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Permeability of glass ribbon-reinforced composites

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An analytical model of the fluid permeability of glass ribbon-reinforced organic matrix composites is presented. The analysis indicates that such composites, with ribbon aspect ratios in the range 50 to 200 offer 100 to 1000 fold improvement in permeation resistance over fibre glass composites. This is pertinent to the application of composites for storage containers, pressure vessels, and pipelines. Permeation characteristics of glass ribbon composites were determined experimentally through mass spectrographic measurements of helium penetration. These measurements qualitatively supported the analytical model.

1. Introduction

Permeability to fluids is a factor which limits the applicability of composite materials in such items as storage containers, pressure vessels and pipelines. In the area of fibre glass-reinforced plastics (FRP) such permeability has meant that FRP chemical storage tanks leak; that rocket motor casings could not be made solely of FRP due to leakage; and that an impervious liner must frequently be employed in FRP pipe.

Intuitively, it seems that a ribbon-reinforced composite would be less permeable than a fibre-reinforced one due to the more tortuous permeation path. An analytical model of permeability of ribbon-reinforced composites is developed to investigate this quantitatively. The analysis presented here goes considerably beyond the treatment of Humphrey [1]; It should be noted that the relative advantage of ribbon over fibre reinforcement in providing composite permeation resistance is due to geometrical factors and does not depend on the mechanical or physical characteristics of the ribbon. The enhancement of mechanical properties of composites due to ribbon reinforcement has been reported by Halpin and Thomas [2], Lewis [3], Chen and Lewis [4] and Gray [5]. The analysis presented here is not limited to permeation resistance, but may be extended for finding thermal or electrical conductivity, magnetic permeability and permittivity of heterogeneous media containing ribbon-like reinforcement since all of these problems are governed by a single equation.

2. Analytical treatment

The objective is to determine the effective coefficient for permeation through a glass ribbon-reinforced composite (Fig. 1a) in the direction normal to the plane of ribbons. The geometrical parameters describing the structure of the composites are identified in Fig. 1b. The plate thickness, L_p, is taken as n multiples of the repeating distance $(a + t)$, where a is the ribbon thickness and t the matrix layer thickness. Similarly, the plate width, W, is considered as m multiples of the distance $(b + 2g)$, where b is the ribbon width and $2g$ the matrix-filled gap between ribbons in the same layer. The ratio b/a is termed the ribbon aspect ratio. The plate depth into the paper is denoted by l. The error introduced by considering the plate thickness and width as integral multiples of the repeating distances $(a + t)$ and $(b + 2g)$ is very small for all practical cases where the composite is many ribbon dimensions thick and wide.

The stacking parameter, $\gamma = x/b$, defines the position of each ribbon layer with respect to the layer underneath, as shown in Fig. 1b. By this definition $\gamma = \frac{1}{2}$ represents the case of maximum offset of ribbons in successive layers: a ribbon in one layer centred over a gap in the layer below.

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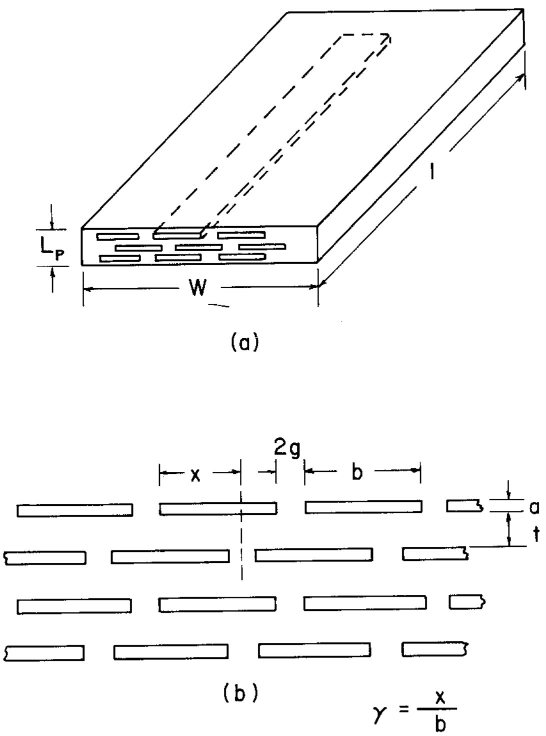

Figure 1 (a) Ribbon-reinforced composite plate. (b) Parameters describing plate construction.

This arrangement will give the highest permeation resistance. Similarly, $\gamma = 0$ implies that ribbons are almost lined up with the permeation resistance at a minimum. Because the permeability of organic resins is many orders of magnitude greater than that of glass, only permeation through the matrix is considered. The effect of this assumption will be examined later in the paper. In lieu of a complete mathematical solution of the diffusion equation for the geometry described, an approximate solution has been obtained by considering the matrix skeleton as a series of interconnecting straight channels. The channel model chosen thus provides a physically acceptable path for flow. Of course, in actual flow the path chosen for flow is the path of least resistance. Thus a permeation coefficient calculated on the basis of a constructed but physically realizable path will be somewhat less than the permeation coefficient for the path of least resistance. The difference between the two values will be less, the more efficiently the modelled flow pattern makes use of the actual area available for flow.

The channel arrangement on which the calculations are based is shown in Fig. 2a. The repeating unit from which the whole channel structure is built is shown in Fig. 2b. The relation-

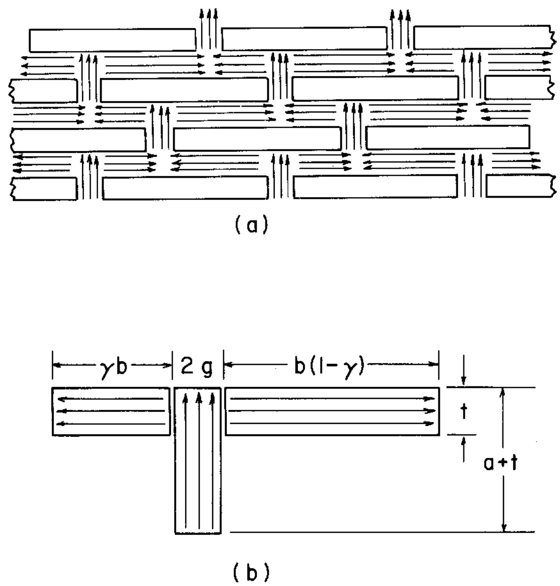

Figure 2 (a) Diffusion channels in composite. (b) Repeating unit in matrix skeleton.

ship describing the permeation of a fluid through a channel of material with permeation coefficient K is given by

$$\dot{Q} = K\left(\frac{A}{L}\right)\Delta P \tag{1}$$

where $\dot{Q}$ is the volume flow rate; A is the channel area normal to flow; L is the channel thickness and ΔP is the pressure drop over the thickness of the channel.

Consider the flow in the repeating unit shown in Fig. 2b. The flow rate through the vertical channel is given by

$$\dot{Q}_{\rm v} = K_{\rm m}\left(\frac{2gl}{a+t}\right)\Delta P_{\rm v}. \tag{2}$$

The horizontal flow has both left and right components. By symmetry, the pressure drops to the left and right are equal because the point reached by flow to the left from one vertical channel is also reached by flow to the right from an adjacent vertical channel. Thus

$$\dot{Q}_{\rm h} = \dot{Q}_{\rm hl} + \dot{Q}_{\rm hr} = K_{\rm m}\left[\frac{tl}{b\gamma(1-\gamma)}\right]\Delta P_{\rm h}. \tag{3}$$

Conservation of mass requires that horizontal and vertical flow rates be equal. Denoting the flow rate through each channel of width $2g$ by $\dot{Q}_{\rm ch}$, we have

$$\dot{Q}_{\rm ch} = \dot{Q}_{\rm v} = \dot{Q}_{\rm h}. \tag{4}$$

The total pressure drop in the repeating unit (and thus for each layer of ribbon in the plate) is the sum $(\Delta P_v + \Delta P_h)$ which by virtue of Equations 2, 3 and 4 is given by

$$\Delta P_{\text{layer}} = \frac{\dot{Q}_{\text{ch}}}{K_m l}\left[\frac{a+t}{2g} + \frac{b}{t}\gamma(1-\gamma)\right]. \quad (5)$$

Since the plate is composed of n layers, the total pressure drop across the plate is $n\Delta P_{\text{layer}}$ or

$$\Delta P_{\text{T}} = \frac{\dot{Q}_{\text{ch}} L_p}{k_m l}\left[\frac{1}{2g} + \frac{b\gamma(1-\gamma)}{t(a+t)}\right]. \quad (6)$$

The total flow rate through the plate is related to the flow rate through the channel by

$$\dot{Q}_{\text{T}} = \left(\frac{W}{b+2g}\right)\dot{Q}_{\text{ch}}. \quad (7)$$

Combining Equations 6 and 7 and noting that Wl is the plate area A_p, we obtain

$$\dot{Q}_{\text{T}} = \left[\frac{K_m}{1+\dfrac{b}{2g}+\dfrac{b}{a}\left(\dfrac{b+2g}{t}\right)\left(\dfrac{a}{a+t}\right)\gamma(1-\gamma)}\right]\left(\frac{A_p}{L_p}\right)\Delta P_{\text{T}}. \quad (8)$$

Comparing this expression with Equation 1, it can be seen that the effective permeation coefficient for flow through the composite plate is given by

$$K_c = \frac{K_m}{1+\dfrac{b}{2g}+\dfrac{b}{a}\left(\dfrac{b+2g}{t}\right)\left(\dfrac{a}{a+t}\right)\gamma(1-\gamma)} \quad (9)$$

It should be pointed out that the stacking parameter γ affects the resistance to horizontal flow only, as would be expected from the model. Moreover, from the form of Equation 9 it is clear that the composite permeation resistance is unaffected if we replace γ by $(1-\gamma)$. The physical interpretation of this symmetry follows from the model and Fig. 2b.

From Fig. 1b it is easy to show that the ribbon volume fraction V_r is given by

$$V_r = \frac{1}{\left(1+\dfrac{t}{a}\right)\left(1+\dfrac{2g}{b}\right)}. \quad (10)$$

For ribbon composites of most interest, $2g/b$ is small compared to unity and Equation 9 by virtue of Equation 10 takes the form

$$\frac{K_c}{K_m} = 1\bigg/\left[\frac{b}{2g}+\left(\frac{b}{a}\right)^2\left(\frac{V_r^2}{1-V_r}\right)\gamma(1-\gamma)\right]. \quad (11)$$

In cases where the aspect ratio b/a is very large (>100) and $2g \sim a$, the above expression can be further approximated by

$$\frac{K_c}{K_m} = \frac{1}{(b/a)^2}\left(\frac{1-V_r}{V_r^2}\right)[\gamma(1-\gamma)]^{-1}. \quad (12)$$

Although this approximation for K_c/K_m has a limited region of applicability, it illustrates clearly the general form of the dependence on b/a, V_r and γ.

The preceding results are shown graphically on a log–log paper in Fig. 3. The straight lines correspond to Equation 12 for $V_r = 0.75, \gamma = 0.5$; $V_r = 0.5$, $\gamma = 0.5$ and 0.25; and $V_r = 0.25, \gamma = 0.5$. The curved line is the exact solution given by Equation 9 for $V_r = 0.5$ and $\gamma = 0.5$ with $2g$ taken equal to a. The departure from the more approximate Equation 12 is evident. It may be noted that for a given value of b/a the more approximate solution predicts a higher permeation coefficient. Thus, predictions of permeation resistance will err on the conservative side when made on the basis of Equation 12. The basis for this difference is that in

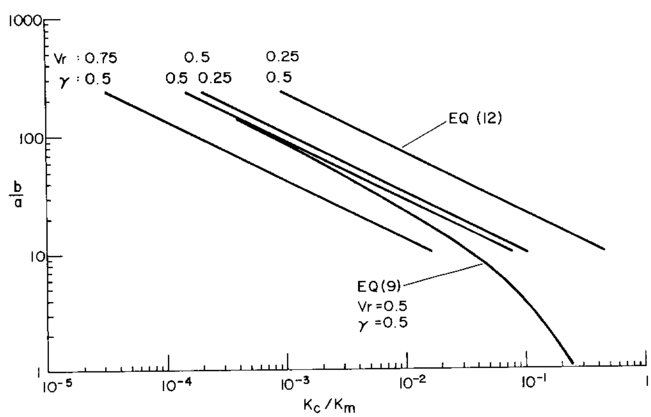

Figure 3 Permeation coefficient of composites as a function of ribbon aspect ratio (b/a), volume fraction (V_r), and stacking parameter (γ).

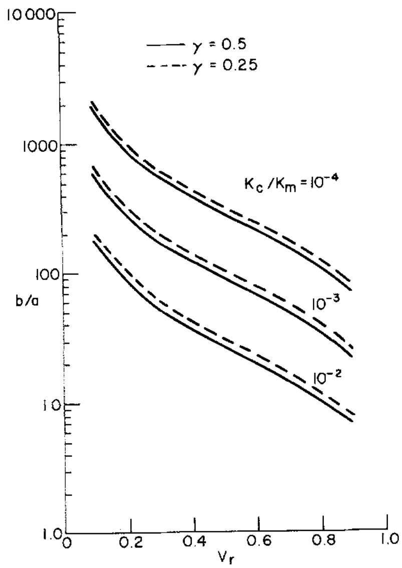

Figure 4 Effect of aspect ratio and volume fraction on permeation coefficient of ribbon composites; $2g/b = 0.1$.

going from Equation 9 to Equation 12, the term reflecting resistance to flow in the vertical channels has been dropped, whereas in practice some resistance will be contributed. Another way of presenting the solution to Equation 9 is shown in Fig. 4 where lines of constant K_c/K_m are plotted for γ values of 0.25 and 0.5. A value of 0.1 has been assumed for $2g/b$. It should be noted that a desired reduction in composite permeation coefficient may be achieved by increasing either the volume fraction or the aspect ratio or both. Accordingly, it might be possible to use a low volume fraction of high aspect ratio ribbon, thereby causing a saving in cost and weight of the composite.

Of the three factors (V_r, b/a, γ) which effect the composite permeation coefficient, the stacking parameter has the least effect. Figs. 3 and 4 illustrate the effect on K_c/K_m of varying γ from 0.5 where each ribbon is centred over the gap in the layer beneath, to 0.25, characteristic of a filament-wound ribbon composite tube. Only when $\gamma = 0$ does it have a strong effect on K_c/K_m. When $\gamma = 0$, vertical flow resistance becomes predominant and an examination of Equation 9 shows that

$$K_c/K_m = 2g/(b + 2g) \quad (13)$$

which is the correct solution for a high volume fraction composite with gaps lined up; this factor may still be of the order of 1/100.

Under the conditions $a = b$ and $2g = t$, the solution of Equation 9 provides an estimate of the permeation resistance of composites containing uniformly spaced fibres. The calculated K_c/K_m ratios for several volume fractions are shown in Table I where the values based on Halpin–Tsai [6] equations are also included for comparison. Although Equation 9 was derived on the basis of diffusion paths characteristic of ribbon composites, it provides a reasonably good solution for fibre composites. In fibre composites the vertical flow resistance outweighs the horizontal flow resistance, and the vertical component is fully accounted for in Equation 9; thus the agreement between the present model and Halpin–Tsai equations is reasonably good.

TABLE I K_c/K_m values for fibre composites

V_r	Present solution; Equation 9 ($2g = t, \gamma = 0.25$)	Halpin–Tsai solution
0.11	0.63	0.79
0.25	0.46	0.59
0.44	0.30	0.38
0.50	0.26	0.33
0.66	0.17	0.20
0.83	0.08	0.09

3. Experimental results

The verification of permeability theory given here was sought experimentally through mass spectrometer measurements of helium permeation through composites of various constructions. Corning Code 8871 glass ribbon was used with either of the two matrices: Shell Epoxy Resin Epon 828 with Z curing agent; and 3M epoxy polyamide film SCOTCHWELD. Specimens from 0.014 to 0.045 in. thick and 3 in. square were prepared in the desired configurations by hand lay-up technique. Helium permeation measurements were carried out in the mass spectrometer by Altemose by the procedures used for measuring permeation through glass [7].

The data are summarized in Table II, and confirm the permeation advantages of ribbon composites. In all cases a lower permeability was measured than was predicted by the theory. In the case of the fibre composite, the agreement between theory and experiment was excellent; for ribbon composites, much less satisfactory agreement was found. One contributing factor may be the probably far from ideal spacing of resin and glass in the composites. Solution of the equations shows that such effects would be far more important for the ribbon than for the fibre con-

TABLE II Helium permeation results – theory versus experiment

Specimen	Helium permeation (measured) (cm³ (STP) mm sec⁻¹ cm⁻² (cm Hg)⁻¹)	K_c/K_m Measured	K_c/K_m Theory (Equation 12)	K_c (measured) / K_c (theory)
Epon 828/Z	1.38×10^{-9}	–	–	–
SCOTCHWELD	6.45×10^{-10}	–	–	–
Code 8871 Glass	5.60×10^{-17}	–	–	–
Code 7740 Glass	1.00×10^{-11}	–	–	–
Ribbon composites				
Epon 828/Z, $V_r = 0.62$ $\gamma = 0.5$, $b/a = 264$	1.09×10^{-14}	7.9×10^{-6}	5.7×10^{-5}	0.14
SCOTCHWELD, $V_r = 0.22$ $\gamma = 0.5$, $b/a = 121$	5.96×10^{-14}	9.2×10^{-5}	4.6×10^{-3}	0.02
SCOTCHWELD, $V_r = 0.54$ $\gamma = 0.5$, $b/a = 121$	3.70×10^{-14}	5.7×10^{-5}	4.4×10^{-4}	0.13
Fibre composite				
Epon 828/Z, $V_r = 0.45$ (E-glass fibre)	3.03×10^{-10}	2.2×10^{-1}	2.9×10^{-1} (Equation 9)	0.76

struction. It is also possible that the resin structures in the ribbon and fibre composites and the glass-free reference specimens may all be different due to differing thermal history and the residual stresses set up during fabrication.

4. Discussion

In the foregoing analysis it was assumed that permeation through the glass phase of the composite was negligible. It is true, as shown in Table II, that permeation coefficients of helium through glass are many orders of magnitude lower than through organics. However, the tortuosity of the organic path in ribbon composites so reduces the permeation through the organic phase that direct permeation through the glass phase may not be negligible. Indeed, Table II shows measured Code 8871 ribbon composite permeation coefficients lower than the permeation through Corning's Code 7740 borosilicate glass.

The measured values of K_c were low because the permeability of Code 8871 ribbon glass is extremely low due to its lead-rich composition with low concentration of network-forming oxides. The general rule for predicting helium permeability of a glass, given the composition, is given by Altemose [7].

Applying the permeability analysis to gas flow in the thickness direction of a ribbon composite, i.e. through alternate layers of glass and organic, the permeability coefficient for straight-through permeation turns out to be

$$K_{\text{through}} = \frac{K_g}{V_r}\left[1 + \frac{t}{a}\left(\frac{K_g}{K_m}\right)\right]^{-1} \tag{14}$$

where K_g is the permeation coefficient of glass ribbon. Thus the ratio of straight-through to tortuous permeability (Equation 12) becomes

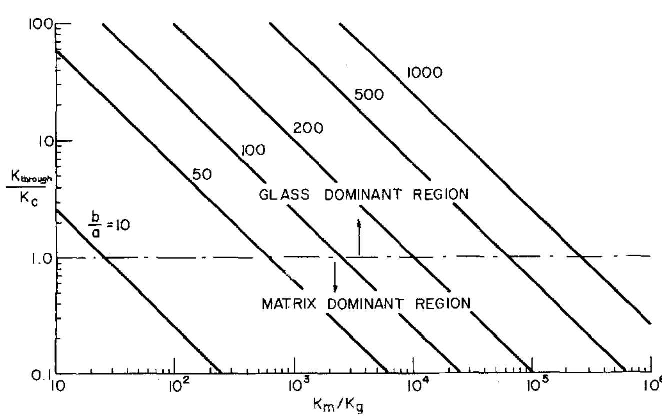

Figure 5 Variation of K_{through}/K_c with K_m/K_g for different aspect ratios (Epon 828/Z matrix; $V_r = \gamma = 0.5$).

$$\frac{K_{\text{through}}}{K_c} = \left(\frac{K_g}{K_m}\right)\left(\frac{V_r}{1-V_r}\right)\left(\frac{b}{a}\right)^2 \cdot \gamma(1-\gamma)\left[1+\frac{t}{a}\left(\frac{K_g}{K_m}\right)\right]^{-1} . \quad (15)$$

The above ratio will be maximum when V_r is maximum. Assuming $V_r = 0.5$ and $\gamma = 0.5$, the variation of K_{through}/K_c with K_m/K_g for different aspect ratios is shown in Fig. 5. It should be noted that the dominance of either straight-through or tortuous permeation in a ribbon composite is dictated by the aspect ratio of the ribbon and K_m/K_g value. For tortuous permeation to be dominant, large aspect ratio ribbons would require large values of K_m/K_g.

For the most tortuous ribbon composite shown in Table II ($V_r = 0.62$) the ratio K_{through}/K_c works out to be 0.0012, thus justifying the neglect of permeation through the glass phase for all of the experimental composites reported here. However, if Code 7740 glass ribbons were used, the above ratio would be unity indicating that straight-through permeation is equal to tortuous permeation and hence is not negligible.

5. Conclusions

An analysis is presented here which indicates quantitatively how the permeation resistance of ribbon composites depends on volume fraction, aspect ratio and the stacking configuration of reinforcing elements.

It is clear from Fig. 3 and Table I that fibres, even at the highest attainable volume fraction, can lower the permeation coefficient of the composite to at most 1/10 the matrix permeation coefficient. In contrast to this, ribbons of readily attainable aspect ratios and volume fraction should offer 100 to 1000 fold improvement over the fibre case.

The assumption of neglecting permeation through the glass ribbon was examined and found to be justifiable in those cases where $K_m/K_g > 10^4$ and ribbon aspect ratio > 100.

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