

Viscoelastic Analysis of Osmotic Blistering Behavior of Coating Film

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The osmotic blistering behavior of polymeric coating film which is in contact with an aqueous environment has been investigated. In this study, the coating film has been assumed to be linearly viscoelastic. Interfacial stresses induced in a laminate model consisting of the viscoelastic film and the elastic substrate as the film absorbs moisture from the ambient environment have been investigated using the time-domain boundary element method. The overall stress intensity factor for interfacial cracks subjected to a uniform osmotic pressure has been computed using the tractions at the crack tip node. The magnitude of stress intensity factors decreases with time due to viscoelastic relaxation, but remains constant at large times.

Keywords : osmotic blistering, polymer, coating film, viscoelastic, moisture, boundary element method

1. Introduction

The adhesion of polymers to a variety of substrates is of great technological importance. Many polymers are widely used as coating films which are in contact with an aqueous environment.¹⁾⁻³⁾ The coating films are semi-permeable membranes, permeable to water, but impermeable to dissolved solids. Under such conditions, after water is absorbed by the film, it is subsequently transferred to the film/substrate interface. There it may come in contact with the soluble material on the substrate and leave the film to dissolve the material. Under fresh water conditions (distilled water or even high humidity), such interface dissolution creates a concentration gradient across the film, which here acts as a semi-permeable membrane. On the downstream side of the film where the solute is dissolved by water from the film, the solute concentration is much higher than the solute concentration at the external (or up-stream) face of the film. Under these conditions, water is drawn through the film towards the concentrated solute, under osmotic pressure. This transfer of water occurs because the water pressure and salt concentrations on either side of the membrane attempt to equilibrate. As solution concentration drops with additional migration of water, osmotic pressure becomes too great for the adhesive forces holding coating film to the substrate and results in interfacial cracks⁴⁾⁻⁶⁾ or the localized delamination of



Fig. 1. Osmotic blistering of coating on concrete

film as a solution-filled blister(Fig. 1).

This paper deals with the osmotic blistering behavior of polymeric coating film which is in contact with an aqueous environment. Polymeric films in general respond in a viscoelastic manner under loads and their time-dependent behavior is affected by moisture. In this study, the coating film is assumed to be linearly viscoelastic. The boundary element method⁷⁾⁻⁹⁾ is employed to investigate the blistering behavior of the coating film.

2. Boundary element analysis

A viscoelastic thin film bonded to an elastic substrate is shown in Fig. 2(a). The osmotic pressure becomes too great for the adhesive forces holding coating film to the substrate and results in the interfacial crack of film as a solution-filled blister. Due to symmetry, only one half of the layer needs to be modeled. Fig. 2(b) represents the

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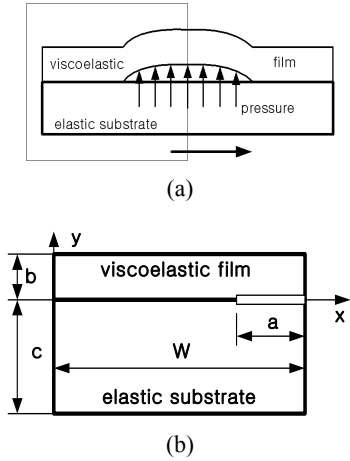


Fig. 2. Interfacial crack of film as a solution-filled blister.

two-dimensional plane strain model for analysis of the interfacial stresses between the film and the substrate. The osmotic pressure is assumed to be uniform along the interfacial crack. It is further assumed that moisture effects are analogous to thermal effects. A uniform moisture change $\Delta mH(t)$ in the film is equivalent to increasing the tractions by $\gamma(t)n_j^{10}$ where

$$\gamma(t) = 3K\beta\Delta mH(t) \quad (1)$$

Here, K is the bulk modulus; n_j are the components of the unit outward normal to the boundary surface; and β is the coefficient of hygral expansion of the viscoelastic film.

The boundary integral equations without any other body forces are written as follows¹⁰:

For viscoelastic thin film,

$$\begin{aligned} & c_{ij}(\mathbf{y})u_j(\mathbf{y}, \xi) \\ & + \int_S \left[u_j(\mathbf{y}', \xi)T_{ij}(\mathbf{y}, \mathbf{y}'; 0+) + \int_{0^+}^{\xi} u_j(\mathbf{y}', \xi - \xi') \frac{\partial T_{ij}(\mathbf{y}, \mathbf{y}'; \xi')}{\partial \xi'} d\xi' \right] dS(\mathbf{y}') \\ & = \int_S \left[t_j(\mathbf{y}', \xi)U_{ij}(\mathbf{y}, \mathbf{y}'; 0+) + \int_{0^+}^{\xi} t_j(\mathbf{y}', \xi - \xi') \frac{\partial U_{ij}(\mathbf{y}, \mathbf{y}'; \xi')}{\partial \xi'} d\xi' \right] dS(\mathbf{y}') \\ & + \int_S \left[\gamma(\xi)n_j U_{ij}(\mathbf{y}, \mathbf{y}'; 0+) + \int_{0^+}^{\xi} \gamma(\xi - \xi')n_j \frac{\partial U_{ij}(\mathbf{y}, \mathbf{y}'; \xi')}{\partial \xi'} d\xi' \right] dS(\mathbf{y}') \end{aligned} \quad (2)$$

For elastic substrate

$$\begin{aligned} & c_{ij}(\mathbf{y})u_j(\mathbf{y}, \xi) + \int_S u_j(\mathbf{y}', \xi)T_{ij}(\mathbf{y}, \mathbf{y}')dS(\mathbf{y}') \\ & = \int_S t_j(\mathbf{y}', \xi)U_{ij}(\mathbf{y}, \mathbf{y}')dS(\mathbf{y}') + \int_S \gamma(\xi)n_j U_{ij}(\mathbf{y}, \mathbf{y}')dS(\mathbf{y}') \end{aligned} \quad (3)$$

where u_j and t_j represent displacement and traction, and S is the boundary of the given domain. $c_{ij}(\mathbf{y})$ is dependent

only upon the local geometry of the boundary. For y on a smooth surface, the free term $c_{ij}(\mathbf{y})$ is simply a diagonal matrix $0.5\delta_{ij}$. The viscoelastic fundamental solutions, $U_{ij}(\mathbf{y}, \mathbf{y}'; \xi)$ and $T_{ij}(\mathbf{y}, \mathbf{y}'; \xi)$, can be obtained by applying the elastic-viscoelastic correspondence principle to Kelvin's fundamental solutions of linear elasticity.

In Eq. 2, ξ is the reduced time defined as follows:

$$\xi = \xi(t) = \int_0^t A_m(m(\lambda))d\lambda \quad (4)$$

where A_m is the shift function, a function of moisture cycle. Under the constant moisture change $\Delta mH(t)$, the reduced time ξ of Eq. 4 becomes

$$\xi = A_m t \quad (5)$$

Eqs. 2 and 3 can be solved in a step by step fashion in time by using the modified Simpson's rule for the time integrals and employing the standard BEM for the surface integrals. Solving Eqs.2 and 3 under boundary conditions leads to determination of all boundary displacements and tractions.

The following viscoelastic model for the film is in this study

$$E(t) = \frac{3200}{1 + 0.0336t^{0.19}} \quad \text{MPa} \quad (6)$$

$$K(t) = 3550 \quad \text{MPa} \quad (t : \text{min.}) \quad (7)$$

where $E(t)$ is a tensile relaxation modulus, $k(t)$ is a bulk modulus.

3. Stress intensity factor for an interfacial crack

The stress field near an interface crack between linear elastic material and linear viscoelastic material in the Laplace transformed space are given as follows⁶:

$$\left[\overline{\sigma}_{yy}(r, \theta, s) + i\overline{\tau}_{xy}(r, \theta, s) \right]_{\theta=0} = \frac{\overline{K}_1 + i\overline{K}_2}{\sqrt{2\pi r}} \exp \left[i\overline{\beta}(s) \ln \left(\frac{r}{d} \right) \right] \quad (8)$$

where

$$\overline{\beta}(s) = \frac{1}{2\pi} \ln[\overline{\gamma}(s)], \quad \overline{\gamma} = \frac{\overline{\kappa}_I(s)\mu_{II} + s\overline{\mu}_I(s)}{\overline{\kappa}_{II}s\overline{\mu}_I(s) + \mu_{II}} \quad (9)$$

$$\overline{\kappa}_I(s) = 3 - 4s\nu_I(s), \quad \overline{\kappa}_{II} = 3 - 4\nu_{II} \quad (10)$$

Here $\overline{\sigma_{yy}}(s)$ and $\overline{\tau_{xy}}(s)$ are the Laplace transformed viscoelastic stresses, $\overline{K_1}(s)$ and $\overline{K_2}(s)$ are the Laplace transformed stress intensity factors, and s is the transform variable. $\overline{\mu}_1(s)$ and $\overline{\nu}_1(s)$ are Laplace transforms of the shear relaxation modulus $\mu_1(t)$ and the viscoelastic Poisson's ratio $\nu_1(t)$.

As can be seen from Eq. 8, the stresses exhibit an oscillating singularity. However, the maximum amplitude of these singular stresses is determined by the overall stress intensity factor as follows:

$$K_O(t) = \lim_{r \rightarrow 0} \sqrt{2\pi r} \sqrt{[\sigma_{yy}(r,0;t)]^2 + [\tau_{xy}(r,0;t)]^2} \quad (11)$$

The overall stress intensity factor $K_O(t)$ for the elas-

tic-viscoelastic interface crack can be determined from the stresses near the crack tip using Eq. 11. It is well known that by using the quarter-point element for displacement fields and the traction singular quarter-point element for the traction field, the variation of the displacements and tractions along the crack tip element is of the correct order as those established in fracture mechanics theory.^{8,9)} The stress intensity factor can be expressed from Eq. 11 as

$$K_O(t) = \sqrt{2\pi L} \sqrt{[t_1^A(t)]^2 + [t_2^A(t)]^2} \quad (12)$$

where t_i^A denote the BEM computed traction on the traction singular crack tip element at the crack tip node and L is the length of the crack tip element.

The problem for interfacial cracks between the viscoe-

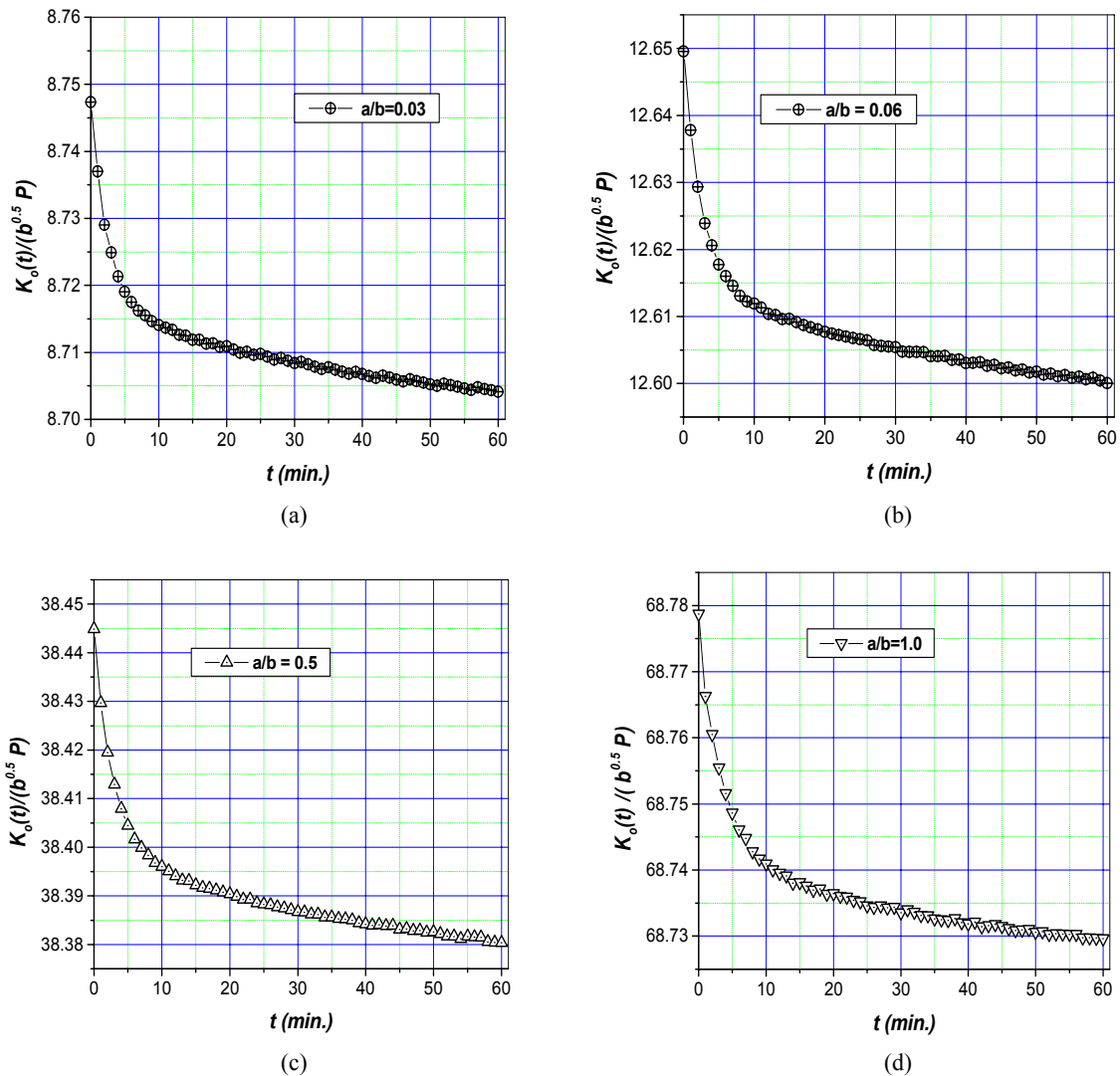


Fig. 3. Variation of overall stress intensity factors

lastic film and the elastic substrate subjected to a uniform pressure $PH(t)$ is solved. The analysis model is shown in Fig. 2. It is assumed that $(W-a) > 9b$. The model has 38 boundary elements for $a/b = 1.0, 0.5, 0.06, 0.03$. The crack tip elements are used with small crack tip element to crack length ratios (L/a) to represent properly both the \sqrt{r} displacement behavior and $1/\sqrt{r}$ traction behavior. As $a \rightarrow 0$ ($a/b < 10^{-3}$), however, the boundary element procedure is inaccurate due to the instability of the crack tip elements to represent the stress singularity.

Fig. 3 shows the BEM results of $K_o(t)$ for crack lengths $a/b = 1.0, 0.5, 0.06, 0.03$, in which $K_o(t)$ increases with increasing crack size. $K_o(t)$ for each crack length is observed to be relaxed with time. To begin with, at time $t = 0$, if K_o is more than the critical value K_C , the crack starts growing before it reaches a stage where $K_o(t)$ drops below that of K_C and then it ceases to grow. In another situation, right at the beginning, if K_o is below the critical value K_C , the crack will never grow.

4. Conclusions

The osmotic blistering behavior of polymeric coating film which is in contact with an aqueous environment has been investigated using the time-domain boundary element method. Polymeric films in general respond in a viscoelastic manner under loads and their time-dependent behavior is affected by moisture. Therefore, a time-dependent stress analysis of the film has been performed to understand and predict failure in coating systems. In this study, the coating film has been assumed to be linearly viscoelastic.

The overall stress intensity factor for interfacial cracks

between the viscoelastic film and the elastic substrate subjected to a uniform osmotic pressure has been computed using the tractions at the crack tip node. The magnitude of stress intensity factors decreases with time due to viscoelastic relaxation, but remains constant at large times. At time $t = 0$, if the overall stress intensity factor is more than the critical value, the crack starts growing before it reaches a stage where the overall stress intensity factor drops below that of the critical value and then it ceases to grow. In another situation, right at the beginning, if the overall stress intensity factor is below the critical value, the crack will never grow. The numerical procedure does not permit calculation of the limiting case for which the crack length vanishes.

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