by both the gel modulus and the gel fraction in the pad, increasing with gel modulus and the gel fraction. This
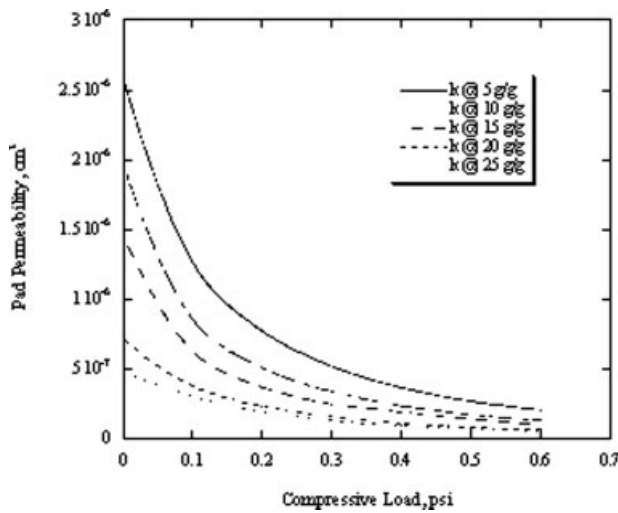
Figure 8 Permeability change with compression and swelling extent (44% SAP load).

means that the stiffness of the pad (i.e., its resistance to compression) increases with the gel content of the pad while the porosity is declining. The contribution of the gel modulus to the compression modulus of the pad is moderated by the fiber fraction and the compression modulus of the wet fiber. Even though the fiber fraction can be quite small in a swollen composite, the compression modulus of wet fiber is about ten times larger than typical gel modulus values. This results in a roughly equal contribution of fiber and gel to the pad compression modulus, and relative insensitivity of pad modulus to gel modulus. This indicates that to improve pad permeability under compression by means of polymer modification, we require high polymer loading, low swelling extent, and a high gel modulus.

IMPLICATIONS OF THIS MODEL

The large number of parameters needed to calculate the permeability illustrates the complexity of the composite pad. The permeability of a pad during swelling can be understood as the net result of the change of porosity with swelling and the change of specific surface area with swelling.

The porosity of a swollen pad decreases as swelling increases. The initial porosity of the dry pad, which is determined by the pad construction details, is quite important to the final result. As swelling proceeds, porosity declines from the initial value. Porosity also declines with increasing compression. The compressibility of the pad depends on the extent of swelling, the amount of gel present in the pad, and the modulus of the gel. Pad compression modulus increases with gel modulus, if all other parameters are held constant. However, the compressibility has only a weak dependence on gel modulus. This is because the gel

modulus and swelling extent generally are not independent parameters (they change in opposing directions and depend on crosslink density). The porosity also depends on the "particle interaction parameter" q, which describes the degree to which the pad bulk volume scales with the gel volume. The values of q for pads is quite small as a result of the restraint of the fibers, which act as cages for the gel particles. Values of q for gel beds are much larger—by a factor of 10–100—than those for pads. It is unclear from this work whether there is any relationship between the q values for pads and gels.

The specific surface (surface area to volume ratio) in a swelling pad decreases with increasing swelling. The initial value of specific surface in a pad depends on the mass fraction of polymer particles and their size. Usually, the specific surface decreases with increasing polymer fraction because the polymer particles are typically larger than the fibers and have a smaller surface-to-volume ratio. In this model, the specific surface does not change with compression; therefore, the permeability change after compression results only from the change in porosity.

The permeability of the swollen pad depends on a ratio of a porosity function to a specific surface function. The porosity function in eq. (2) is roughly equal to $\phi,^{4.5}$ and the specific surface dependence is S_0^2. Therefore, the permeability in pads is more sensitive to factors that affect the porosity of the pad, such as the initial dry porosity, the mass fraction of polymer in the pad, and the swelling extent of the polymer.

The model shows that over a certain range of q values for gel beds, the pad permeability correlates positively to gel bed permeability. However, above a certain threshold value of q, pad permeability will correlate negatively to the gel bed permeability. Therefore, as swelling increases in gel beds, some
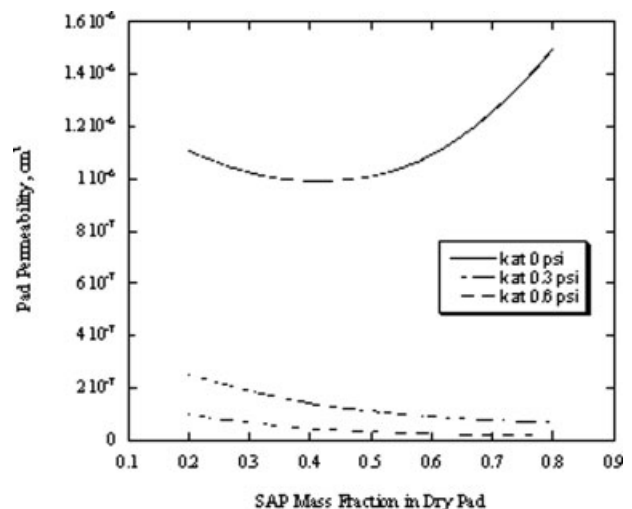

Figure 9 Pad permeability as a function of SAP fraction and applied pressure, at low gel modulus.

samples may increase in permeability while other decrease, depending on which side of the threshold they are on. This would clearly weaken any expected general correlation between pad and gel bed permeability. At the present time, there is no known relationship between the q values of gel beds and pads made with the same polymer. Unless such a relationship can be established, gel bed permeability cannot be reliably used as a guide for pad permeability or for polymer property targets.

The general compression behavior of pads and gel beds are similar because the compression of both is taken as a loss of porosity. The compression modulus of pads is generally larger (stiffer) than for gel beds because the fiber component resists compression much better than do the gel particles. The fiber component serves to minimize differences in gel modulus between different SAPs. Therefore, in order to observe an effect of gel modulus on pad compression, the differences between polymers must be quite large.

In terms of SAP development, this work indicates that high permeability in pads depends first on the porosity fixed in the pad in the dry state. If pads are highly compressed in the dry state, they will have poor permeability. Increasing swelling of the polymers decreases permeability; therefore, permeability can be improved by limiting the swelling of SAP. Permeability under compression depends on both the swelling extent and the gel modulus, which are inversely related through the crosslink density of the polymer. Compressibility is improved (made smaller) by increasing modulus and decreasing the swelling extent. Smaller compressibility lessens the drop in permeability under compression from its value at no load.

Various surface treatments of SAP that change the gel bed permeability most likely act on the ''particle interaction parameter'' q. For example, others have observed that surface treatment of polymer with alum solutions can dramatically increase the gel bed permeability. The model shows that a part of this effect is the lower swelling extent of the SAP. The gel modulus of some of the treated samples is also very large, but the model suggests only a weak dependence of permeability under compression on the gel modulus. What remains is the scaling of gel bed volume with swelling extent, indicated by the value of q, and the degree to which this is ''transferred'' into the blend of polymer and fiber. Too high a gel bed permeability may be accompanied by lower pad permeability, depending on the balance of these factors.

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