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Rheological properties and adhesive failure of thin viscoelastic layers

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Synopsis

Methods have been developed for measuring the linear viscoelastic properties of thin adhesive layers, and for determining the stress intensity factor characterizing the driving force for adhesive failure. Both methods involve bringing a hemispherical indenter in contact with the adhesive layer while simultaneously monitoring the load, displacement, and radius of contact between the indenter and the adhesive. Dynamic moduli for the adhesive layer are obtained by oscillating the indenter, and the adhesive properties are obtained by pulling the indenter completely out of contact with the adhesive layer. Existing theories of viscoelastic contact mechanics were extended to account for the fact that the adhesive layer thickness is not substantially larger than the contact radius, as is generally assumed. A variety of correction factors were introduced that depend on the ratio of the contact radius to the adhesive layer thickness. These methods were applied to a model adhesive based on an acrylic triblock copolymer. Determination of the time-dependent creep and relaxation functions for this material was simplified by the power-law frequency response of the dynamic moduli. The large stress intensity factors observed were related to a Dugdale model of the cohesive zone at the contact edge. © 2002 The Society of Rheology. [DOI: 10.1122/1.1428316]

I. INTRODUCTION

It is well-known that the behavior of thin, viscoelastic adhesive layers such as pressure sensitive adhesives is dependent upon both the interfacial and bulk properties of the adhesive [Creton (1997); Pocius (1997)]. An understanding of the quantitative relationship between surface and interfacial effects has been difficult to achieve, however. Linear elastic fracture mechanics and the specific derivation of Johnson, Kendall, and Roberts in 1971 [Johnson *et al.* (1971)] has been used effectively to quantify adhesion for many materials, [Barquins and Maugis (1981); Crosby and Shull (1999); Maugis and Barquins (1978), Shull *et al.* (1998)], but certain underlying assumptions have limited its influence over the entire field of adhesion. The two most critical assumptions are (1) the contact radius must be much smaller than the dimensions of the two contacting bodies and (2) the materials must be linearly elastic. We have recently addressed the first assumption by developing semianalytical corrections to extend the fracture mechanics equations to thin

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samples [Shull *et al.* (1998)]. The second assumption continues to play a significant role in the general applicability of the fracture mechanics technique to describe polymer adhesion, and is the focus of this paper.

Polymers are generally viscoelastic materials. The ability to use elastic mechanical models to describe polymer behavior is largely dependent upon the length and time scales over which the viscous component plays a role. When ideally elastic materials are used as adhesives, all of the applied energy is used to propagate the interfacial crack and create new surface area. Linear elastic fracture mechanics formally applies to this case. If the mechanical response of the material has a weak viscoelastic component, the applied energy will be shared between creating new surfaces and being dissipated in regions near the crack tip where stress levels are elevated. As long as the region of dissipation is small relative to the sample volume, then linear elastic fracture mechanics can still be used to describe the failure process. In this case the majority of applied energy still works to propagate the interfacial crack, but the critical energy release rate for crack propagation will no longer be simply the work of adhesion of the two surfaces. Rather, the critical energy release rate for crack propagation exhibits a dependence on the crack tip velocity. This approach has been demonstrated for a variety of crosslinked elastomers [Ahn and Shull (1996); Ahn and Shull (1998b); Barquins and Maugis (1981); Maugis and Barquins (1978)] and for pressure-sensitive adhesives [Crosby and Shull (1999)]. As the region of viscous dissipation increases in size relative to the overall sample dimensions, more of the applied energy is dissipated throughout the bulk of the material and is not used to propagate the crack. Consequently, elastic fracture mechanics arguments are no longer valid in this regime.

In this paper, we extend a previous treatment of viscoelastic contact mechanics [Hui and Baney (1998); Lin *et al.* (1999)] to account for the small thickness of the adhesive layer. The model is applied to studies of a model adhesive system that has been studied with two different experimental techniques. First, we introduce a rheometric test that allows us to determine the bulk rheological properties of thin adhesive layers. An axisymmetric adhesion test is then used to determine the overall adhesion of this material. Information obtained from both of these tests enables us to develop a quantitative adhesive failure criterion for this material based on the relationship between the stress intensity factor and the detachment rate.

II. EXPERIMENTAL METHOD

Our model adhesive is a blend of diblock and triblock copolymers, referred to here as D/T. The triblock copolymer (MW = 167 000 g/mol) consists of poly(methylmethacrylate) (PMMA) end blocks coupled to a carboxylated poly(*n*-butylacrylate) (PnBa) mid-block (82 wt %). The diblock is poly(methylmethacrylate)–poly(*n*-butylacrylate) and is half as large as a triblock molecule. The diblock corresponds to 35% by weight of the overall polymer. A more detailed structural characterization of this polymer has been provided previously [Flanigan *et al.* (1999)]. These adhesives are generally elastic materials, but their linear and nonlinear viscoelastic properties play an important role in determining their adhesive properties.

The layers of D/T used in our experiments are processed with a gel casting technique that produces very reproducible samples with a well-defined microstructure. This technique involves first dissolving D/T in a solvent that is preferential for the PnBa segment. For the samples described in this paper, the solvent was 2-ethylhexanol, but a wide variety of alcohols can be used for this purpose. When dissolved in a preferential solvent, the polymer solution will form a swollen gel at room temperature with the morphology

FIG. 1. The morphology of the D/T blend when swollen by a preferential solvent for the PnBA.

shown in Fig. 1. This morphology has been confirmed by small angle x-ray scattering measurements as reported in a previous publication [Flanigan *et al.* (1999)]. The PnBA blocks of the diblock copolymer exist in a solvent-rich matrix, and provide elasticity by spanning the PMMA domains. This physically-crosslinked network of PMMA aggregates connected by PnBA segments behaves as an elastic solid in the swollen state. To form the model PSA layers, we place a quantity of the swollen gel on a glass slide that has a nylon washer attached to it. Using the thermoreversible nature of these gels, we heat the glass slide to allow the polymer solution to flow and conform to the volume within the inner diameter of the nylon washer. After cooling the sample to room temperature, the microstructure shown in Fig. 1 is recovered in our uniform layer of swollen gel. This uniform layer is slowly dried at room temperature until the solvent has been completely removed.

The experimental tests that we have utilized involve a glass hemispherical indenter that is placed in contact with the thin adhesive layer as illustrated in Fig. 2. A linear stepping motor is used to control the motion of this indenter. This motor has a velocity range of 4.0 nm/s–2.0 mm/s. While the two bodies are in contact, a load transducer

FIG. 2. A schematic of the experimental apparatus used to test the adhesive and rheological properties of thin viscoelastic layers.

monitors the normal force and a fiber optic displacement sensor records the normal displacement. Additionally, the contact radius is observed through an optical microscope and recorded digitally with a charge coupled device camera. All of these devices are controlled and integrated by National Instruments Labview software, using a personal computer.

A variety of displacement histories can be applied to the indenter. In this paper we focus on two specific displacement histories. Each history involves bringing the rigid indenter into contact with the polymer until an arbitrarily-specified maximum compressive force is reached. At this point, the displacement is applied in the form of either (1) a sine wave or (2) a monotonic unloading curve where the indenter is pulled away from the adhesive layer.

The monotonic unloading history is commonly applied in adhesive testing (i.e., peel tests, probe-tack tests, etc.). This history yields a force versus displacement curve that is commonly referred to as a tack curve. The total energy dissipated during this test is given by the area enclosed by the tack curve. This energy is a combination of the energy required to create the new surfaces and the energy dissipated by viscoelastic mechanisms in the bulk of the material. Qualitatively, this information has been analyzed by several researchers for a variety of materials [Chuang *et al.* (1997); Creton (1997); Lakrout *et al.* (1999)], but a quantitative analysis has been limited to elastic systems where energy dissipation is limited to a small region that is very close to the contact edge [Ahn and Shull (1998a); Barquins and Maugis (1981); Gent and Petrich (1969); Maugis and Barquins (1978); Shull and Crosby (1997)]. As the region of viscoelastic dissipation becomes large relative to the sample volume, a more complicated analysis must be used to interpret the information contained within a tack curve. This analysis requires that the bulk viscoelastic properties of the material be determined. In the linear viscoelastic regime, these properties are obtained by the oscillatory experiments described in the following section.

III. LINEAR VISCOELASTIC PROPERTIES

To experimentally measure the bulk rheology, we apply a small-strain amplitude sine wave to the indenter after a maximum compressive force has been achieved. For sufficiently adhesive materials the contact area remains constant and the relationship between load and displacement remains constant for each cycle, as illustrated by the representative data plotted in Fig. 3. By measuring the phase lag between the applied displacement and the resulting force, we quantify the storage and loss moduli for these tests.

The applied displacement varies in time with the following form:

$$\delta = \delta_0 \sin(\omega t), \quad (1)$$

where δ_0 is the displacement amplitude and ω is the applied angular frequency. The resulting force has the form

$$P = P_0 \sin(\omega t - \lambda), \quad (2)$$

where P_0 is the load amplitude and λ is the phase angle. Note that our notation for the phase angle is different from the conventional notation of δ , which in our case represents the displacement. We know from conventional linear viscoelastic relations that the magnitude of the frequency dependent complex modulus, $E^*(\omega)$, is related to the storage [$E'(\omega)$] and loss [$E''(\omega)$] moduli by the following relations [Ward and Hadley (1993)]:

FIG. 3. Load-displacement relationship for a rigid spherical indenter in contact with a high molecular weight poly(*n*-butyl acrylate) homopolymer. The frequency of the applied displacement is 0.01 Hz.

$$\begin{aligned} E'(\omega) &= E^*(\omega) \cos \lambda, \\ E''(\omega) &= E^*(\omega) \sin \lambda. \end{aligned} \quad (3)$$

E^* is determined by using the relation between the compliance (C) and the modulus at a specified contact radius (a) [Shull *et al.* (1998)]:

$$C(\omega) = \frac{\delta_0(\omega)}{P_0(\omega)} = \frac{3}{8E^*(\omega)a} f_c(a/h), \quad f_c(a/h) = \left[1 + 1.33 \left(\frac{a}{h} \right) + 1.33 \left(\frac{a}{h} \right)^3 \right]^{-1}, \quad (4)$$

where h is the thickness of the polymer layer, which has been assumed to be incompressible. (Poisson's ratio, $\nu = 0.5$). Rearrangement of Eq. (4) gives the following expression for the complex modulus as a function of the measured load and displacement amplitudes:

$$E^*(\omega) = \frac{3P_0(\omega)}{8\delta_0(\omega)a} \left[1 + 1.33 \left(\frac{a}{h} \right) + 1.33 \left(\frac{a}{h} \right)^3 \right]^{-1}. \quad (5)$$

To validate these relations, we can compare the rheological data collected by conventional shear rheometry and our contact mechanical technique. The material that we used for validation is a high molecular weight homopolymer of poly(*n*-butylacrylate). The time dependence of the load and displacement are obtained directly, enabling us to measure t , P_0 , δ_0 , and λ at different frequencies, as described in a previous publication [Fabbro *et al.* (2001)]. The results are shown in Fig. 4, where storage and loss moduli obtained in this way are compared to data obtained from a conventional parallel plate rheometer. The contact mechanical data and the parallel plate data nearly overlay, thus we can confidently use the contact mechanical technique to measure rheological properties of thin adhesive layers that are not conducive to conventional shear rheometric measurements.

FIG. 4. Frequency dependence of the storage modulus (E' , circles) and loss modulus (E'' , squares) for the poly(*n*-butylacrylate) control sample. The filled symbols correspond to data obtained from our contact mechanical test, and the open symbols correspond to data obtained from conventional shear rheometry.

Rheological data obtained in this way for the D/T model adhesive are plotted in Fig. 5. The power law form of these data suggests that the relaxation modulus of the polymer can also be expressed as a power law. In this case the time dependent relaxation modulus, $E(t)$, is completely specified by the exponent, Δ , and by the value of the modulus at an arbitrary reference time, t_{ref} :

FIG. 5. The storage [E' (●)] and loss [E'' (■)] moduli of the D/T adhesive layer. The solid and dashed lines correspond to the respective power law forms for the storage and loss moduli given by Eqs. (7) and (8), with $E_{\text{ref}} = 1.6 \text{ MPa}$, $t_{\text{ref}} = 1 \text{ s}$ and $\Delta = 0.077$.

$$E(t) = E_{\text{ref}}\phi(t), \quad E_{\text{ref}} \equiv E(t_{\text{ref}}), \quad \phi(t) = \left\{ \frac{t}{t_{\text{ref}}} \right\}^{-\Lambda}. \quad (6)$$

In this case the dynamic moduli are given by the following expressions [Chambon and Winter (1987); Ferry (1980)]:

$$\begin{aligned} E'(\omega) &= \omega \int_0^\infty E(t) \sin(\omega t) dt = E_{\text{ref}} (\omega t_{\text{ref}})^\Lambda (-\Lambda)! \cos \lambda, \\ E''(\omega) &= \omega \int_0^\infty E(t) \cos(\omega t) dt = E_{\text{ref}} (\omega t_{\text{ref}})^\Lambda (-\Lambda)! \sin \lambda, \end{aligned} \quad (7)$$

where the phase angle, λ , is related to the exponent, Λ , by the following relationship:

$$\lambda = \frac{\pi\Lambda}{2}. \quad (8)$$

Note that for a purely elastic material, $\Lambda = \lambda = 0$, whereas for a Newtonian fluid, $\Lambda = 1$ and $\lambda = 90^\circ$. The creep compliance function, $E^{-1}(t)$ can also be obtained. The relaxation and creep compliance functions are not simply inverses of one another, but are related to one another through the following expression:

$$s^2 \mathcal{L}[E(t)] \mathcal{L}[E^{-1}(t)] = 1, \quad (9)$$

where $\mathcal{L}$ is the Laplace transform and s is the Laplace transform variable. When the relaxation modulus has the power law form of Eq. (6), the creep compliance function has a similar form

$$E^{-1}(t) = \frac{\psi(t)}{E_{\text{ref}}}; \quad \psi(t) = \frac{(t/t_{\text{ref}})^\Lambda \sin \lambda \cos \lambda}{\lambda}. \quad (10)$$

From the data in Fig. 5 we obtain $\Lambda = 0.077$, corresponding to $\lambda = 6.9^\circ$. Fitting the magnitude of the storage modulus, we obtain $E_{\text{ref}} = 1.6 \times 10^6$ Pa, with $t_{\text{ref}} = 1$ s. These data confirm that D/T is primarily elastic at low strains, but a slight viscoelastic component does exist, as indicated by the finite value of E'' and the frequency dependence of the dynamic moduli. In the following section we develop a viscoelastic fracture mechanics formalism that can be applied in this situation.

IV. VISCOELASTIC FRACTURE MECHANICS MODEL

Viscoelasticity enters into our analysis in two ways. The first of these, which we refer to as “large scale viscoelasticity,” refers to the situation in the previous section, where the overall bulk response of the adhesive layer is characterized by a time-dependent elastic modulus. Small-scale viscoelasticity refers to effect that are confined to a small region of the sample at the edge of the contact zone. These effects determine the rate at which the contact radius shrinks or grows, but they do not affect relationships between load and displacement of the sort that were developed in the previous section. This previous section was essentially a description of large-scale viscoelasticity in the case where the contact radius remains constant during an oscillatory experiment. The present section is devoted to a discussion of large-scale viscoelasticity during a tack test, where the contact area grows and then decreases as the indenter is brought into contact with the adhesive layer and is then removed. Our discussion of large-scale viscoelasticity as it applies to a tack test is divided into five subsections. The purely elastic case is described

first, to provide the relevant background on geometric effects. We then describe the approach for nonadhesive, viscoelastic contact, followed by a description of the approach for adhesive, viscoelastic contact. In our discussion of nonadhesive and adhesive viscoelastic contact, the advancing and receding cases are treated separately.

A. Elastic contact

We begin with a summary of the expressions for elastic contact, where the elastic modulus, E , is independent of time and frequency. In the absence of adhesive interactions, the loads and displacements are given by the Hertzian values [Johnson (1985)], taking into account the appropriate geometric correction factors [Shull *et al.* (1998)]:

$$P'_{el} = \frac{16Ea^3}{R} f_p(a/h), \quad f_p(a/h) = [1 + 0.25(a/h)^3], \quad (11)$$

$$\delta'_{el} = \frac{a^2}{R} f_\delta(a/h), \quad f_\delta(a/h) = [0.4 + 0.6 \exp(-1.8a/h)], \quad (12)$$

where P'_{el} is the nonadhesive load and δ'_{el} is the nonadhesive displacement. Poisson's ratio is assumed to be equal to 0.5 in these expressions, an assumption that we maintain throughout our discussion.

For an adhesive system, the actual loads and displacements are less than the nonadhesive values. The difference between the actual and nonadhesive displacements for an elastic system is given by the product of the compliance and the difference between the actual and nonadhesive loads

$$\delta_{el} = \delta'_{el} - C(P'_{el} - P) = \delta'_{el} - \frac{3f_c}{8Ea}(P' - P), \quad (13)$$

where C is the compliance of the loading system, which depends on the thickness and elastic modulus of the elastic layer, and on the contact radius. The relationship between C , E , a , and h for an elastic layer is given by Eq. (4) with $E^*(\omega)$ replaced by E . The region outside the indenter and the elastic layer can be viewed as an external crack. Thus, advancing and receding contact correspond to crack closure and crack growth, respectively. Here advancing contact refers to the case where the contact radius is increasing with time, and receding contact refers to the case where the contact radius is decreasing with time. Adhesive forces give a nonzero energy release rate, which for a linearly elastic material is obtained from the following general expression [Crosby and Shull (1999)]:

$$\mathcal{G} = -\frac{(P'_{el} - P)^2}{2} \frac{\partial C}{\partial A} = -\frac{(P'_{el} - P)^2}{4\pi a} \frac{\partial C}{\partial a}, \quad (14)$$

from which we obtain the following for the energy release rate:

$$\mathcal{G} = \frac{3(P'_{el} - P)^2}{32\pi Ea^3} f_{kp}(a/h), \quad f_{kp}(a/h) = \left[\frac{0.56 + 1.5(a/h) + 3(a/h)^3}{(0.75 + (a/h) + (a/h)^3)^2} \right]. \quad (15)$$

The expressions used throughout this paper for the geometric correction factors f_p , f_c , f_{gp} , and f_{kp} [defined in Eq. (19)] correspond to a full-friction boundary condition for the interface between the adhesive layer and the indenter, and for the interface between the adhesive layer and the supporting substrate. Because interfacial shear stresses can be supported at the indenter/adhesive interface, a mode II component to the stress

field will generally be present. In this case the stresses near the edge of contact are characterized by K_I and K_{II} , the mode I and mode II components of the stress intensity factor

$$\sigma_{zz} = \frac{K_I}{(2\pi x)^{1/2}}, \quad \sigma_{xz} = \frac{K_{II}}{(2\pi x)^{1/2}} \quad x \rightarrow 0. \quad (16)$$

Here σ_{zz} is the normal stress, σ_{xz} is the interfacial shear stress, and x is the distance from the edge of contact. The magnitude, K , of the stress intensity factor is related to K_I and K_{II} through the phase angle, Θ :

$$K_I = K \cos \Theta, \quad K_{II} = K \sin \Theta. \quad (17)$$

The phase angle is relatively small for $\nu \approx 0.5$, increasing from 0 for $a/h = 0$ to a plateau value near 30° for very high values of a/h [Lin *et al.* (2000)].

For the plane strain conditions that are relevant to our experiment, and for $\nu \approx 0.5$, K is related to $\mathcal{G}$ by the following expression [Lin *et al.* (2000)]:

$$K = \left(\frac{8E\mathcal{G}}{3} \right)^{1/2}. \quad (18)$$

Substitution of Eq. (15) for $\mathcal{G}$ into this expression gives

$$K = \frac{P'_{el} - P}{2\pi^{1/2} a^{3/2} f_{kp}(a/h)}, \quad f_{kp}(a/h) = \frac{[0.56 + 1.5(a/h) + 3(a/h)^3]^{1/2}}{0.75 + (a/h) + (a/h)^3}. \quad (19)$$

For systems where the large-scale response is completely elastic, treatments based on the energy release rate and on the stress intensity factor are equivalent, since these two quantities are related to one another by Eq. (18). Small-scale viscoelastic losses occurring in a region very close to the crack tip enter the problem by determining the relationship between $\mathcal{G}$ or K and the resultant crack velocity. For systems where large-scale viscoelastic effects become important, a well-defined energy flow to the crack tip no longer exists, and one must use treatments based on the stress intensity factor [Hui and Banay (1998); Lin *et al.* (1999); Schapery (1975); Schapery (1989)]. This formalism is developed in the following subsections, beginning with a discussion of some relevant expressions for the nonadhesive case, where $K = 0$.

B. Viscoelastic, nonadhesive advancing contact

The problem of nonadhesive contact involving curved viscoelastic half-spaces ($a/h = 0$) has been formulated by Ting [Ting (1966); Ting (1968)]. The treatment here is equivalent, although it has been generalized in order to account for finite size effects and the eventual inclusion of adhesive interactions. Because the elastic modulus does not appear in the relationship between contact radius and the nonadhesive displacement, this quantity is equal to the elastic displacement from the previous section

$$\delta'(t) = \delta'_{el}(t). \quad (20)$$

The effects of stress relaxation can be accounted for by first defining a reference elastic load P'_{ref} , which depends only on the reference modulus and the current value of the contact radius

FIG. 6. Time dependence of the contact radius, including actual measured values (●), and fits to the data used in the calculations of the stress intensity factor (solid and dashed lines).

$$P'_{\text{ref}}(t) = \frac{16f_p(t)E_{\text{ref}}a^3(t)}{9R}, \quad (21)$$

where $f_p(t)$ denotes the value of $f_p(a/h)$ evaluated at t . Incremental changes in the contact radius produce incremental changes in the reference elastic load. These contributions to the load then relax with a time dependence that is described by the relaxation function $\phi(t)$. The actual measured load for this nonadhesive case is obtained as the superposition of the loads imposed at different loading times, giving the following convolution integral for $P'(t)$:

$$P'(t) = \int_0^t \phi(t-t') \frac{\partial}{\partial t'} [P'_{\text{ref}}(t')] dt'. \quad (22)$$

C. Viscoelastic, nonadhesive receding contact

A specific example of advancing and receding contact is shown in Fig. 6, where the contact radius is plotted as a function of time. At the time t_m , the contact radius reaches its maximum value. For some time t larger than t_m , the contact radius will be equal to the value it had at a corresponding time $t_1(t)$ during the advancing portion of the experiment. In the absence of adhesion, Ting showed that the load at t is independent of the contact history for the intermediate times between $t_1(t)$ and t , and can be written in the following form:

$$P'(t) = \int_0^{t_1(t)} \phi(t-t') \frac{\partial P'_{\text{ref}}(t')}{\partial t'} dt'. \quad (23)$$

This equation is valid because the contact stresses are equal to zero outside the current contact area. Prior forces outside the current contact area do not affect the present value of the load. These forces do affect the displacement however, which is given by the following expression:

$$\delta'(t) = \delta'_{el}(t) - \int_{t_m}^t \psi(t-t') \frac{\partial \Delta'(t')}{\partial t'} dt', \quad (24)$$

with

$$\Delta'(t) = \int_{t_1(t)}^t \phi(t-t') \frac{\partial \delta'_{el}}{\partial t'} dt'. \quad (25)$$

D. Viscoelastic, advancing adhesive contact

In the presence of adhesive interactions between a viscoelastic material and a rigid surface, the stress intensity factor has a positive value, and the actual load is no longer equal to P' . For $a/h = 0$, the relationships between P , P' , and K have been considered by Schapery for advancing contact [Schapery (1989)], and more recently by Hui and Baney for both advancing contact [Hui and Baney (1998)] and receding contact [Lin *et al.* (1999)]. The description given here is based largely on the work of Hui and Lin *et al.* and readers are referred to these references for details.

For a viscoelastic material, we need to introduce the relaxation function to obtain the relationship between P' , P , and K . The procedure is similar to the procedure used to develop equation 20 for P' . For an elastic material Eq. (19) can be rearranged to give $P'_{el} - P$ as a function of K . If the reference time is chosen to correspond to the shortest meaningful time scale in the experiment, then contributions to $P' - P$ decay with a time dependence determined by the relaxation function, $\phi(t)$. The current value of $P' - P$ is obtained from the following convolution integral:

$$P'(t) - P(t) = 2\sqrt{\pi} \int_0^t \phi(t-t') \frac{\partial}{\partial t'} \left[\frac{Ka^{3/2}}{f_{kp}}(t') \right] dt'. \quad (26)$$

Because $\psi(t)$ and $\phi(t)$ are related to one another by Eq. (9), Eq. (26) can be inverted to give the following expression for $K(t)$:

$$K(t) = \frac{f_{kp}(t)}{2\sqrt{\pi}[a(t)^{3/2}]} \int_0^t \psi(t-t') \frac{\partial}{\partial t'} [P'(t') - P(t')] dt'. \quad (27)$$

The displacement is given by an equation analogous to Eq. (13), but with a convolution integral involving the creep function ψ being used to describe the influence of $P'(t) - P(t)$ on the evolution of the displacement. The expression for the displacement can be written in either of two equivalent ways

$$\begin{aligned} \delta(t) &= \delta'(t) - \frac{3f_c(t)}{8E_{\text{ref}}a(t)} \int_0^t \psi(t-t') \frac{\partial}{\partial t'} [P'(t') - P(t')] dt', \\ \delta'(t) - \delta(t) &= \frac{3f_c(t)\sqrt{\pi}[a(t)]^{1/2}}{4E_{\text{ref}}f_{kp}(t)} K(t), \end{aligned} \quad (28)$$

where $\delta'(t)$, is still given by Eq. (24).

E. Viscoelastic, receding adhesive contact

Receding adhesive contact, where the contact radius is decreasing with time, is the most important and also the most complicated situation. With the inclusion of the finite size correction factor f_{kp} the expression given by Lin *et al.* [Lin *et al.* (1999)] for the stress intensity factor for the debonding phase of the experiment can be written in the following form:

$$K(t) = \phi[t-t_1(t)]K[t_1(t)] + \frac{f_{kp}}{2\sqrt{\pi}[a(t)]^{3/2}} \int_{t_m}^t \psi(t-t') \frac{\partial}{\partial t'} [P'_{\text{eff}}(t') - P(t')] dt' \quad (29)$$

with

$$P'_{\text{eff}}(t) = \int_0^{t_1(t)} \phi(t-t') \frac{\partial}{\partial t'} [P_{el}(t')] dt', \quad (30)$$

and

$$P_{el}(t) = \int_0^t \psi(t-t') \frac{\partial}{\partial t'} [P(t')] dt'. \quad (31)$$

The first term in Eq. (29) describes the relaxation of the stress field established during the advancing phase of the experiment, when the contact radius is increasing. For systems exhibiting a substantial adhesion hysteresis, the second term will be much larger than the first term. This second term describes the additional stress fields formed in the vicinity of the crack tip during the debonding phase of the experiment.

After accounting for the geometric correction factor, the following equivalent expressions for the displacement are obtained from the results of Hui and Lin [Lin *et al.* (1999)]:

$$\begin{aligned} \delta(t) &= \delta'_{\text{eff}}(t) - \frac{3f_c(t)}{8E_{\text{ref}}a(t)} \int_{t_m}^t \psi(t-t') \frac{\partial}{\partial t'} [P'_{\text{eff}}(t') - P(t')] dt', \\ \delta'_{\text{eff}}(t) - \delta(t) &= \frac{3f_c(t)\sqrt{\pi}[a(t)]^{1/2}}{4E_{\text{ref}}f_{kp}(t)} \{K(t) - \phi[t-t_1(t)]K[t_1(t)]\}, \end{aligned} \quad (32)$$

with

$$\delta'_{\text{eff}}(t) = \delta[t_1(t)] - \int_{t_m}^t \psi(t-t') \frac{\partial}{\partial t'} [\Delta(t')] dt', \quad (33)$$

and

$$\Delta(t) = \int_{t_1(t)}^t \phi(t-t') \frac{\partial}{\partial t'} \{\delta[t_1(t')]\} dt'. \quad (34)$$

These general expressions are simplified substantially in the case where the stress intensity factor is zero during the loading portion of the experiment. As derived in the appendix, $P'_{\text{eff}} = P'$ in this limit, where P' is the nonadhesive load for adhesive contact given by Eq. (23). With this simplification, and with $K = 0$ during the loading portion of the experiment ($t < t_m$), we have

FIG. 7. Tensile load as a function of the experimentally measured displacement (open symbols), and as a function of the displacement calculated from Eq. (36) (solid and dotted lines). The solid and dotted lines correspond to contact radii given by the respective solid and dashed lines of Fig. 6.

$$K(t) = \frac{f_{kp}(t)}{2\sqrt{\pi}[a(t)]^{3/2}} \int_{t_m}^t \psi(t-t') \frac{\partial}{\partial t'} [P'(t') - P(t')] dt'. \quad (35)$$

Similar simplifications apply for the calculation of the displacement, which reduces to the following:

$$\delta(t) = \delta'(t) - \frac{3(f_c/f_{kp})(t)}{4E_{\text{ref}}} K(t) \sqrt{\pi}[a(t)]^{1/2}, \quad (36)$$

with $\delta'(t)$ given by Eq. (24). The ratio f_c/f_{kp} that appears in this equation [and also in Eqs. (28) and (32)] can be obtained directly from the definitions given in Eqs. (4) and (19):

$$\frac{f_c}{f_{kp}} = [1 + 2.66(a/h) + 5.32(a/h)^3]^{-1/2}. \quad (37)$$

F. General comments

An axisymmetric test where a rigid, spherical indenter is brought into contact with a linearly viscoelastic adhesive layer of thickness h and then removed is described by the equations given in the previous sections. In the absence of adhesion, $K = 0$, and the results of Secs. III B and III C are recovered, with $P = P'$ and $\delta = \delta'$ for both advancing and receding contact. Equations (28) and (32) give the displacement in terms of the applied load and the contact area. In principle, these viscoelastic properties can be obtained from an experiment where P , δ' , and a are all independently measured. In practice it is often more useful to measure the viscoelastic properties independently, and use Eqs. (28) and (32) to verify that these properties accurately describe the measured values for the displacement. If agreement between the measured and predicted values of the displacement is obtained, then one can be confident that accurate values for the stress

FIG. 8. Stress intensity vs contact radius as obtained from Eqs. (10) and (35) with $\Delta = 0$ (dashed line) and with $\Delta = 0.077$, $t_{\text{ref}} = 1$ s (solid line), using values for the contact radius corresponding to the solid line in Fig. 6. The dotted line represents the stress intensity factor obtained with $\Delta = 0.077$, but with the contact radii given by the dashed line in Fig. 6. The data correspond to receding contact (decreasing contact radius with time), as indicated by the arrow.

intensity factor are also obtained. The magnitude of this stress intensity factor determines how fast the contact area either advances or recedes, as described in the discussion later.

V. ADHESIVE PERFORMANCE AND APPLICATION OF THE MODEL

For the D/T adhesive layers, a representative tack curve is shown in Fig. 7. This tack curve corresponds to the contact history from Fig. 6. Tack curves are normally plotted as a tensile load, P_t , as a function of a tensile displacement, δ_t , and this is the convention we have used. Note that $P_t = -P$ and $\delta_t = -\delta$. For our test, the crosshead velocity is $2.5 \mu\text{m/s}$, the radius of curvature for the spherical indenter is 6.0 mm , and the thickness of the adhesive layer is $83 \mu\text{m}$. The maximum contact radius, achieved at a compressive force of 20 mN , is $182 \mu\text{m}$. As justified in more detail in the discussion section, the stress intensity factor is very close to zero during the loading portion of the experiment, so that $P \approx P'$. Because the loading takes place over a period of about 1 s , corresponding roughly to our reference time t_{ref} , we can use Eq. (11) to estimate E_{ref} using $P' = 20 \text{ mN}$, $a = 182 \mu\text{m}$, $h = 83 \mu\text{m}$, and $R = 6 \text{ mm}$. From this we obtain $E_{\text{ref}} \approx 3 \text{ MPa}$, which is in reasonably good agreement with the value of 1.6 MPa obtained from the oscillatory measurements.

Values for the contact radii during the receding portion of the experiment are obtained by fitting the measured values (obtained at 1 s intervals) to the following fitting function:

$$a = a_{\text{max}} \left[1 - \left(\frac{t - t_m}{t_{\text{tot}}} \right)^n \right]. \quad (38)$$

This function is represented by the solid line in Fig. 6, where we have used $n = 2.4$, $t_m = 2 \text{ s}$, $t_{\text{tot}} = 23 \text{ s}$, and $a_{\text{max}} = 182 \mu\text{m}$. While accurate values of the contact radius can easily be obtained during the initial portions of the test, it becomes increasingly difficult to visualize the contact perimeter during the later portions of the test. We were not able to obtain values for times greater than about 18 s , and the uncertainty in the our

FIG. 9. Stress intensity from Fig. 8, plotted as a function of the crack velocity, ν ($\nu = -da/dt$) for $\Delta = 0.077$. The solid and dotted lines correspond to contact radii given by the respective solid and dashed lines of Fig. 6.

determination of the contact radius increases as the tensile strain applied to the adhesive layer increases. The dashed line in Fig. 6 is a representation of Eq. (38) with $n = 2.0$, and the remaining parameters identical to those given earlier for the solid line. This alternate contact history gives a better description of the measured tack curve, and is within our experimental uncertainty for the determination of the contact radius.

The detailed analysis of the receding part of the experiment begins with a calculation of the stress intensity factor from Eq. (35). Note that the stress intensity factor is independent of the absolute value of the modulus, and that viscoelasticity enters through the time dependence of the creep function, $\psi(t)$. The effect of viscoelasticity on the calculated stress intensity factor is illustrated in Fig. 8, where values of K obtained with the assumption that $\Delta = 0$ (elastic behavior) are compared to values of K obtained using our experimental value of 0.077 for Δ . In order to illustrate our overall uncertainty in the values of the stress intensity factor, results obtained assuming both contact histories from Fig. 6 are included for the case where $\Delta = 0.077$.

The stress intensity factor describes the stress field in the vicinity of the contact edge. For elastomers, this stress distribution has been shown to determine the rate at which the crack advances [Maugis and Barquins (1978)]. Our assumption here is that this principle is valid for viscoelastic systems as well, in which case the appropriate adhesive failure criterion is the relationship between K and the crack velocity, ν . We obtain this crack velocity by differentiating Eq. (38), so that the following interpolated value for ν is obtained for each experimental point:

$$\nu = -\frac{da}{dt} = \frac{na_{\max}}{t-t_{\max}} \left(\frac{t-t_{\max}}{t_{\text{tot}}} \right)^n. \quad (39)$$

Our calculated values for K are replotted as function of ν in Fig. 9, where the two separate curves correspond to the two contact histories from Fig. 6.

The relationship between K and ν determines the rate at which the indenter will separate from the adhesive layer, and sets the overall load that the adhesive layer is able to support during a tack test. While this relationship can be measured experimentally, it

FIG. 10. Average tensile stress under the indenter as a function of the tensile displacement.

cannot be predicted from the “large scale” viscoelastic treatment that we are using. This relationship depends on “small scale” viscoelastic properties of the adhesive, and is discussed in more detail in the following section. For a given applied load, the resultant displacement, and hence, the overall flow of energy into the system, is determined by the bulk viscoelastic properties of the system. If the average tensile stress is low enough so that the response is adequately described by linear viscoelasticity, the displacement will be given by Eq. (36). For our system, a value of 1.8 MPa for E_{ref} gives an excellent description of the early portions of the tack curve, as shown in Fig. 7. The agreement between this value and the value of 1.6 MPa obtained from the oscillatory results is not surprising, since the oscillatory measurements correspond to measurements that are made in this same region of the tack curve. Finally, note that the entire predicted tack curve [actual load as a function of predicted displacement from Eq. (36)] is described by $E_{\text{ref}} = 1.8 \text{ MPa}$ if we use the contact history represented by the dashed line in Fig. 6. In the nonlinear regime, the displacements will begin to exceed the values predicted by linear elasticity. The dashed line in Fig. 6 should therefore be regarded as a set of lower bounds for the contact radius. Lower values for the contact radii give larger predicted displacements, and it is not possible for the values predicted from linear viscoelasticity to exceed the actual measured values.

VI. DISCUSSION

The procedure that we have used to analyze our data is very similar to the procedure utilized by Unertl *et al.*, who have used these methods in the analysis of data obtained from the indentation of viscoelastic latex films [Giri *et al.* (2000); Giri *et al.* (2001)]. Hui and Baney [Hui and Baney (1998)] have also used this approach in an their analysis of the previously published data of Falsafi and Tirrell [Falsafi *et al.* (1997)] for viscoelastic advancing contact. In both of these cases, however, the values of a/h were quite small, so the various confinement corrections developed in Sec. IV were not necessary. In addition, the adhesive forces were relatively weak in these experiments, and had a much smaller effect on the overall tack curve than is observed in our experiments. The overall importance of adhesive forces can be obtained by calculating the average tensile stress, σ_{avg} ,

FIG. 11. Calculated stress distribution for a flat punch that is adhesively bonded to a thin elastic layer, for $a/h = 2$. A schematic illustration of the flat punch geometry with $a/h = 2$ is also shown (bottom left), as is a blowup of the plastically formed zone near the contact edge where the stress is assumed to be equal to the yield stress (bottom right).

given by $P_t/\pi a^2$. As shown in Fig. 10, the average stress increases to a plateau value of 1.3 MPa, which is very close to the reference elastic modulus for this system. For $a/h > \sim 1$, the condition $\sigma_{avg} \approx E$ corresponds to the onset of instabilities, which include internal cavitation and elastic fingering associated with the early stages of fibrillation [Shull *et al.* (2000)]. In fact, evidence for the early stages of fingering are observed in the images from the later portions of the test.

Confinement effects associated with non-negligible values of a/h also affect the nature of the stress distribution, as illustrated in Fig. 11. This figure shows the normal stress distribution underneath a flat punch for $a/h = 2$, as calculated from finite element methods [Shull *et al.* (2000)]. The two important features of this stress distribution are the stress singularity characterized by K that exists near the contact edges ($r/a \approx 1$), and the stress maximum at the center of the contact zone ($r/a = 0$). This stress maximum is a consequence of the hydrostatic stress that is maximized in the center of a confined elastic layer ($a/h > 1$) [Gent (1994)]. Clearly, the stress intensity factor only characterizes the stress distribution in a region outside the minimum in the contact stress shown in Fig. 11. For $a/h = 2$, this minimum is removed from the contact edge by a distance of $0.2a$ (i.e., it occurs at $r/a = 0.8$), which is also equal to $0.4h$. This distance is actually controlled by the thickness of the film, so we can expect the stress distribution near the edge of contact to be described by the stress intensity factor only for distances from the contact edge that are less than a few tenths of the film thickness. The adhesive layer thickness therefore imposes an upper limit on the distance from the contact edge, $x(x = a - r)$, where the stress field is adequately represented by Eq. (16).

A lower limit for x on the applicability of Eq. (16) is imposed by the fact that the stress cannot diverge to infinity but must be truncated at some meaningful value. The simplest model that accounts for this is a Dugdale model, where the stress within a region of width d is fixed at a constant value, which we assume here to be the yield stress of the material. If d is relatively small then Eq. (16) for the normal stress is replaced by the following expression: [Maugis (1992)]:

$$\sigma_{zz}(x) = \sigma, \quad 0 < x < d,$$

$$\sigma_{zz}(x) = \frac{2\sigma_y}{\pi} \arctan\left(\frac{d}{x-d}\right)^{1/2} \quad d < x \ll h. \quad (40)$$

For regions that are removed from the contact edge by several cohesive zone widths, the stress field is still described by Eq. (16), with K_I given by the following expression:

$$K_I = 4\sigma_y \left(\frac{d}{2\pi}\right)^{1/2}. \quad (41)$$

As mentioned earlier, we assume that the phase angle is relatively small, so that $K \approx K_I$. An estimate for the minimum value of K can be obtained by further assuming that our system is essentially elastic, so that Eq. (18) can be used to relate K to $\mathcal{G}$. Given the relatively low value of the exponent, Λ , this elastic approximation is expected to be reasonable. The minimum value of $\mathcal{G}$ for receding contact (and the maximum value of $\mathcal{G}$ for advancing contact) is the thermodynamic work of adhesion, which for our systems is close to 60 mJ/m² [Mowery *et al.* (1997)]. With this value of $\mathcal{G}$, and with $E = 3 \times 10^6$ Pa we obtain $K \approx 700 \text{ Pa m}^{1/2}$ from Eq. (18). The actual value of the stress intensity factor for rapid advancing contact will be less than this value, thereby justifying our assumption that the stress intensity factor for the advancing part of the experiment is small in comparison to the values obtained from the receding portion of the experiment.

While we do not have an accurate measurement of the yield stress for the D/T polymer used in our experiments, we assume a value of approximately 3 MPa. This value is consistent with preliminary tensile tests performed on adhesive layers that have been removed from a substrate, and is also consistent with published values for similar block copolymers [Tong *et al.* (2001)]. Using this value for σ_y in Eq. (41), we obtain a value for d that increases from 21 nm to 10 μm as K increases from 700 to 15 000 Pa m^{1/2}. With this in mind, we can develop a qualitative description of the deformation process. Equilibrium forces originating from outside the contact zone give rise to a stress intensity factor, which for our system is estimated to be about 700 Pa m^{1/2}. Yielding occurs near the contact edge if the stress intensity factor is large enough to form a cohesive zone of some critical length, d_{crit} . This critical length is the minimum length for which the macroscopic yield stress of the material is meaningful. Because yielding occurs by the breakup of individual PMMA domains, the PMMA domain spacing, equal to about 25 nm for our system [Flanigan *et al.* (1999)], is one estimate of this critical length scale. Our results are consistent with a critical cohesive zone length that is less than 20 nm. In this case the value of 700 Pa m^{1/2} for K that is associated with the equilibrium surface forces is large enough to cause plastic deformation in a localized zone near the edge of the contact. As the overall tensile forces increase, K increases as well, and the size of this deformed zone, illustrated schematically in Fig. 11, increases according to Eq. (41). Strain hardening within the plastically deformed zone will limit its deformation, and determine the nature of the measured $K(\nu)$ curve. While some progress has been made recently in the development of theories that would enable the $K(\nu)$ curve to be related to the viscoelastic properties of the adhesive, [Johnson (2000)], this problem is a very difficult one that remains well beyond the scope of this work.

As a final point, it is useful to put our criterion for cohesive zone yielding (and the substantial levels of adhesion that are subsequently observed) in the context of a critical value of the energy release rate that can be applied to elastic systems. Neglecting numerical prefactors that are close to one, we can use the definition of d_{crit} along with Eqs. (18) and (41) to obtain $\mathcal{G}_{\text{crit}}$, the critical energy release rate corresponding to the onset of yield behavior in the cohesive zone

$$\mathcal{G}_{\text{crit}} \approx \frac{d_{\text{crit}} \sigma_y^2}{E}. \quad (42)$$

Many of the important characteristics of adhesives with a strong elastic character can be understood in terms of this equation. Thermoplastic elastomers, including the acrylic systems described here and the much more commonly utilized styrenic systems, are excellent examples. In these cases very high levels of adhesion are obtained when the threshold adhesion energy $\mathcal{G}_0$, commonly given by the thermodynamic work of adhesion, exceeds the critical value given by Eq. (45). The effect on the overall adhesion energy is highly nonlinear, with small changes in $\mathcal{G}_0$ or σ_y producing a dramatic effect on the overall adhesive performance. In thermoplastic elastomers, the yield stress can be modified by blending diblock copolymers with triblock copolymers, thereby decreasing the number of bridging molecules between physical crosslinks in the microstructure. These materials adhere well to a wide variety of surfaces, provided that the threshold adhesion energy exceeds the critical value associated with Eq. (45). If the threshold adhesion energy is very low, as is the case with appropriately designed release liners, then the practical adhesion is also very low. For a system with a more complicated viscoelastic character, it is necessary to employ the formalism based on the stress intensity factor that has been developed in this paper.

VII. SUMMARY

The contributions from this work to our understanding of the behavior of viscoelastic adhesive layers can be divided into three areas, each of which are summarized.

A. Experimental method for the determination of viscoelastic properties of thin layers

Viscoelastic properties of thin, adhesive layers can be measured by bringing an indenter in contact with the material and applying an oscillatory displacement while monitoring the load response. The primary experimental requirement is that adhesive forces are sufficient to maintain a constant contact radius between the indenter and the adhesive layer during the oscillation. With our experimental device, we are able to measure the response to frequencies as high as 1 Hz, with the lower frequency limit being limited primarily by longest time scales that are of practical interest. Quantitative agreement was obtained between the dynamic moduli obtained by this method for a thin PnBA layer, and for a bulk material characterized by standard shear rheometry. This method was used to obtain the dynamic modulus for a model pressure sensitive adhesive based on an acrylic triblock copolymer. In the linear regime, the dynamic modulus exhibited a weak power-law dependence on the frequency, from which we were able to obtain the time dependent creep and relaxation functions for this material.

B. Extension of viscoelastic fracture mechanics methods to the treatment of thin layers

Existing viscoelastic contact mechanics methods have been modified to account for the geometric constraints associated with the confinement of a thin, incompressible, compliant layer between two rigid surfaces. A variety of correction factors involving the ratio of the contact radius to the film thickness were developed. These correction factors are valid for axisymmetric geometries, for the case where the contact radius is small in comparison to the radius of curvature of the indenter. Expressions were developed for the stress intensity factor and for the normal displacement of the indenter as a function of

linear viscoelastic properties of the adhesive and of the complete history dependence of the contact radius and applied load. The adhesive failure criterion for the material is a relationship between the stress intensity factor and the resultant crack velocity. This relationship was obtained for our model triblock adhesive adhering to a glass substrate.

C. Cohesive zone model

A simple cohesive zone model was developed, based on the assumption that the system behaves as a linear viscoelastic material up to the yield stress. Equilibrium surface forces define a critical stress intensity factor that must be exceeded in order for crack motion to be initiated. Yielding initially occurs throughout a small region near the contact edge when this stress intensity factor exceeds a critical value defined by the yield stress and a critical cohesive zone size. As the tensile load increases, the size of this cohesive zone also increases, as does the stress intensity factor and the resultant crack velocity.

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APPENDIX: SIMPLIFICATION FOR THE CASE WHERE $K=0$ DURING THE BONDING PHASE

The general expressions from Sec. IV E are simplified substantially in the case where the stress intensity factor is zero during the loading portion of the experiment. Because the expression for P'_{eff} involves an integral involving times that are restricted to the loading portion of the experiment, we can substitute the non-adhesive load, $P'(t')$ for the actual load $P'(t')$ in the definition of $P_{el}(t)$ [Eq. (31)]:

$$P_{el}(t) = \int_0^t \psi(t-t') \frac{\partial}{\partial t'} [P'(t')] dt' = \psi * P', \quad (\text{A1})$$

where $*$ denotes the convolution operator. The nonadhesive load is in turn defined in terms of a convolution of the reference elastic load with the relaxation function [Eq. (22)]:

$$P'(t) = \int_0^t \phi(t-t') \frac{\partial}{\partial t'} [P'_{\text{ref}}(t')] dt' = \phi * P'_{\text{ref}}. \quad (\text{A2})$$

One then obtains $P_{el}(t) = \psi * (\phi * P'_{\text{ref}}) = P'_{\text{ref}}(t)$, which follows from the inverse relationship between $\phi(t)$ and $\psi(t)$. Substitution of $P'_{\text{ref}}(t)$ for $P_{el}(t)$ in Eq. (30) gives

$$P'_{\text{eff}}(t) = \int_0^{t_1(t)} \phi(t-t') \frac{\partial}{\partial t'} [P'_{\text{ref}}(t')] dt', \quad (\text{A3})$$

which is identical to the expression for $P'(t)$ for receding, nonadhesive contact [Eq. (23)]. The expression for the stress intensity factor Eq. (29), simplifies to the following expression:

$$K(t) = \frac{f_{kp}(t)}{2\sqrt{\pi}[a(t)]^{3/2}} \int_{t_m}^t \psi(t-t') \frac{\partial}{\partial t'} [P'(t') - P(t')] dt'. \quad (\text{A4})$$

The displacement expression is simplified by using Eq. (A2) to substitute K for the integral in Eq. (32), giving the following expression for δ :

$$\delta(t) = \delta'_{\text{eff}}(t) - \frac{f_c(t)}{2E_{\text{eff}}f_{kp}} K(t) 2\sqrt{\pi}[a(t)]^{1/2}. \quad (\text{A5})$$

Because K is assumed to be zero during the loading portion of the experiment, we can substitute $\delta'_{el}(t)$ for $\delta[t_1(t)]$ in Eqs. (33) and (34), to obtain

$$\delta'_{\text{eff}}(t) = \delta'_{el}(t) - \int_{t_m}^t \psi(t-t') \frac{\partial \Delta(t')}{\partial t'} dt', \quad (\text{A6})$$

and

$$\Delta(t) = \int_{t_1(t)}^t \phi(t-t') \frac{\partial \delta'_{el}(t')}{\partial t'} dt'.$$

These expressions for δ'_{eff} are identical to those given for δ' [Eq. (24)].

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