**Dynamic Indentation Modulus of Viscoelastic Films**

**Discussion**

The aim of this work is to analyze the dynamic indentation modulus of viscoelastic films that overlay rigid and elastic substrates. To this end, theoretical modeling and finite element simulations were employed to identify analytical formulae linking the dynamic modulus of the pristine film to that of the film-substrate laminate. This was achieved by applying a shape function of the indentation state parameter $ϕ\left(H/a\right)$ and determining the ratio between the modulus magnitude of the film and the elastic modulus of the substrate ($E\_{f}/E\_{s}$). The analytical relationships correspond well to finite element simulation results for a wide range of geometrical parameters (i.e., from ultra-thin to semi-infinite films), as well as for various mechanical characteristics (i.e., from distinctive to comparable film-substrate moduli, and from highly dissipative to nearly elastic film loss coefficients). They are insensitive to the specific flat, spherical, and conical indentation tip shapes that were analyzed.

This work expands on previous studies of dynamic indentations of viscoelastic materials that focused on semi-infinite films [\*]. Its results enable a new approach, using a standard nano-DMA testing method, to determine the dynamic modulus of finite-thickness, and even ultra-thin films. These kinds of materials are widespread in advanced nanomaterials and biological materials, but were not within the bounds of the analytical frameworks of previous studies. In this study, the effect of the film thickness was quantified via a non-dimensional indentation state parameter ($H/a$) that is consistent with previous elastic thin-film indentation theories [\*]. Broadly analogous non-dimensional parameters dominate indentation mechanics of other composite systems. Examples include indentations of spherical polymeric inclusions in synthetic composites (dominated by the inclusion-radius/contact-radius ratio), and interfacial indentations of biocomposites (dominated by the interface-width/contact-radius ratio) [\*]. The shape function $ϕ\left(H/a\right)$ connects the geometrical state of the film indentation to the mechanical effect of the film dynamic modulus. For infinitely rigid substrates, this shape function takes the film thickness into account by direct scaling of the film dynamic modulus. For elastic substrates, the shape function serves as a weighting factor that connects the film and substrate moduli to the dynamic modulus of the film-substrate laminate via an inverse-rule-of-mixtures. Both the analytical exponential form of the shape function, and its phenomenological mechanical role are consistent with previous studies on elastic thin films [\*].

Environmental conditions have a significant effect on the dynamic modulus of viscoelastic films. For example, temperature changes may result in the transition of synthetic polymers from a glassy to a rubbery state, and humidity changes may result in a hydration state of biological polymers [\*]. Both temperature and humidity changes cause a decrease in the modulus magnitude and an increase in the loss coefficient of the film. These effects link to variations in the dynamic indentation modulus of the film-substrate laminate that are described by the resultant analytical formulae of our theoretical modeling. Qualitatively, an increase in temperature or in humidity progressively reduces the film-to-substrate modulus ratio ($E\_{f}/E\_{s}$), which increases the effect of the indentation state parameter on the storage and loss moduli, modulus magnitude, and loss coefficient of the film-substrate laminate. These effects become more dominant as the indentation state parameter decreases (i.e., the film thickness decreases), and are especially pronounced for $H/a\ll 1$. Under these conditions, the storage and loss moduli, and the modulus magnitude of the film-substrate laminate are significantly greater than those of the pristine film, while the loss coefficient of the film-substrate laminate is much smaller than that of the pristine film. Notably, variations in the absolute values of the modulus magnitude and loss coefficient do not affect these normalized variations of the film-laminate dynamic modulus connections. However, they do have a significant effect on the absolute magnitudes and loss coefficients of the laminate.

The dynamic functional capabilities of the film-substrate laminate are significant for a number of engineering applications in terms of resistance of local impact loadings, which are indicated by the storage and loss moduli of the laminate, normalized by those of the pristine film (namely, $E\_{L}^{'}/E\_{f}^{'}$ and $E\_{L}^{''}/E\_{f}^{''}$). Previous studies introduced analogous considerations in the framework of viscoelastic interfaces, and for film substrates with uniform, far-field mechanical loadings (not localized, indentation loadings) [\*]. Upon increasing the substrate elastic modulus and decreasing the film thickness, the storage modulus of the laminate progressively increases compared to that of the pristine film, resulting in greater energy storing capabilities. In contrast, similar changes may lead to qualitatively different variations in the loss modulus of the laminate and may be either greater or lesser than that of the pristine film. This indicates that the energy dissipation characteristics of the laminate can be calibrated by varying the film thickness and substrate modulus. A material’s energy dissipation characteristics may also reach extremum for a specific indentation state parameter, which is consistent with analogous extremum effects of viscoelastic interfaces [\*].